

## THE THERMAL WATERS OF THE UNION OF SOUTH AFRICA AND SOUTH WEST AFRICA.

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### ABSTRACT.

In the Union of South Africa seventy-four springs are regarded as thermal, i.e., issuing at temperatures exceeding 25°C. the year round. Those above 37°C. are classed as hot, whilst a special group styled scalding waters has been created for those with temperatures exceeding 50°C. The combined discharge is estimated to be 8,000,000 gallons (36,290 cbm.) a day, one spring alone being responsible for almost a third of this total. Thermal water also flows from several boreholes, in five of which it was struck at depths greater than 2,500 feet (762 m.).

Twenty-five analyses representative of all the types of thermal water known in the country are given, and of these seventeen have not been published previously. The waters contain up to 86 mgm. per litre of silica, the possible states of which are discussed.

Sulphuretted waters, which are defined as containing more than 10 mgm. of dissolved hydrogen sulphide per litre, are uncommon in South Africa. It is suggested that the terms "moderately sulphuretted" and "slightly sulphuretted" should be used for those containing from 5 to 10 and from 1 to 5 mgm. per litre of the dissolved gas respectively.

Fluorine is a prominent minor constituent, up to 13.2 mgm. per litre being present. Strontium, an element seldom sought in waters, occurs to the extent of 7.2 mgm. per litre in water from a deep borehole near Trompsburg.

Residues obtained by evaporation were spectrographically examined by Dr. B. Wasserstein of the Geological Survey. Selected minor elements seemed to characterise waters issuing from certain geological formations. Rough quantitative data indicated that the elements Li, Sr and Ba did not form more than 0.1 per cent. of the residues, while Pb and Mo both had maximum values around 0.005 per cent.

The gas associated with the waters is of two types; one is mainly air from which most of the oxygen has been abstracted and the other mainly methane, accompanied in some cases by hydrogen. Thirteen new analyses are given.

Spring deposits are not common and are represented only by ferruginous ochres and sinters formed by springs in the Cape system. Manganese is an important constituent of these deposits. Four new analyses are given.

In most cases a close relationship in composition exists between the thermal waters and waters struck in shallow boreholes or issuing as cold springs from the same geological formations. When differences other than in degree of concentration were noted, it was found that the thermal waters were characteristic of the deeper underlying rock formations.

All the thermal waters are considered meteoric. Geological sections illustrate the structures upon which the emergence of thermal waters depends. These are artesian basin, artesian slope, barrier, and faults. The source of the heat is probably the normal geothermal gradient in the crust. It is calculated that the total amount of heat being brought to the surface by the South African thermal springs is approximately  $5.8 \times 10^{10}$  cal. cm.<sup>2</sup> sec. or about a two-thousandth of that normally dissipated by conduction through the crust.

Less is known about the thermal springs of the Territory of South West Africa. Twenty-four springs are known to be thermal, of which nine are scalding, a much higher proportion than in the Union of South Africa. Thermal water has been struck in many fairly shallow boreholes.

A few analyses are given, all old. The potassium content greatly exceeds that of the thermal waters of the Union; this is attributed to the higher potassium content of the granites of South West Africa.

The Windhoek springs have deposited extensive layers of calcareous tufa.

The South West African thermal springs, too, are believed to represent the return of meteoric water to the surface mainly through fault fissures, and in some cases fractures, associated with volcanicity possibly of Cretaceous age.

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## PART I.—THE UNION OF SOUTH AFRICA.

## I. INTRODUCTION.

For a non-volcanic country the Union of South Africa is relatively well-endowed with thermal springs. There are no definite thermal regions, and with few exceptions the springs occur sporadically throughout those parts of the country where the annual rainfall exceeds 10 inches (25.4 cm.), i.e. in all save the arid North of the province of the Cape of Good Hope.

The natural hot waters of the western Cape Province attracted the early explorers and travellers, and Caledon and some of the other springs have been health resorts since the early 19th century. The first scientific account of them, by T. E. Gumprecht,<sup>15</sup> is now almost a hundred years old. His descriptions included temperature measurements but no chemical analyses. The first attempt at a chemical classification of all the known South African "medicinal" springs was published by M. M. Rindl<sup>26</sup> in 1916, and the work was continued as a series of papers. These deal essentially with the chemical composition of the waters. In most geological accounts of areas where thermal springs are found they have

either been completely ignored, or their existence has merely been noted. Reasonably detailed descriptions by geologists of only the Lilani,<sup>7</sup> Amanzi,<sup>8</sup> Tugela valley,<sup>14</sup> Letaba,<sup>17</sup> Loubad,<sup>18</sup> Souting,<sup>19</sup> and Buffelshoek<sup>20</sup> springs are available in print, but several others have been investigated recently, and it is hoped within a few years to publish a Geological Survey Memoir on the thermal waters of South Africa.

Artesian supplies of thermal water have been struck in several boreholes; most of them are deep, having been drilled in search of gold reefs or oil. Warm waters have also been encountered in a few of the deeper mines.

## II. CLASSIFICATION OF THERMAL WATERS ON THE BASIS OF TEMPERATURE.

It appears to be largely a matter of opinion where the dividing line should be drawn between thermal and non-thermal waters. Kirk Bryan<sup>3</sup> mentioned that it is usually taken as 70°F. (21.1°C.), but that 20° to 25°F. (11.1°-13.9°C.) above the mean for the region might be preferable. In the most recent general account of the thermal springs of the United States, however, some are included "whose temperatures may not be more than 10°F. (5.6°C.) above the mean annual temperature of the locality where they issue."<sup>32</sup> In an official Canadian publication<sup>10</sup> thermal springs are defined as those issuing at above 70°F. (21.1°C.) the year round, those above 90°F. (32.2°C.) being described as hot. In Southern Rhodesia, the Union's neighbour to the north, the dividing temperature of 20°C. (68°F.) has been chosen.<sup>22</sup> This follows climatological usage as 68°F. is regarded as the temperature separating "mild" from "warm," whereas 80°F. (26.7°C.) is used to separate "warm" from "hot." Most balneotherapists regard 80°F. as the division between cool and tepid waters, and they class waters between 92° and 98°F. (33.3°-36.7°C.) as warm, between 98° and 104°F. (36.7°-40.0°C.) as hot, and above 104°F. as very hot. On an Italian classification<sup>23</sup> waters below 20°C. are regarded as cold, those between 20° and 30°C. as hypothermal, those between 30° and 40°C. as thermal, and those above 40°C. as hyperthermal. The scheme proposed by the International Society of Medical Hydrology is rather similar—waters below 20°C. are termed cold, between 20° and 37°C. subthermal, from 37° to 42°C. thermal, and above 42°C. hyperthermal.

