HOT SPRINGS OF THE IGNEOUS TERRAIN OF SWAZILAND

Their noble gases, hydrogen, oxygen and carbon isotopes and dissolved ions

E. MAZOR*, B. T. VERHAGEN
Nuclear Physics Research Unit,
University of Witwatersrand,
Johannesburg, Republic of South Africa

E. NEGREANU
Isotope Department,
The Weizmann Institute of Science,
Rehovot, Israel

Abstract

HOT SPRINGS OF THE IGNEOUS TERRAIN OF SWAZILAND: THEIR NOBLE GASES, HYDROGEN, OXYGEN AND CARBON ISOTOPES AND DISSOLVED IONS.

The hot springs of Swaziland are of great interest as they occur in an area devoid of recent volcanism and issue in igneous, rather than in sedimentary rocks. An origin from directly infiltrating rain water is concluded from the Ne, Ar, Kr and Xe concentrations, and the δD and $\delta^{18}O$ values. The noble gases are shown to have been kept in closed system conditions, and their concentrations lead to the deduction of paleotemperatures at infiltration of 21°C to 31°C, which are similar to the present local summer temperatures. The ^{14}C age of the waters is calculated to be 4500 to 5400 years, and tritium concentrations are very low, indicating that the bulk of groundwater is indigenously deep seated. The chemical composition is unique, the total dissolved salts being 120 ppm, reflecting contact with igneous as opposed to sedimentary rocks.

1. INTRODUCTION

Hot springs are common all over the world, many of them being situated in regions of recent volcanic activity, to which their heat is often ascribed. In addition, many of the world's hot waters issue in sedimentary rocks and most, if not all, of their salt constituents are often attributed to dissolution from these rocks. Swaziland offers hot springs in a different geological setting, unassociated with any recent volcanism, and issuing in igneous rather than sedimentary rocks.

About ten hot springs are known in Swaziland (Fig. 1 and Table I), a few of them with several eyes. Seven of these have been sampled for detailed analysis of their dissolved noble gases, their stable hydrogen and oxygen isotopes, tritium and the composition of their dissolved ions. ^{14}C dating and stable carbon isotope analysis were carried out on three of the springs. In addition four adjacent rivers have been sampled for comparison.

The geology of Swaziland has been studied by Hunter [1] and a general description of the Swaziland hot springs has been given by the same investigator [2]. A number of chemical analyses are given by Rindl [3] and by

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* On sabbatical leave from the Israel Atomic Energy Commission and the Weizmann Institute of Science, Rehovot, Israel, during 1972.

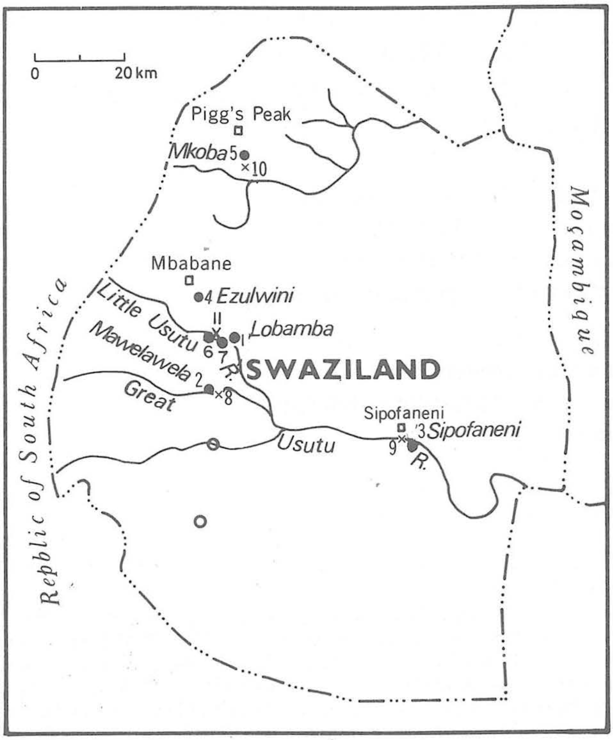

FIG. 1. Location map of sampled hot springs (●) and adjacent rivers (x). Known hot springs which were not included in the present study are marked by open circles.

the Geological Survey of Swaziland [4]. A physical description of the thermal Mkoba spring, in the Pigg's Peak region, is given by Spargo [5]. The springs are all situated in Precambrian granite or gneiss [2]. The springs, apart from Sipofaneni, are regarded by King [6] and Temperley [7] to lie on a line of crustal weakness, on whose South African extension four of the Natal hot springs are situated, namely Sulphur Springs (30.1°C), Warmbad (37.2°C), Frischgewaag (29.5°C) and Natal Spa (41.1°C). These springs are described also by Kent [8].

The Swaziland Springs are rather low yielding, with outputs varying from 3 to 19 m^3 hourly [2].

2. THE NOBLE GASES

The water samples for noble gas analysis were carefully collected in 1 cm^3 glass tubes with high vacuum stopcocks at both ends. These were sealed to an extraction system, the gas phase was separated and purified over a titanium getter and the noble gases were introduced into a Reynold's type 60°, 4.5'' glass mass spectrometer (Nuclid Co.) and measured against atmospheric standards. Details of the sampling technique, the mass spectrometric measurements and the analytical errors (± 5% or less for elemental concentrations in the present work) are given by Mazor [9].