The mean annual air temperature of the Union of South Africa ranges between approximately 55° and 70°F. (12.8°-21.1°C.). Most of the country falls between the 55° and 65°F. isotherms, but many of the thermal springs lie in the 65° to 70°F. (18.3°-21.1°C.) belt.<sup>24</sup> Thus it would appear to be inadvisable to set a limit below 25°C. (77°F.) as the division between thermal and non-thermal waters. Even for geologists human blood-heat appears a most satisfactory temperature for dividing warm from hot waters. In a subtropical country like South Africa warm waters therefore have a range of 12°C. A new dividing line is proposed at 50°C. (122°F.) to separate hot from scalding waters. On this basis the hot waters have a range of 13°C. Thus the classification proposed is:

Warm .. .. .	25°—37°C.
Hot or hyperthermal .. .. .	37°—50°C.
Scalding .. .. .	above 50°C.

Natural waters with temperatures between the mean air temperature and 25°C. may be classed as tepid. Provision may be made in the classification for boiling and superheated waters, but these are not known in South Africa. On the basis of the above classification there are seventy-four thermal springs and nine thermal artesian boreholes, or groups of boreholes, known in the Union of South Africa (area 472,550 sq. miles or 122,394,230 hectares). On the map (Fig. 1) only seventy-two springs are shown, the additional ones occur near the Loskop dam and the village of Roos Senekal, both in the central Transvaal.

SPRINGS.			THERMAL ARTESIAN BOREHOLES.	
Warm ..	..	39		6
Hot ..	..	24		2
Scalding ..	..	6		1
Temperature unknown ..	..	5		
		<u>74</u>		<u>9</u>

### III. DISCHARGES OF SPRINGS.

The spring at Brandvlei in the south-west of the Cape Province is by far the strongest thermal spring in South Africa, having a daily discharge of 2,430,000 gallons. (11,022 cbm.). Of the others only Aliwal North exceeds a cusec (540,000 gallons or 2,450 cbm. per day). Brandvlei is also the hottest spring in the country, while Aliwal North has a higher temperature than the other springs in the north-eastern Cape Province and adjacent Orange Free State.

Of the springs that have been gauged only the two mentioned above attain third magnitude on Meinzer's classification, whereas there are eight of fourth magnitude, and fourteen of fifth magnitude.

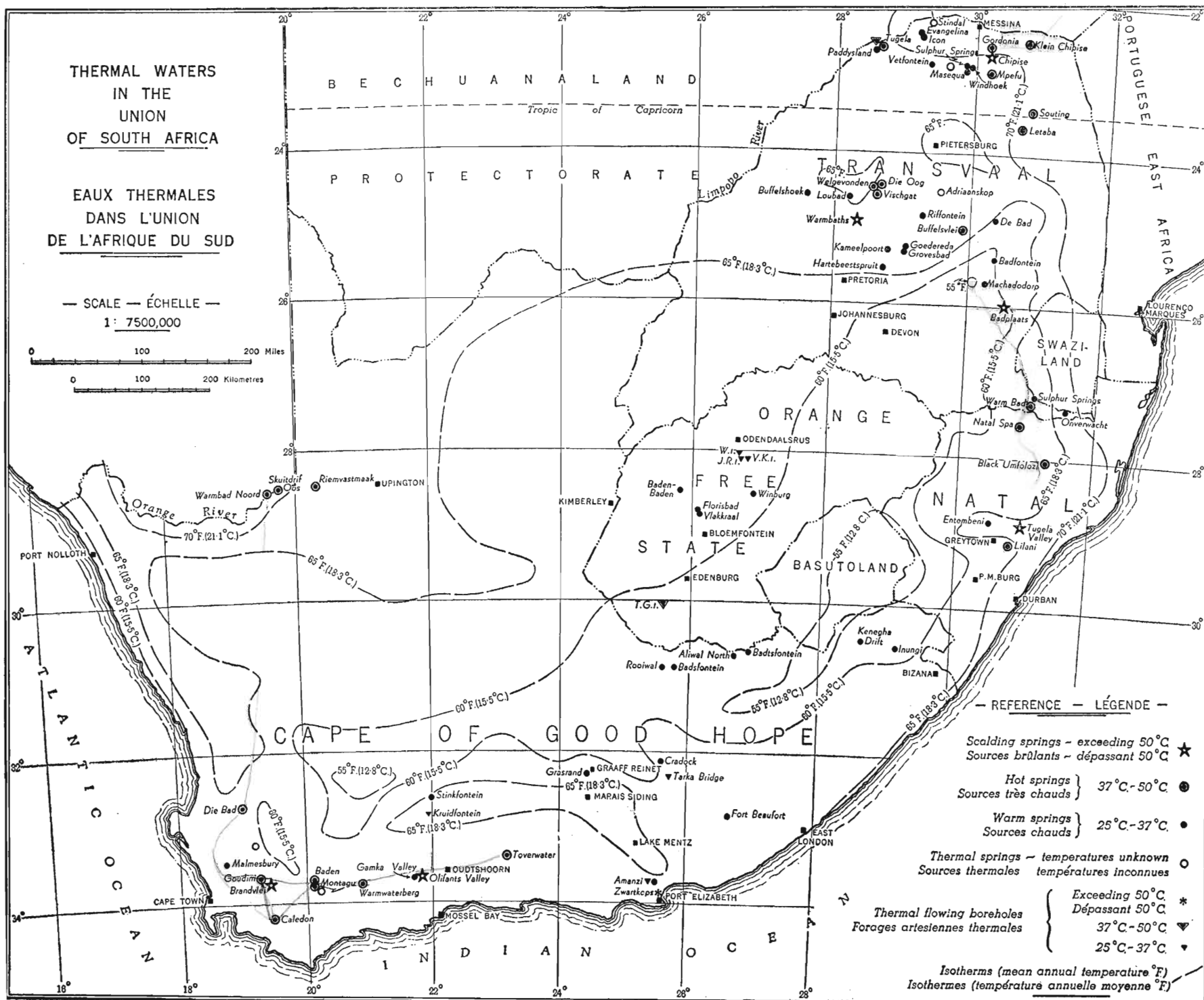
A preliminary estimate gives the combined discharge of all the thermal springs in the Union of South Africa as 8,000,000 gallons (36,290 cbm.) per day. There are few figures available from other countries that can be quoted for comparison. In the United States of America, which has an area six and a half times greater than that of the Union, the thermal springs have a daily discharge of 720,000,000 U.S. gallons. (2,719,000 cbm.)<sup>32</sup>