The solubility of He and Ne in water is relatively independent of temperature, but the solubility of Ar, Kr and Xe is highly temperature-dependent (Fig. 2). Dissolved helium is often enriched by radiogenic helium, flushed out of the country rocks, but Ne enters groundwaters via contact with the air alone. As may be seen in Fig. 2, the maximum possible Ne content in air-equilibrated water at temperatures of 10°C to 60°C is 2.3×10^{-7} cm^3STP/cm^3 water. Air bubbles trapped during sampling may increase this amount significantly, the contamination caused by free air being highest for Ne and progressively lower for the heavier noble gases. Samples with Ne contents significantly higher than the above-mentioned value of 2.3×10^{-7} cm^3 STP/cm^3 water may thus be rejected as contaminated, whereas samples with Ne at or below this value may be regarded as free from any significant contamination. Fifteen of the measured samples are uncontaminated by this criterion (Table II) and only one, run No. 239, is a borderline case. The accompanying Ar, Kr and Xe values are slightly lower than those of the twin sample, No. 236, however, and hence this case also appears to be uncontaminated (the Ne is probably high because of an analytical error somewhat above average). The air contamination problem is further discussed by Mazor [9].

The noble gas data are given in Table II. The following characteristics are seen.

2.1. Noble gas air-supersaturation at the time of sampling

In Fig. 3 the air-saturation percentages for the various samples are plotted for Kr and Xe. These values were obtained by multiplying the measured values by 100 and dividing by the amount expected in air-saturated water at the sampling temperature, the value being read for each case from the solubility curve (Fig. 2). It is seen that the samples (except for the Xe value of run No. 237) were air-supersaturated when sampled. The values are 100-150% for Ar, 115-152% for Kr and 96-158% for Xe. Hence, some losses could occur from the springs before sampling. For this reason each spring has been sampled two to three times, and in further discussions the sample of highest noble gas contents has been selected from each spring, assuming it to be closest to the indigenous state. The similar values obtained in this way for the various springs lead us to believe that the noble gas escape was indeed low for the selected samples.

2.2. Radiogenic helium enrichments

The ^{4}He contents are several orders of magnitude higher than the corresponding air-saturation value, i.e. up to $17\,000 \times 10^{-8}$ cm^3 STP/cm^3 water. These large excesses are attributed to flush-out of radiogenic helium from the decay of uranium and thorium, present in the ppm range in all common rocks. Such radiogenic He is often observed in hot waters and seems to be a useful indicator for slow moving, or static, water.

TABLE I. DESCRIPTION OF SPRINGS

Station	Spring	Location	Temperature (°C)	Geology
1	Lobamba 3	31°13'E; 26°27'S	44.0	Grey granodiorite
2	Mawelawele	31°09'E; 26°35'S	35.0	Porphyrite granite
3	Sipofaneni	31°41'E; 26°39'S	44.0	Alluvial valley in granodioritic terrain
4	Ezulwini ("Spa")	31°10'E; 26°24'S	45.0	Alluvial valley in granitic terrain
5	Mkoba	31°15'E; 26°01'S	51.5	Small acidic pink intrusion into grey coarse-grained granite
6	Lobamba 1	31°12'E; 26°26'S	44.0	Alluvial valley in granodioritic terrain
7	Lobamba 2	31°12'E; 26°26'S	45.5	Alluvial valley in granodioritic terrain

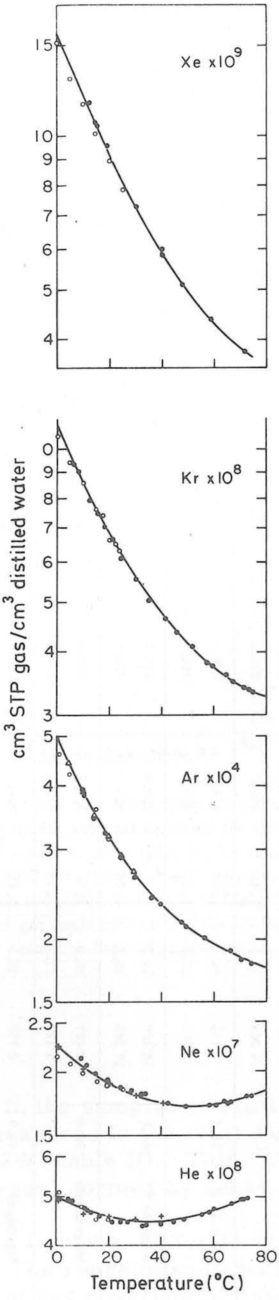

FIG. 2. Solubility of noble gases in fresh water. Source of data: ● - [10]: multiplying his sea-water data by his given ratios for solubility in distilled water to solubility in sea-water; + - [11]; ○ - [12]; and △ - [13]: multiplying their data by the atmospheric abundances.

ORGREB
Institut für Kraftwer
7544 Vetscha

TABLE II. NOBLE GASES (cm^3 STP/cm^3 WATER)[a]

Station No.	Run No.	Spring	Temp. (°C)	He × 10^8	Ne × 10^8	Ar × 10^4	$\frac{^{40}Ar}{^{36}Ar}$ sample	$\frac{^{40}Ar}{^{36}Ar}$ standard	$\frac{(^{40}Ar/^{36}Ar)\ sample}{(^{40}Ar/^{36}Ar)\ standard}$	Atmospheric ^{40}Ar × 10^4	Radiogenic ^{40}Ar × 10^4	Kr × 10^9	Xe × 10^9
4	234	Ezulwini ("Spa")	45.0	12 266	19.5								
	235			9 519	19.8	3.17	312.5	296.8	1.053	3.01	0.16	58.0	7.20
	238			9 711	21.2	3.18	311.5	289.4	1.076	2.95	0.23	64.3	8.20
6	228	Lobamba 1	44.0	11 720	17.9	2.76	352.4	286.4	1.23	2.24	0.52	51.1	6.65
	237			10 068	18.8	3.00	323.7	292.5	1.11	2.70	0.30	52.7	5.30
7	226	Lobamba 2	45.5	8 198	14.0	2.93	312.1	288.9	1.080	2.71	0.22	53.8	7.23
	231			5 083	12.3	2.65	309.5	292.7	1.057	2.51	0.14	51.9	7.25
1	236	Lobamba 3	44.0	14 400	20.9	3.63	320.0	291.2	1.10	3.30	0.33	64.8	8.34
	239			17 545	25.8	3.65	325.3	289.6	1.12	3.26	0.43	61.6	8.20
2	229	Mawelawele	35.0	8 427	22.6	3.39	312.2	298.6	1.046	3.23	0.13	60.7	7.32
	233			6 422	17.1	3.33	313.3	282.1	1.110	3.00	0.33	61.7	7.84
3	224	Sipofaneni	44.0	8 759	18.2	3.22	326.4	290.0	1.12	2.88	0.34	60.1	8.70
	230			7 172	17.5	3.05	326.3	292.7	1.11	2.75	0.30	56.6	6.61
	240			8 560	20.3	3.38	323.7					55.7	6.20
5	227	Mkoba	51.5	14 478	13.5	3.37	352.9	296.7	1.19	2.83	0.54	47.1	5.54
	232			17 464	17.8	3.76	354.9	298.5	1.19	3.16	0.60	61.4	7.42
		Air-saturated water	25.0	4.5	18.5					2.85		60.5	8.0

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[a] Elemental concentration errors are ± 8% or less [9], and the ^{40}Ar/^{36}Ar ratio is assigned an error range of up to ± 2%.

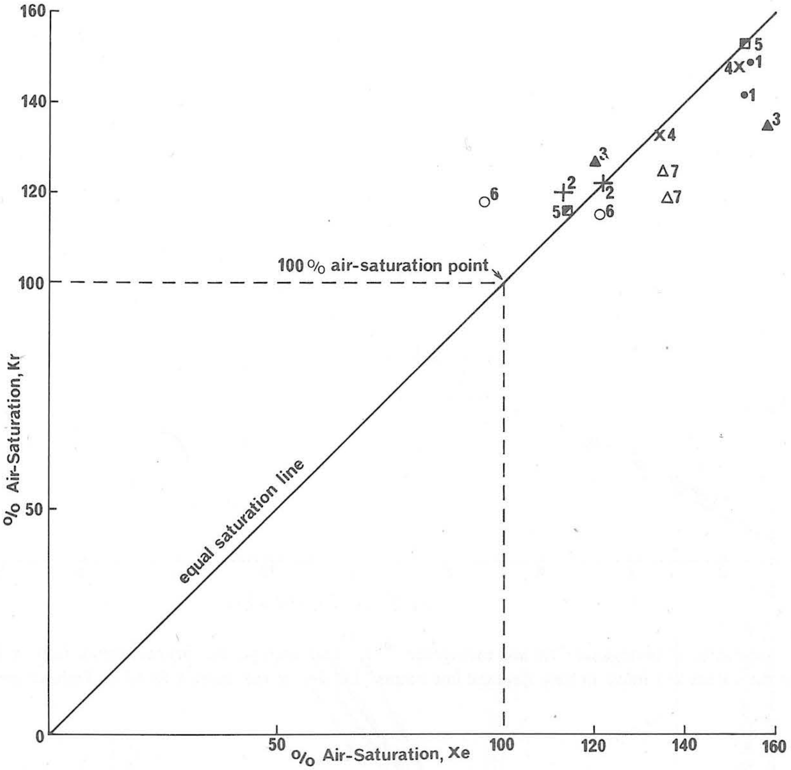

FIG. 3. Percentage air saturation of Kr and Xe. The values were obtained by multiplying the measured values (Table II) by 100 and dividing by the amounts expected for air-equilibrated water (Fig. 2) at the sampling temperature (Table I). All samples, apart from the Xe value of sample No. 6, are supersaturated. The corresponding values for Ar are similar to those of the Kr and Xe. This supersaturation at the time of sampling is taken as an indication that the waters were kept in the ground in closed system conditions with respect to their noble gases, but some gas could escape into the air before sampling. The highest values for each spring are therefore taken to be closest to the indigenous values.

2.3. Radiogenic argon

The $^{40}Ar/^{36}Ar$ ratio in the samples is significantly higher than in the atmospheric standards measured in the same runs. The ^{40}Ar enrichments are in the range of 5 to 23% (Table II). This ^{40}Ar excess is attributed to flush-out of radiogenic argon, formed by decay of ^{40}K, present in the ppm level in all common rocks.

A positive correlation is observed for the radiogenic He and Ar enrichment, as seen in Fig. 4. The range of radiogenic He/Ar ratio is 2.6 to 5. This is similar to ratios of 2-4 observed in New Zealand hot springs [14] and equal to a value of 4 found in Yellowstone hot waters [15]. This value is also in the range of the average He/Ar radiogenic production ratio of about 10, calculated by Zartman and co-workers [16] for common crustal rocks.