In the Table (pp. 235-237) the results are given of recent measurements of flow and temperature, together with geological and chemical data. Only those springs for which reliable information is available are included.

The flows of the thermal artesian boreholes are given in the Table on page 248.

### IV. CLASSIFICATION OF THERMAL WATERS ACCORDING TO CHEMICAL COMPOSITION.

The therapeutic value of thermal waters is often ascribed to constituents of relatively minor importance chemically, and waters are commonly classed as "arsenical," "lithia," "iodine," etc. Under the heading "sulphur springs" Rindl<sup>26</sup> included several containing less than 1 mgm. per litre of dissolved hydrogen sulphide and hydrosulphide ions. According to Matsuo<sup>21</sup> sulphur springs should contain at least 10 mgm. per litre of free hydrogen sulphide. It is not known if this definition has been found generally acceptable; if it has, then as far as our present knowledge goes there is only one thermal sulphur spring in



# SOUTH AFRICAN THERMAL SPRINGS.

	Spring.	Latitude °S.	Longitude °E.	Temperature °C.	Flow.		Chemical Classification (Bond System).*	Geological structure determining origin.	Observer of temperature and flow, or (reference) and date.
					Imp. Galls./ 24 hrs.	Cu. metres/ 24 hrs.			
SCALDING SPRINGS. SOURCES BRULANTS.	Brandvlei ..	33° 43'	19° 25'	64·2	2,430,000	11,022	E	Middle Cretaceous fault in Cape system (Devonian - Lower Carboniferous).	C. Preston, 1947 (flow) L. E. Kent, 1947 (temp.)
	Chipise ..	22° 37'	30° 10'	57·2	100,000	454	D, B	Intersection of two post-Permian faults in Upper Karroo.	H. N. Visser, 1948.
	Tugela valley ..	28° 52'	31° 0'	52—53	—	—	A (SO <sub>4</sub> )	Fault in Archaean amphibolites and gneisses.	T. W. Gevers, 1942.
	Warmbaths ..	24° 53'	28° 18'	51·9	160,000	726	D	Post-Karroo fault in Bushveld granite (pre-Cambrian).	(M. Rindl, 1931.)
HOT SPRINGS. SOURCES TRÈS CHAUDS.	Olifants valley ..	33° 40'	21° 46'	50—51	144,500	655	E (Fe)	Middle Cretaceous fault in Table Mountain series, Cape system.	L. E. Kent and P. G. du Plessis, 1947.
	Badplaats ..	25° 57'	30° 35'	50	180,000	817	D	Fracture in Archaean granite.	Baths Superintendent, 1948.
					<u>3,014,500</u>	<u>13,674</u>			
	Caledon ..	34° 15'	19° 27'	49	180,000	817	E (Fe)	Middle Cretaceous fault in Cape system.	(M. Rindl, 1931.)
	Warmwaterberg	33° 44'	20° 54'	45·6	174,000	789	E (Fe)	Fault at nose of anticline of Table Mountain series.	L. E. Kent, 1947.
	Warmbad Noord	28° 32'	19° 33'	44·4	15,000	68	—	Fracture zone in Archaean granodiorite.	D. J. L. Visser, 1943.
	Natal Spa ..	27° 32'	30° 52'	44·4	64,800	294	D	—	Owners, 1936.

\* Bond classes the underground waters of South Africa into five groups designated A to E. For the significance of these letters, see page 238 of this paper. The small symbols added in brackets, i.e., SO<sub>4</sub>, Fe and S, denote respectively sulphate-rich waters, chalybeatic waters, and waters containing more than 1 mgm. per litre of H<sub>2</sub>S.