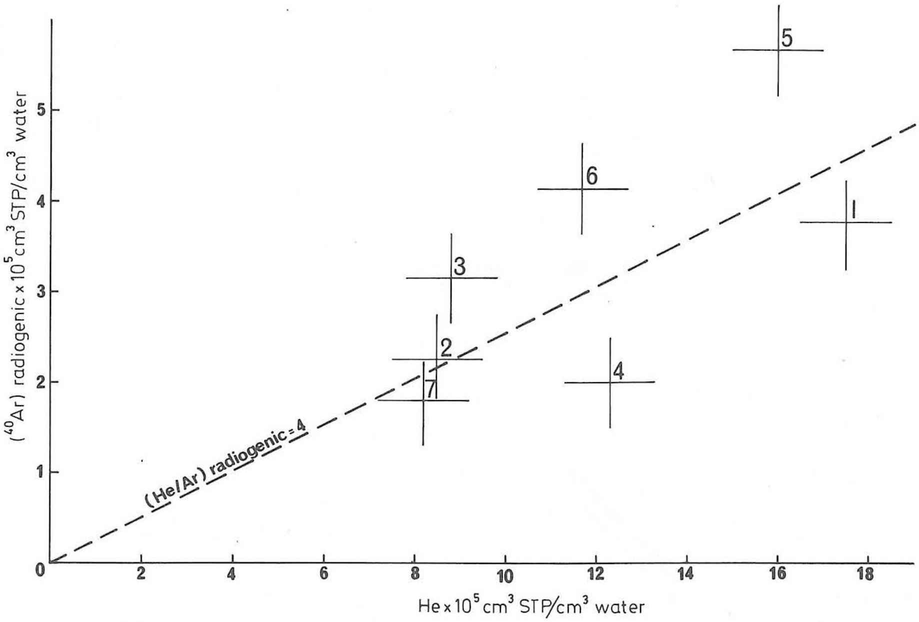

FIG. 4. Correlation of radiogenic ^{4}He and radiogenic ^{40}Ar. The average (He/Ar) radiogenic ratio is 4, similar to the values 2-4 found in New Zealand hot waters [14] and to the value 4 found in Yellowstone [15].

2.4. Atmospheric relative abundances indicating meteoric origin

The relative aboundance of Ne, atmospheric Ar (i.e. after correction for radiogenic additions (Table II) by use of the $^{40}Ar/^{36}Ar$ ratio in the accompanying standard measurement), Kr and Xe closely resemble those in air-saturated water. In Fig. 5 the selected samples (richest in noble gases for each spring) were plotted along with the abundance values of air-saturated water at 25°C, and the similarity of the lines is obvious.

This is taken as proof that we are dealing with meteoric water, which penetrated the ground after equilibration with air at the then prevailing ambient temperature. No other process is likely to exist in nature that can load these waters by noble gases in near atmospheric proportion. This meteoric nature is independently revealed by the stable isotopes, as discussed below.

2.5. Deduction of paleotemperatures

Thermal waters were air-supersaturated with respect to their noble gases when sampled. This is taken as an indication that once the meteoric water entered the ground it was kept in closed system conditions with respect to its atmospheric gas content, even though the water was subsequently heated.

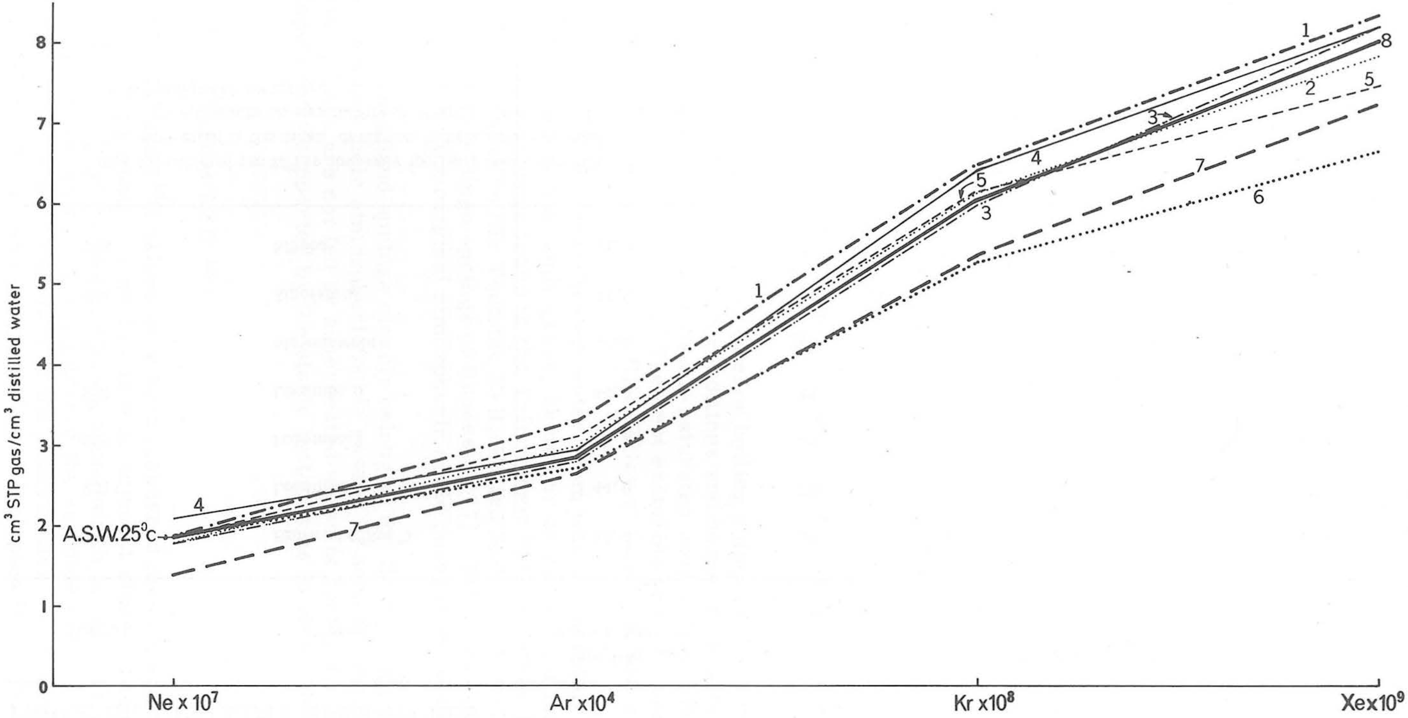

FIG. 5. The noble gas pattern (in the samples of highest noble gas contents in each spring, see text). The values are seen to group closely around the line of air-equilibrated water at 25°C (solid line). This is taken as a proof for the meteoric origin of the waters, as no other mechanism could load them with noble gases in atmospheric-like abundances.

TABLE III. PALEOTEMPERATURES

Run No.	Spring	Sampling temperature (°C)	Paleotemperatures (°C)			
			Ar	Kr	Xe	Mean [b]
238	Ezulwini ("Spa")	45.0	23	22	24	23 ± 1
237	Lobamba 1	44.0	28	32	33 [a]	31 ± 2
226	Lobamba 2	45.5	28	31	29	29 ± 1
236	Lobamba 3	44.0	17	22	23	21 ± 3
233	Mawelawele	35.0	22	23	26	24 ± 2
224	Sipofaneni	44.0	24	25	22	24 ± 1
232	Mkoba	51.5	19	24	28	24 ± 3

[a] The Xe value of run 237 is obviously too low, hence the value of run 228 was applied.

[b] The error cited is the mean deviation between the measurements of Ar, Kr and Xe. The estimated analytical error of ± 5% or better of these elements introduces an uncertainty of about ± 2°C. Thus the deviations observed between the Ar, Kr and Xe paleotemperatures are in the range of the analytical accuracy.

Hence, the atmospheric Ar and Kr and Xe concentrations may be used to calculate the "paleotemperatures" of the waters, i.e. the ambient temperatures that prevailed on the ground at the time of infiltration. These temperatures can be read from the solubility graph in Fig. 2. The paleotemperatures may be calculated for each spring independently from its Ar, Kr and Xe contents. Good agreement is seen (Table III) between the results of calculations for these three gases. The mean deviations of the three values for each spring vary from ± 1°C to ± 3°C. The mean paleotemperatures themselves vary from 21°C to 31°C.

The time, or age, to which these paleotemperatures are relevant can be deduced from ^{14}C measurements (see below). In any case it is interesting to note that the average "paleotemperatures" are close to the average summer temperatures of Swaziland (and it is the summer temperature that counts, as Swaziland is, and probably has been for some millenia, a summer rainfall area). In addition this origin from rain water is borne out by the stable isotope composition of the springs.

2.6. Average temperature in the aquifers feeding the hot springs

The noble gas contents enable us to make general deductions on the temperature of the water reservoirs that feed the springs.

Two basic types of atmospheric noble gas patterns have so far been found in hot springs. These are:

(a) Springs with temperatures below boiling point, in which the noble gases are kept in closed system conditions and hence issue with gas contents equivalent to those found in air-saturated waters at common surface temperatures (10°-30°C). The best examples of such cases so far studied occur in the Jordan Rift Valley in Israel [9] and a few hot springs in Rhodesia [17].

(b) Springs fed by superheated water from which separating steam can strip most of the noble gases, before or at the point of issue. Examples of this type were found in the Yellowstone National Park [15], in Sulfur Bank of the Pacific Tectonic Belt, United States of Ameria [18] and in the boiling Binga springs of Rhodesia [17]. In these cases as little as 10% of the original atmospheric noble gases may remain.

The Swaziland springs clearly belong to the first group, i.e. waters that retained their atmospheric noble gases. It seems, tentatively, that these springs are not fed by superheated water at depth, a conclusion independently supported by the stable isotopes as is shown below.

3. DEUTERIUM AND ^{18}O

The δD and $\delta^{18}O$ values have been measured mass-spectrometrically in the springs studied as well as in four adjacent rivers (Table IV and Fig. 6).

The four river values plot along a line which is typical for rain and derived surface water. The lightest of the samples is No. 10, collected from the short Mkoba tributary of the Komati River, in the mountainous area of Piggs Peak which might well have isotopically relatively light rains.

TABLE IV. CHEMICAL AND ISOTOPIC DATA

Station	Source	pH	K[a]	Na[a]	Mg[a]	Ca[a]	F[a]	Cl[a]	SO$_4$[a]	HCO$_3$[a]	Total ions	δD‰	δ^{18}O‰	Tritium (TU)
4	Ezulwini ("Spa")	8.6	1[b]	35	2	4	6	11	11	53	123	-14.8 ± 1.6	-4.05 ± 0.09	0.5 ± 0.2
			0.026[c]	1.52	0.16	0.20	0.32	0.31	0.23	1.09	3.85			
6	Lobamba 1	7.9	1	48	1	4	6	14	8	81	163	-15.5 ± 1.6	-4.62 ± 0.09	1.3 ± 0.2
			0.026	2.09	0.082	0.20	0.32	0.40	0.17	1.44	4.70			
7	Lobamba 2	7.9	1	45	1	4	6	14	6	81	158	-18.1 ± 1.3	-4.11 ± 0.08	0.4 ± 0.2
			0.026	1.96	0.082	0.20	0.32	0.40	0.13	1.44	4.55			
1	Lobamba 3	8.0	1	45	1	4	7	14	6	74	152	-14.4 ± 1.6	-4.48 ± 0.09	0.6 ± 0.2
			0.026	1.96	0.082	0.20	0.37	0.40	0.13	1.33	4.48			
2	Mawelawele	7.9	1	45	2	9	7	14	6	87	171	-18.8 ± 1.6	-4.05 ± 0.09	0.2 ± 0.2
			0.026	1.96	0.16	0.45	0.37	0.40	0.13	1.54	5.03			
3	Sipofaneni	7.9	4	135	1	2	7	121	30	101	401	-14.7 ± 1.6	-4.09 ± 0.09	0.4 ± 0.2
			0.10	5.87	0.082	0.10	0.37	3.41	0.62	1.77	12.3			
5	Mkoba	8.3	1	58	1	4	6	21	6	93	190	-18.6 ± 1.6	-3.96 ± 0.09	1.1 ± 0.2
			0.026	2.52	0.082	0.20	0.32	0.59	0.13	1.74	5.61			
11	River at Lobamba Little Usutu R.	7.4	-	7	4	2	1	7	5	27	53	-12.1 ± 1.1	-3.27 ± 0.08	46.9 ± 1.8
				0.30	0.33	0.10	0.053	0.20	0.10	0.44	1.53			
8	River at Mawelawele Great Usutu R.	7.5	1	11	4	4	1	11	9	40	81	-10.5 ± 1.3	-2.60 ± 0.08	53.2 ± 3.5
			0.026	0.48	0.33	0.20	0.053	0.31	0.19	0.66	2.30			
9	River at Sipofaneni Great Usutu R.	7.6	1	9	7	4	1	11	8	47	88	- 4.5 ± 1.1	-2.16 ± 0.08	46.1 ± 2.5
			0.026	0.39	0.58	0.20	0.053	0.31	0.16	0.77	2.50			
10	River at Mkoba Mkoba R. (into the Komati)											-13.6 ± 1.1	3.40 ± 0.08	