# SOUTH AFRICAN THERMAL SPRINGS

	Spring.	Latitude °S.	Longitude °E.	Temperature °C.	Flow.		Chemical Classification (Bond System).	Geological structure determining origin.	Observer of temperature and flow, or (reference) and date.
					Imp. Galls./ 24 hrs.	Cu. metres/ 24 hrs.			
HOT SPRINGS. SOURCES TRÈS CHAUDS.	Toverwater ..	33° 24'	23° 10'	44·3	216,000	980	E (Fe)	Middle Cretaceous fault in Cape system.	L. E. Kent (temp.) and D. Wallace (flow), 1946.
	Welgevonden ..	24° 27'	28° 34'	44	12,500	57	—	Diabase dyke along post-Karoo (post-Permian) fault in Rooiberg felsites.	J. W. von Backström, 1938.
	Souting ..	23° 25'	30° 51'	43·9	30,000	136	A	Fault in Archaean granite.	T. W. Gevers, 1945.
	Mpefu ..	22° 55'	30° 10'	42·8, 43·7	—	—	E	Pre-Karoo (pre-Carboniferous) fault.	L. E. Kent, 1939.
	Die Bad ..	32° 45'	19° 2'	42·2-43·2	—	—	—	Barrier spring on west limb of syncline in Cape system. (See Fig. 2).	M. Rindl, 1916.
	Tugela† ..	22° 34'	28° 37'	42·8	2,650	12	A(SO <sub>4</sub> )	Joints in Archaean gneiss.	L. E. Kent, 1948.
	Letaba ..	23° 39'	30° 40'	40·4-42	91,000	413	A	Dolerite dyke in Archaean gneissic granite.	L. E. Kent, 1936-1937.
	Black Umfolosi	28° 2'	31° 18'	41	—	—	B (S)	Fissures in Dwyka tillite (U. Carboniferous) overlying Archaean rocks.	G. Molengraaff, 1898.
	Goudini ..	33° 40'	19° 16'	40·1	—	—	E	Middle Cretaceous graben in Cape system (see Fig. 2)	L. E. Kent, 1945.
	Lilani ..	29° 7'	30° 51'	38-40	—	—	D (S)	Fracture zone in Archaean gneisses and amphibolites.	A. L. du Toit, 1916.
	Die Oog ..	24° 26'	28° 37'	39·5	32,000	145	E	Diabase dyke along post-Karoo fault in Rooiberg felsites.	J. W. von Backström, 1938.
	Vischgat ..	24° 34'	28° 36'	39·5	20,000	91	—	Post-Karoo fault in Bushveld granite.	„ „
	Skuitdrif Oos ..	28° 30'	19° 43'	±38	—	—	—	Fracture zone in Archaean granite.	D. J. L. Visser, 1943.
	Gordonia ..	22° 35'	30° 10'	37·7	—	—	—	Fault in Archaean gneiss.	H. N. Visser, 1948.

† Borehole near spring flows at the rate of 15,600 galls. (71 cbm.) per 24 hours, the temperature of the water being 48·9°C.

## SOUTH AFRICAN THERMAL SPRINGS

	Spring.	Latitude °S.	Longitude °E.	Temperature °C.	Flow.		Chemical Classification (Bond System).	Geological structure determining origin.	Observer of temperature and flow, or (reference) and date.
					Imp. Galls./ 24 hrs.	Cu. metres/ 24 hrs.			
WARM SPRINGS. SOURCES CHAUDS.	Aliwal North ..	30° 43'	26° 43'	36.9	840,600	3,813	A	Dolerite dyke in Beaufort series (L. Triassic).	S. V. R. Lewis, 1927.
	Loubad ..	24° 36'	28° 11'	27.1-34.1	414,300	1,879	E	Artesian basin in Waterberg system (pre-Cambrian ?) (See Fig. 2).	L. E. Kent, 1940-1943.
	Gamka valley ..	33° 40'	21° 43'	32.3-33.2	65,500	297	E (Fe)	Middle Cretaceous fault in Table Mountain series.	L. E. Kent and P. G. du Plessis, 1947.
	Malmesbury ..	33° 28'	18° 43'	32.8	180,000	816	A (S)	Fracture zone in Cape granite (pre-Cambrian ?).	J. Muller, 1922.
	Grovesbad ..	25° 21'	29° 2'	32.8	—	—	—	Fissures in Bushveld granite.	L. E. Kent, 1942.
	Evangelina ..	22° 25'	29° 11'	32.5	—	—	A(SO <sub>4</sub> )	Diabase dyke in Archaean gneiss.	L. E. Kent and O. R. van Eeden, 1941.
	Sulphur springs	27° 11'	31° 6'	31	120,000	544	E (S)	Dolerite dykes in Beaufort series sediments.	J. K. Marais, 1946.
	Cradock ..	32° 8'	25° 27'	29-31.3	18,300	83	D (S)		L. E. Kent, 1946.
	Buffelshoek ..	24° 34'	27° 36'	30.6	17,000	77	D	Diabase dyke as barrier on artesian slope of Bushveld granite. (See Fig. 2).	L. E. Kent and H. D. Russell, 1944.
	Rcoiwal ..	30° 52'	25° 35'	30	56,000	254	D	Dolerite dyke in Beaufort series.	D. J. L. Visser, 1947.
	Badsfontein ..	30° 53'	25° 47'	25.5-30.0	51,000	231	B	Dolerite dyke in Beaufort series.	D. J. L. Visser, 1947.
	Winburg ..	28° 33'	26° 55'	29.5	4,000	18	A	—	M. Rindl, 1918.
	Vetfontein ..	22° 47'	29° 23'	29.5	—	—	—	Post-Karoo fault.	L. E. Kent, 1945.
	Knegha Drift ..	30° 28'	28° 39'	29.3	—	—	—	Dolerite dyke in Beaufort series.	L. E. Kent, 1947.
	Riffontein ..	24° 50'	29° 18'	28.3-29.0	8,000	36	A-B	Fault in Rooiberg series (pre-Cambrian).	L. E. Kent, 1942, and J. T. Wessels, 1948.
	Machadodorp ..	25° 39'	30° 15'	27.5-28.5	45,000	204	D	—	(M. Rindl, 1916.)
	Fort Beaufort ..	32° 50'	26° 40'	27.0-29.0	17,300	79	D (S)	Fissure in Beaufort series.	L. E. Kent, 1947.
	Stinkfontein ..	32° 40'	21° 59'	28.7	7,500	34	D (S)	Major joint in syncline of L. Beaufort sediments.	L. E. Kent, 1949.
	Etembeni ..	28° 51'	30° 29'	28	—	—	—	Dolerite sill in Ecca series (Permian) shales.	A. L. du Toit, 1931.
	Grasrand ..	32° 19'	24° 27'	26	3,600	16	B	Joints in L. Beaufort sediments.	L. E. Kent, 1949.