[a] Geological Survey, Botswana.

[b] mg/litre.

[c] meq/litre.

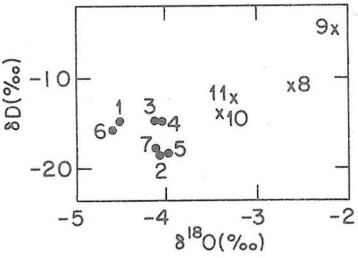

FIG. 6. Isotopic composition. The river samples (x) lie on a line which is common for rain. The sequence of the river samples along this trend is understood from their locations and reveals slight progressive evaporation (see text). The hot springs (●) may well originate from non-evaporated infiltrating rain water. The stable isotopes seem to reveal, independently, the meteoric origin of the hot springs studied.

TABLE V. CARBON ISOTOPES AND INFERRED AGES

Source	^{14}C (pmc) [a]	$\delta^{13}C$‰ [b]	Age I (years) [c]	Age II (years) [d]
Ezulwini ("Spa")	47.6 ± 2.1	-13.6 ± 0.07	4660	1080
Lobamba 2	43.5 ± 1.8	-14.48 ± 1.8	5400	2300
Sipofaneni	48.5 ± 2.5	-12.4 ± 0.07	4500	200

[a] In per cent modern carbon (pmc).

[b] Isotope Department, Weizmann Institute of Science.

[c] Assuming groundwater initially contains 85 pmc [19].

[d] ^{14}C value applied as initial content derived by dividing measured value by $\delta^{13}C/-25$.

See text for evaluation of Ages I and II.

The next in the sequence is sample No. 11, collected at a tributary of the Little Usutu, and this is followed by samples 8 and 9, both from the Great Usutu, No. 9 being about 220 km downstream from No. 8. The four river samples thus reveal isotopic values resulting from slight progressive evaporation. The average rain composition seems to be close to, or very slightly lighter than, the values of sample No. 10.

The results of the hot springs are grouped around δD - 17‰ and $\delta^{18}O$ - 4.2‰, and are slightly lighter than the river waters, probably close to the composition of the local rain at the time of infiltration.

The stable isotope data therefore lead independently to the following conclusions:

(a) The hot springs are fed by rain water that did not undergo evaporation and, hence, infiltrated directly into the ground.

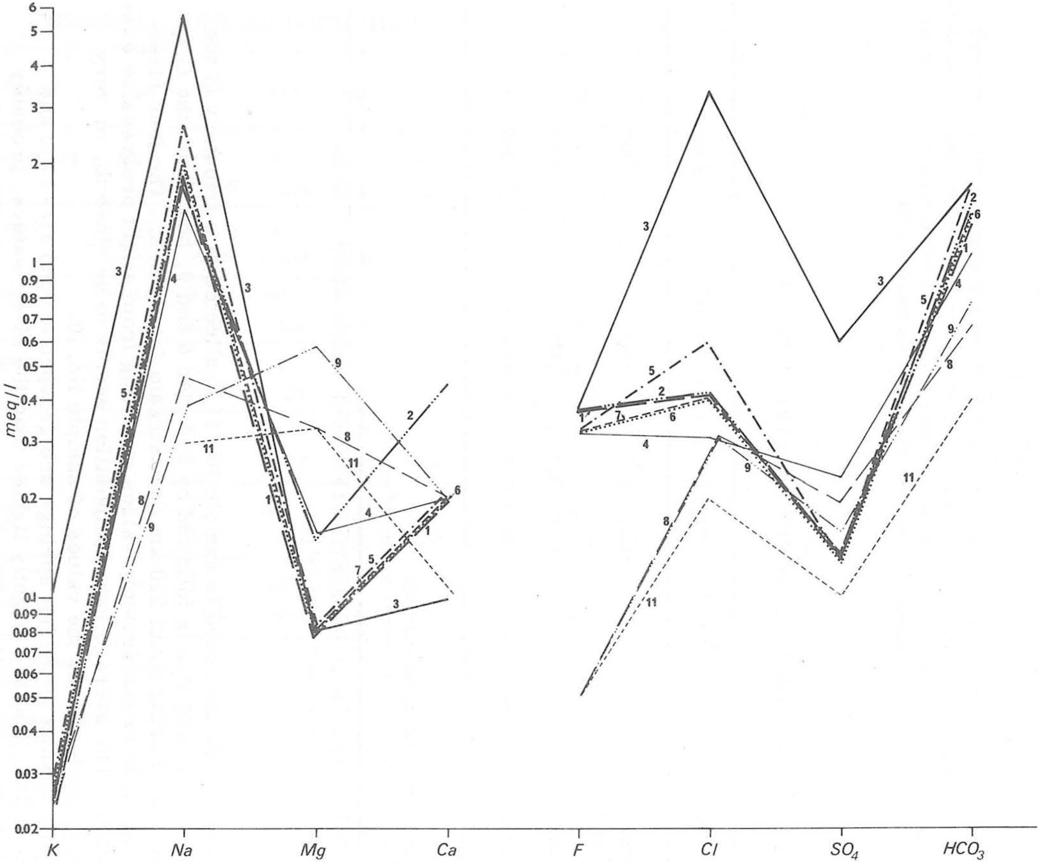

FIG. 7. The chemical composition. The hot spring waters (1 - 7) are higher in their salt contents than the adjacent river waters (8, 9, 11). If the rivers are taken to represent in their composition the original infiltrating meteoric water, then the hot springs must have picked up from the igneous and metamorphic country rocks, Na, F and HCO_3, and have lost Mg, perhaps by exchange reactions. The higher NaCl value of Sipofaneni (sample 3) might be caused by brief contact with Karroo sediments (see text).

(b) The hot springs did not suffer from partial losses of a steam phase, which would result in an isotopically heavier residual water phase. These waters are fed by reservoirs at temperatures that are significantly below boiling, a conclusion already reached on the basis of dissolved noble gas data.

4. TRITIUM CONCENTRATIONS

The tritium values for three measured rivers are 46-53 TU. The values found in the hot springs are, however, only 0.0-1.3 TU (Table IV). This suggests that the spring waters are virtually not mixed with river, or other very recent water met during their ascent. An upper limit for such additions may be reached if it is assumed that the indigenous hot waters are devoid of tritium. Even in such a case the additions from intermixing surface water will be limited to 0-2%. Hence, the spring waters may justifiably be regarded as indigenous, deep-seated when discussing their noble gas contents, stable isotope composition, ^{14}C values or composition of the dissolved ions.

5. CARBON ISOTOPES AND INFERRED AGES

Water from three springs has been extracted at the field for its carbon extraction. The measured $\delta\,^{13}C$ and ^{14}C values are given in Table V.

The measured springs issue in igneous terrain and in two of them $NaHCO_3$ is the dominant dissolved salt species. However, the observed $\delta\,^{13}C$ values of 12-14‰ are close to values known elsewhere from sedimentary terrain.

Two types of age calculations were applied in Table V. Age I was based on the assumption that the groundwaters had an initial ^{14}C content of 85 pmc [19, 20]. Age II was calculated by correcting for initial dilution by fossil carbon by dividing the observed ^{14}C value by $\delta\,^{13}C/-25$ [21]. The set of Ages I seems to reveal a better internal consistency than those of Ages II (Table V). There are, however, no criteria at hand with which to decide on the correct ^{14}C ages. These may perhaps be re-calculated in the future, once the art of ^{14}C age deduction reaches a more advanced state.

In conclusion, the ^{14}C content seems to indicate that the hot spring water studied in Swaziland is a few thousand years old, i.e. older than the water in the active cycle of shallow groundwater but not entirely fossil.

An age of a few thousand years would be in good agreement with the elevated contents of radiogenic He and Ar, which reached the observed level by prolonged contact with aquifer rocks.

6. THE CHEMICAL COMPOSITION

The chemical composition of the springs studied and the adjacent rivers is given in Table IV and Fig. 7. Comparison with a number of chemical analyses previously published [3, 4] reveal a general similarity;

a detailed comparison is not possible, as these sampling sites could not be accurately identified. The following features emerge from the chemical data:

(a) Remarkably low salt contents. The springs, though thermal, are surprisingly low in their salt contents, the total ions ranging from one case of 400 ppm. This is definitely to be attributed to the igneous rock environment composed mainly of granites (Table I), which contain very little soluble material. This is in remarkable contrast to most hot springs in the world, which are frequently loaded with salts, originating from sedimentary rocks.

In spite of the very low salinity, some of the waters are not palatable because of a sulphur taste and an occasional H_2S smell.

(b) Reactions with the igneous host rocks. The rivers have a total ion content of 53 to 88 ppm, whereas the hot springs have a content of 120 to 400 ppm. It has been shown from the noble gas and stable isotope data that the springs are of meteoric origin. It seems reasonable that the initial salt content of this meteoric water was, at most, as high as in the rivers. Hence, the additional ions result from the igneous rocks or their derived soils. The various springs, except Sipofaneni, have much in common in their dissolved salts (Fig. 7), their cations being $Na \gg Ca > Mg$, and their anions being $HCO_3 > Cl > F > SO_4$ and the dominant salt species being $NaHCO_3$.

The enrichments above river water are in Na, F, HCO_3 and very slightly in Cl. Magnesium has been depleted, possibly because of ion exchange, a process seen elsewhere, also in other water associations.

Sipofaneni has more than twice the T.D.S. of the other springs, the dominant addition being NaCl (Table IV and Fig. 7). This might well be explained by the location of this spring on a post-Karroo joint and adjacent Karroo outcrops. It seems likely that, although Sipofaneni issues in igneous rocks, its water comes into contact with Karroo sediments, which contribute additional salts [22].

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DISCUSSION

J.Ch. FONTES: To what extent was the rain water saturated in noble gases?

E. MAZOR: In the few rain-water analyses which we performed, we observed slight oversaturation, attributable to lower temperatures in the clouds. In that connection, I would mention that, when the rain water reached the ground surface, its temperature equilibrated rapidly with the ambient temperature.

P. FRITZ: The solubility of a gas depends not only on temperature but also on the ionic strength of the solution. Was the concentration of rare gases in your samples affected by the dissolving of salt underground?

E. MAZOR: No, for our samples contained a total of only 120 ppm T.D.S.

R.R. LETOLLE: With regard to Fig. 4, was the helium excess determined using the ^{3}He/^{4}He ratio?