South Africa, Stinkfontein in the Cape Province. In special samples taken at various springs smelling quite strongly of hydrogen sulphide this fugitive constituent was fixed immediately as cadmium sulphide. Despite this precaution the highest figures obtained for dissolved hydrogen sulphide were 16.0 and 6.2 mgm. per litre—for the springs at Stinkfontein and near Fort Beaufort respectively. At Badplaats and Zwartkops, where the odour of hydrogen sulphide is only very slight, analyses showed only 0.2 and 0.5 mgm. per litre of the dissolved gas respectively.

In view of the importance attached by balneotherapists to the presence of dissolved hydrogen sulphide in waters, the following definitions are suggested:—

Sulphuretted waters contain over 10 mgm. per litre dissolved  $H_2S$  (including  $HS'$ )

Moderately sulphuretted waters contain between 5 and 10 mgm. per litre dissolved  $H_2S$  (including  $HS'$ )

Slightly sulphuretted waters contain between 1 and 5 mgm. per litre dissolved  $H_2S$  (including  $HS'$ )

Sulphurous waters, i.e. those containing dissolved sulphur dioxide, are not known from South Africa, but the same limiting values could be used.

Waters that deposit hydroxides of iron present rather a difficult problem as regards classification. The  $Fe^{++}$  content of these so-called chalybeate springs is often surprisingly low. A recent series of analyses gave values of 0.7, 2.3, 2.9, 3.8, and 7.7 mgm. per litre for the  $Fe^{++}$  content of the Warmwaterberg, Olifants valley, Caledon, Zwartkops, and Gamka valley springs respectively. Manganese is actually present in slight excess over iron in the Warmwaterberg, Caledon and Olifants valley thermal waters.

The iron is almost certainly present as ferrous bicarbonate, and, as is well known, such waters seldom contain more than 30 mgm. per litre of  $Fe^{++}$ . Sulphate waters, on the other hand, may contain as much as 1 gm. per litre of  $Fe^{++}$  in the form of ferrous sulphate. The only thermal springs of this latter type known in the Union are at Amanzi<sup>8</sup> (Balmoral), near Port Elizabeth, and Inungi; their waters contain 48.5 and 52.9 mgm. per litre of  $Fe^{++}$  respectively.<sup>16</sup>

With the exception of these two it is proposed to term the iron-depositing springs "chalybeatic" rather than "chalybeate."

In his "Geochemical Survey of the Underground Water Supplies of the Union of South Africa," published in 1946, Bond<sup>2</sup> recognised five distinct classes:

- A—Highly mineralised Chloride-Sulphate waters.  
Total solids > 1,000 mgm. per litre.  $Cl' > 27$  per cent.  $SO_4'' > 5$  per cent.
- B—Slightly saline Chloride Waters.  
Total solids > 300 < 500 mgm. per litre.  $Cl' > 27$  per cent.  $SO_4'' < 3$  per cent.
- C—Temporary hard Carbonate Waters.  
Total solids < 800 mgm. per litre.  $pH > 7.6$ .
- D—Alkaline Soda Carbonate Waters.  
Total solids < 1,000 mgm. per litre.  
 $Na_2CO_3$  or  $NaHCO_3 > 15$  per cent. Permanent hardness, nil.
- E—"Pure" Waters.  
Total solids < 150 mgm. per litre.  $pH < 7.1$ .

Bond's<sup>2</sup> investigations were mainly in connection with the utilisation of underground water in power production and industry, and his analyses thus are not detailed and are expressed in accordance with technological conventions.

However, as his Memoir includes the first map showing the distribution of various types of underground water in the Union of South Africa, it was thought advisable not to depart from his scheme of classification. It was though slightly modified to enable waters with total dissolved solids up to 200 mgm. per litre to be placed in group "E."

#### V. NOTES ON THE WATER ANALYSES.

The Tables facing page 240 contain twenty-five analyses representative of the various types of thermal water occurring in South Africa. Three are from deep, artesian boreholes, the remainder of springs. Several were made expressly for this paper, and no less than seventeen have not been previously published.\* They have all been recalculated, when necessary, in terms of mgm. of ions per litre, and the millinormalities (N/1,000) have been worked out. This follows the recommendations of the International Society of Medical Hydrology (I.S.M.). One departure from the Society's recommendations has been the determination whenever possible of both  $\text{CO}_3''$  and  $\text{HCO}_3'$ . A review of the literature showed that most chemists return the total carbonate as either  $\text{CO}_3''$  or  $\text{HCO}_3'$ . Several of our thermal waters contain both (e.g. Badplaats, Chipise, and the alkaline Upper Karroo springs), and separate determination is essential in waters of fairly high pH.

The place to be assigned to silica is problematical. Analysts return it variously as  $\text{SiO}_2$ ,  $\text{SiO}_3''$ ,  $\text{H}_2\text{SiO}_3$ ,  $\text{HSiO}_3'$ , etc.; but these are mere conventions and, as a rule, no definite reason can be given for the selection of one as opposed to another. The point is of great importance, for if the silica is present as  $\text{SiO}_3''$  or  $\text{HSiO}_3'$  it should be included amongst the anions.

From a study of recent chemical literature Roy<sup>30</sup> has concluded that at the concentrations characteristic of natural surface waters silica is probably present in the ionic condition. This is probably so at low concentrations only, of the order of 10 mgm. of silica per litre. Stumfer<sup>34</sup>, for example, found that at concentrations of up to 5 mgm. per litre all the silica was molecularly dispersed, but that above this limiting figure there was an increasing proportion of "colloidal" silica. For thermal springs with rather high silica contents the dialysis experiments of Fresenius<sup>12</sup> suggest that the silica is probably present as di-silicic acid ( $\text{H}_2\text{Si}_2\text{O}_5$ ), and that only a small fraction of up to 1 per cent. is colloidal. Unlike most chemists who have done research on the state of silica dissolved in water Fresenius worked not on artificial solutions, but with actual spring waters having  $\text{SiO}_2$  contents ranging from 33.2 to 180.2 mgm. per litre.