E. MAZOR: No, we are not able to measure ^{3}He with our methods. We decided that the helium was radiogenic because its concentrations was four orders of magnitude higher than in air-equilibrated water.

H. OESCHGER (Chairman): Could you use the radiogenic helium and argon as a basis for dating?

E. MAZOR: I do not think so, for we do not know the volume ratio of water to flushed rock.

D. B. SMITH: Any loss of dissolved gas from the thermal water before obtaining the sample will apparently lead to an overestimate of the temperature of the recharge water. For two springs (Lobamba 1 and 2) Table III gives significantly higher recharge temperatures. Are there any geohydrological features associated with these particular springs which could cause a higher loss of gas than might occur in the other springs which were sampled?

E. MAZOR: Not as far as I am aware. In this connection I would stress, however, that our figures represent maximum temperatures and that additional data would be helpful.

F. J. PEARSON: Hydraulic models of hot spring systems in regions with no recent volcanism show that a source of heat greater than that supplied by a normal geothermal gradient is required for some of the systems to function. The source may be slightly higher than normal concentrations of such radioisotopes as ^{40}K or uranium in the aquifer material. If you have sufficient knowledge of the hydrology of your system, you may be able to make an order-of-magnitude estimate of aquifer radioisotope concentrations from your excess ^{4}He and ^{40}Ar concentrations. Such an estimate would be of great interest to those working with geothermal systems elsewhere.

E. MAZOR: I agree. However, the rise of hot water is often attributable to a head of fresh water, and we believe this may be the case in Swaziland.

V. T. DUBINCHUK: The reference data on gas solubility are for equilibrium states. Did you take into account the kinetics of gas dissolution in atmospheric water or did you assume that the saturation of the atmospheric moisture was complete and in equilibrium? In other words, was there sufficient time to establish equilibrium between atmospheric moisture and noble gases from the moment of condensation up to the moment of precipitation?

E. MAZOR: The saturation values were taken from the literature, where carefully conducted experiments have been reported. As regards the second part of your question, we found that the surface waters were generally in equilibrium.

M. LEVIN LIPSIN: In Section 6 of your paper you mention a sulphur taste and an occasional H_2S smell. If the waters are not magmatic, what in your opinion is the origin of the H_2S?

E. MAZOR: We assume that the H_2S derives from biogenic decomposition of the dissolved sulphate.

M. LEVIN LIPSIN: Is there any carbonate or sulphate mineralization in the fractured zone mentioned by you in your oral presentation?

E. MAZOR: I doubt it, judging by the very low salt contents of the spring waters.

T. FLORKOWSKI: In your oral presentation you mentioned gas bubbles escaping from the water of some of the hot springs. Did you attempt to collect the gas and determine its composition?

E. MAZOR: Not in this study. We did do so, however, in our study in the Yellowstone National Park and observed fractionation which can be explained in terms of a partial loss of dissolved gases.

W. G. MOOK: In your oral presentation you mentioned briefly the problem of correcting the conventional ^{14}C ages of groundwater. I should like to make a comment in this connection.

From a theoretical point of view the situation is quite clear. If you assume that the only source of inorganic carbon in the groundwater is soil limestone dissolved by the action of soil CO_2, that there is in the aquifer no isotopic exchange between the dissolved carbon and solid limestone and no addition of CO_2 (of magmatic origin or released from limestone by H^+ ions), and that there occurs no mixing of water masses of widely different ^{14}C ages, a straightforward calculation gives the original ^{14}C content of the groundwater. I presented this approach at the conference on radiocarbon dating held in New Zealand in 1972 (W.G. Mook, "On the reconstruction of the initial ^{14}C content of groundwater from the chemical and isotopic composition").

Two processes are taken into account: the dissolution of $CaCO_3$ by CO_2; isotopic exchange between the bicarbonate formed and the soil CO_2 in the unsaturated zone. It is irrelevant in what order these processes occur, whether they occur stepwise or even whether they occur continuously at the same time. The result is:

$$A_\Sigma = \frac{1}{a+b}\left[aA_{ao} + bA_{bo} + (A_{be} - A_{bo})\frac{(a+b)\delta_\Sigma - a\delta_{ao} - b\delta_{bo}}{\delta_{be} - \delta_{bo}}\right]$$

where

$A_{bo} = \frac{1}{2}(A_{ao} + A_{\ell o})$ and $\delta_{bo} = \frac{1}{2}(\delta_{ao} + \delta_{\ell o})$; $\delta_{be} = \delta_{go} - \epsilon_g$ and $A_{be} = A_{go} - 2\epsilon_g/10$;

ϵ_g is the carbon isotope fractionation (in per mille) between gaseous CO_2 and dissolved bicarbonate;

A is the ^{14}C content as a percentage of the modern standard;

δ is the ^{13}C value relative to PDB;

a and b refer to the concentrations of dissolved CO_2 and bicarbonate respectively, ℓ refers to the soil limestone and Σ refers to the total carbon content.

Of the nine variables, one is known (ϵ_g), and three can be determined (a and b — on the basis of pH, temperature and salinity — and δ_Σ). To calculate the original ^{14}C content of the sample, A_Σ, four values have to be assumed: A_{ao}, $A_{\ell o}$, δ_{ao} and $\delta_{\ell o}$. The conventional assumptions (100%, 0%, -25‰ and 0‰ respectively) are not necessarily correct.

Although the model is clear, this does not directly lead to a successful correction procedure. The advantage, however, is that one can play around with the figures and determine, for instance, age limits. Also, it often turns out that the assumption of A_Σ = 85% cannot be true. Conversely, assuming a value for A_Σ, one can calculate A_{ao}, as was done in a paper presented earlier in this Symposium.[1]

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