The present analyses show that the content of silica, expressed as  $\text{SiO}_2$ , ranges from 11.0 to 86.0 mgm. per litre. In nearly all of the waters with a high pH value (i.e. the alkaline waters) the total millinormality of the anions exceeds

\* Those credited to Messrs. W. Sunkel, P. Kok, C. F. J. van der Walt, C. J. Liebenberg and H. S. Schoeman were made in the laboratories of the Division of Chemical Services, Department of Agriculture. Those by Messrs. J. Gray, J. Muller and McLachlan and Lazar, consulting chemists, are included by kind permission. The remainder were taken from Dr. Rindl's publications.<sup>26</sup>

that of the cations; silica can thus hardly be present as anions or the ionic balance would be completely disturbed. In the neutral or only slightly alkaline waters, on the other hand, there is generally a deficiency of anions and some of the silica may be present in the form of ions. Unfortunately no acidic thermal spring waters are known in South Africa. It is interesting to note that Diénert and Wandenbulcke<sup>6</sup>, working with made-up solutions of sea water, found in neutral and alkaline solutions that the conversion of colloidal to non-colloidal silica is accelerated, but acids tend to prevent conversion. The conclusion reached was that in natural waters silica is almost exclusively non-colloidal, because the alkaline carbonates in the water would convert any colloidal silica to the non-colloidal form. Another possibility is that complexes may be present, in which silica is linked with elements like fluorine.

This line of argument is only valid if the cations are accurately determined. In many cases analysts arrive at their Na' figures by calculations based on the linking of positive and negative ions to form hypothetical salts. In several of the waters the Na' (and incidentally also the Mg'') was also determined gravimetrically by Mr. E. C. Haumann of the Division of Chemical Services, Pretoria. His results agreed remarkably closely with those previously obtained by calculation, as is shown by the following examples:—

Water.	Na (calculated).	Na (gravimetrically).
Warmwaterberg .. .. .	18.9 mgm. per litre	22.3 mgm. per litre
Zwartkops .. .. .	141.8 " "	145.4 " "
Riffontein .. .. .	234.7 " "	233.5 " "
T.G.I. (Trompsburg) .. ..	2,629 " "	2,665.3 " "

After a consideration of all these facts it was decided to express the total dissolved silica as  $\text{SiO}_2$ , the form in fact in which it was determined by the gravimetric method employed in the Government laboratories. To show the effect of regarding it as being present in the form of ions, millinormalities have been calculated as if it were present as  $\text{SiO}_3$ ".

The figures for dissolved hydrogen sulphide in the recent analyses (credited to W. Sunkel and P. Kok) are quite reliable, as special samples were taken in which it was immediately fixed as insoluble cadmium sulphide.

The chalybeatic waters deposited ferric hydrates in the bottles en route to Pretoria. Thus the pH values determined by the analysts do not refer to the water as discharged by the springs. The iron and accompanying aluminium were returned as oxides by the analysts; in the Tables they are expressed as ions, but the millinormalities are enclosed in brackets to show that these items were not in solution when analysed. In the waters from Warmwaterberg, Fort Beaufort, Olifants valley, and Natal spa the total amount of iron and aluminium oxides did not exceed 4 mgm. per litre, and they were not returned separately. To arrive at an approximately figure for the millinormality it was assumed that half consisted of iron oxide.

Fluorine was determined in most of the waters. It ranges from mere traces up to 13.2 mgm. per litre. It is often present in fairly large amounts in borehole waters in South Africa,<sup>2</sup> and its presence can no longer be assumed to indicate juvenile origin.

# ANALYSES OF SOUTH AFRICAN THERMAL WATERS.

Locality.	Natal Spa, Natal.		Badplaats, Transvaal.		Evangelina, Transvaal.		Tugela, Transvaal.		Paddysland, Transvaal.		Sulphur Springs, Transvaal.		Machadodorp, Transvaal.		Die Oog, Transvaal.		Riffontein, Transvaal.	
Formation.	Archaean granite.		Archaean granite.		Archaean gneiss.		Archaean gneiss.		Archaean hornblende-gneiss.		Pongola system.		Pretoria series.		Rooiberg series (felsites).		Rooiberg series.	
Temperature of water °C. ..	44·4		50·0		32·5		40—41		26		31		27·5—28·5		39·5		28·3—29·0	
Ions	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre†	N/1,000	mgm. per litre†	N/1,000	mgm. per litre	N/1,000
NH <sub>4</sub> <sup>+</sup> .. .. .	0·05	0·003	nil	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	0·1	0·006	nil	—
Li <sup>+</sup> .. .. .	n.d.	—	n.d.	—	tr.	—	nil	—	nil	—	nil	—	0·35	0·050	0·074	0·011	n.d.	—
Na <sup>+</sup> .. .. .	75·7	3·29	119·1	5·18	343·8	14·95	364·3	15·84	98·7	4·29	26·5	1·15	54·7	2·38	46·4	2·02	235·0	10·22
K <sup>+</sup> .. .. .	n.d.	—	3·7	0·092	n.d.	—	6·6	0·17	5·8	0·15	n.d.	—	2·0	0·051	0·38	0·010	6·0	0·18
Mg <sup>++</sup> .. .. .	1·5	0·13	1·8	0·15	29·4	2·43	0·6	0·05	56·7	4·66	2·0	0·17	3·2	0·27	0·84	0·070	3·0	0·25
Ca <sup>++</sup> .. .. .	5·7	0·29	8·0	0·40	78·8	3·94	123·7	6·18	58·6	2·93	4·7	0·23	12·8	0·64	18·6	0·93	30·1	1·51
Al <sup>+++</sup> .. .. .	2·5	(0·18)	n.d.	—	0·53	0·06	nil	—	nil	—	nil	—	1·5	(0·10)	n.d.	—	n.d.	—
Fe <sup>++</sup> .. .. .			n.d.	—	1·4	0·05	tr.	—	tr.	—	1·2	0·043			n.d.	—	tr.	—
Mn <sup>++</sup> .. .. .			nil	—	n.d.	—	n.d.	—	n.d.	—	nil	—			n.d.	—	nil	—
Sum of cations .. .. .	85·45	3·893	132·6	5·822	453·93	21·43	495·2	22·24	219·8	12·03	34·4	1·593	74·55	3·491	66·394	3·047	274·1	12·16
F <sup>-</sup> .. .. .	n.d.	—	10·5	0·55	3·2	0·17	0·4	0·021	4·0	0·21	nil	—	n.d.	—	5·7	0·30	8·8	0·46
Cl <sup>-</sup> .. .. .	46·0	1·30	134·9	3·80	443·0	12·49	418·0	11·79	106·0	2·99	5·0	0·14	52·2	1·49	24·8	0·70	248·5	7·01
Br <sup>-</sup> .. .. .	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	nil	—	n.d.	—
NO <sub>3</sub> <sup>-</sup> .. .. .	nil	—	nil	—	n.d.	—	n.d.	—	n.d.	—	0·56	0·009	n.d.	—	0·01	0·0002	nil	—
SO <sub>4</sub> <sup>==</sup> .. .. .	23·4	0·49	24·0	0·50	215·9	4·49	503·9	10·49	16·8	0·35	7·0	0·15	5·3	0·11	8·2	0·17	38·4	0·80
PO <sub>4</sub> <sup>===</sup> .. .. .	n.d.	—	n.d.	—	nil	—	nil	—	nil	—	nil	—	n.d.	—	nil	—	n.d.	—
HCO <sub>3</sub> <sup>-</sup> .. .. .	—	—	33·6	0·55	191·3	3·14	27·0	0·44	506·0	8·30	—	—	54·9	0·90	109·8	1·80	237·9	3·90
CO <sub>3</sub> <sup>==</sup> .. .. .	54·6†	1·82	18·0	0·60	—	—	—	—	—	—	39·0†	1·30	—	—	—	—	nil	—
Sum of anions .. .. .	124·0	3·61	221·0	6·00	853·4	20·29	949·3	22·741	632·8	11·85	51·56	1·599	112·5*	2·503	148·51	2·9702	533·6	12·17
SiO <sub>2</sub> (with N/1,000 as SiO <sub>3</sub> <sup>==</sup> ) ..	63·2	2·11	55·0	1·83	48·2	1·61	73·0	2·43	86·0	2·87	44·0	1·47	26·7	0·89	42·0	1·40	48·2	1·61
Dissolved H <sub>2</sub> S .. .. .	n.d.	—	0·21	—	nil	—	nil	—	nil	—	nd.	—	0·67	—	nil	—	nil	—
Total sum of items .. .. .	272·65	—	408·81	—	1,355·53	—	1,517·5	—	938·6	—	129·96	—	214·42	—	256·904	—	855·9	—
NaHCO <sub>3</sub> .. .. .	—	—	—	—	n.d.	—	n.d.	—	n.d.	—	nd.	—	nd.	—	nd.	—	202	—
Na <sub>2</sub> CO <sub>3</sub> .. .. .	—	—	32	—	n.d.	—	n.d.	—	n.d.	—	—	—	—	—	—	—	nil	—
pH .. .. .	n.d.		8·95		7·15		7·85		7·45		9·1		n.d.		n.d.		7·8	
Sought but not found .. .. .	NO <sub>2</sub> <sup>-</sup>		NO <sub>2</sub> <sup>-</sup>		Cu, SO <sub>3</sub> <sup>==</sup> , B		Cu, B		Cu, B		Ba <sup>++</sup> , Sr <sup>++</sup> , NO <sub>2</sub> <sup>-</sup> , B		—		Cr, As, Br <sup>-</sup> .		NO <sub>2</sub> <sup>-</sup>	
Date and Analyst .. .. .	c. 1946, J. Gray		1948, W. Sunkel & P. Kok		1941, C. J. Liebenberg		1941, C. F. J. van der Walt		1941, C. F. J. van der Walt		1946, Messrs. McLachlan and Lazar		1913, P. D. Hahn		1939, C. F. J. van der Walt		1948, W. Sunkel and P. Kok	

† Total Carbonates expressed as CO<sub>3</sub><sup>==</sup>.

\* Includes 0·10 mgm. per litre of SH<sup>-</sup> with N/1,000=0·003.

‡ Also determined—CuO 0·016, and B 0·08 mgm. per litre.

Locality.	Warmbaths, Transvaal.		Buffelshoek, Transvaal.		Malmesbury, C.P.		Loubad, Transvaal.		Brandvlei, C.P.		Warmwaterberg, C.P.		Olifants valley, C.P.		Zwartkops, C.P. (borehole).	
Formation.	Bushveld granite.		Bushveld granite (see p. 255).		Cape granite.		Waterberg system.		Cape system.		Table Mt. series.		Table Mt. series.		Cape system (see p. 257).	
Temp. of water °C.	51·9		30·6		32·9		32·4-33·0		64·2		45·6		50-51		54·5	
Ions	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000
NH <sub>4</sub> ·	n.d.	—	n.d.	—	n.d.	—	nil	—	nil	—	nil	—	nil	—	nil	—
Li·	n.d.	—	nil	—	n.d.	—	nil	—	nil	—	n.d.	—	n.d.	—	n.d.	—
Na·	132·5	5·76	151·6	6·59	371·3	16·15	8·2	0·36	14·5	0·63	22·3	0·79	23·0	1·00	145·8	6·30
K·	2·9	0·07	5·7	0·15	tr.	—	2·8	0·07	2·3	0·06	8·9	0·23	8·9	0·23	10·2	0·26
Mg·	1·8	0·15	4·7	0·39	3·8	0·31	5·6	0·46	1·0	0·082	6·0	0·49	6·1	0·50	16·4	1·35
Ca·	13·0	0·65	27·1	1·35	51·6	2·58	26·4	1·32	2·9	0·15	18·0	0·90	12·0	0·60	10·0	0·50
Ba·	n.d.	—	n.d.	—	n.d.	—	nil	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Al·	n.d.	—	nil	—	1·5	0·17	tr.	—	0·85	0·094	} 0·6	(0·04)	} 2·1	(0·15)	2·8	(0·31)
Fe·	n.d.	—	nil	—	0·77	0·028	tr.	—	0·14	0·005					3·2	(0·11)
Mn·	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	0·9	(0·033)	2·9	(0·11)	1·0	(0·036)
Sum of cations	150·2	6·63	189·1	8·48	428·97	19·238	43·0	2·21	21·69	1·021	56·7	2·663	55·0	2·59	189·4	8·866
F'	11·0	0·58	6·6	0·35	n.d.	—	0·49	0·03	nil	—	0·20	0·015	0·30	0·016	0·50	0·036
Cl'	85·2	2·40	138·5	3·91	561·1	15·81	3·6	0·10	16·5	0·47	37·3	1·05	37·6	1·06	237·9	6·71
Br'	n.d.	—	n.d.	—	0·91	0·011	n.d.	—	nil	—	n.d.	—	n.d.	—	nil	—
NO <sub>3</sub> '	nil	—	nil	—	n.d.	—	nil	—	nil	—	nil	—	nil	—	nil	—
SO <sub>4</sub> '	12·1	0·25	35·1	0·73	52·2	1·09	tr.	—	2·8	0·06	10·6	0·22	12·0	0·25	33·6	0·70
PO <sub>4</sub> '	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	0·4	0·013
HCO <sub>3</sub> '	—	—	213·5	3·50	79·7	1·31	122·0	2·00	24·2	0·40	85·4	1·40	61·0	1·00	82·4	1·36
CO <sub>3</sub> '	102·0*	3·40	nil	—	—	—	nil	—	—	—	nil	—	nil	—	nil	—
Sum of anions	210·3	6·63	393·7	8·49	693·91	18·221	126·09	2·13	43·5	0·93	133·5	2·685	110·9	2·326	354·8	8·819
SiO <sub>2</sub> (with N/1,000 as SiO <sub>3</sub> '")	48·2	1·61	44·8	1·49	56·0	1·86	18·9	0·63	29·5	0·982	15·0	0·50	31·0	1·12	18·0	0·60
Dissolved H <sub>2</sub> S	nil	—	nil	—	7·44	—	nil	—	nil	—	nil	—	nil	—	0·53	—
Total sum of items	408·7	—	627·6	—	1186·32	—	187·99	—	94·69	—	205·2	—	196·9	—	562·73	—
NaHCO <sub>3</sub>	—	—	—	—	—	—	—	—	—	—	16·8	—	nil	—	nil	—
Na <sub>2</sub> CO <sub>3</sub>	137·8	—	93·3	—	—	—	15·9	—	9·5	—	nil	—	nil	—	nil	—
pH	8·65		7·1		n.d.		7·20		n.d.		7·5		7·35		6·95	
Sought but not found	—		—		—		NO <sub>2</sub> ', AsO <sub>4</sub> '		NO <sub>2</sub> ', I'		—		—		—	
Date and Analyst	1940, W. Sunkel		1944, W. Sunkel		1922, J. Muller		1941, C. F. J. van der Walt		1946, J. Muller		1947, W. Sunkel and P. Kok		1947, W. Sunkel and P. Kok		1948, W. Sunkel and P. Kok	

\* Total carbonates expressed as CO<sub>3</sub>'.

Locality	J.R.I. nr. Oden- daalsrus, O.F.S. (borehole).		T.G.I. nr. Tromps- burg, O.F.S. (borehole).		Florisbad, O.F.S.		Stinkfontein, C.P.		Cradock, C.P.		Fort Beaufort, C.P.		Aliwal North, C.P.		Chipise, Transvaal.	
Formation	Ventersdorp system (lavas) (see pp. 248 & 253).		Pre-Karoo norite (see pp. 248 & 253).		Ecca series.		Beaufort series (Lower stage).		Beaufort series (Lower stage).		Beaufort series (Lower stage).		Beaufort series (Upper stage).		Karoo system (see p. 253).	
Temp. of water °C.	34		37·2		28-30		28·7		29·0-31·3		27·0-29·0		36·9		65	
Ions	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000
NH <sub>4</sub> ·	n.d.	—	nil	—	0·62	0·035	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Li·	n.d.	—	n.d.	—	0·69	0·099	n.d.	—	nil	—	n.d.	—	2·3	0·33	n.d.	—
Na·	1246·0	54·20	2665·3	115·88	744·1	32·35	209	9·12	49·9	2·17	163·7	7·12	344·5	14·98	140·9	6·13
K·	9·0	0·23	16·1	0·41	nil	—	3	0·08	0·6	0·015	2·2	0·051	6·2	0·16	2·2	0·06
Mg·	7·3	0·60	20·0	1·65	0·79	0·065	15	1·25	0·6	0·049	3·0	0·25	5·5	0·46	1·3	0·11
Ca·	97·8	4·88	473·2	23·66	93·4	4·66	4	0·20	3·0	0·150	11·0	0·55	83·8	4·19	6·0	0·30
Sr·	n.d.	—	7·2	0·16	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Ba·	n.d.	—	n.d.	—	0·74	0·011	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Al·	n.d.	—	n.d.	—	0·85	0·094	nil	—	nil	—	n.d.	—	7·3	0·81	n.d.	—
Fe·	n.d.	—	n.d.	—	0·33	0·012	nil	—	nil	—	1·2	(0·09)	n.d.	—	1·4	0·05
Sum of cations	1360·1	59·91	3181·8	141·76	841·52	37·326	231	10·65	54·1	2·384	181·1	8·061	449·6	20·93	151·8	6·65
F·	1·0	0·053	3·6	0·19	n.d.	—	6·0	0·32	5·8	0·30	13·2	0·69	n.d.	—	n.d.	—
Cl·	2101·6	59·27	4245·8	119·74	1304·6	36·79	82	2·31	24·9	0·70	189·9	5·36	605·3	17·05	139·1	3·92
Br·	n.d.	—	nil	—	n.d.	—	n.d.	—	n.d.	—	nil	—	1·6	0·02	n.d.	—
I·	n.d.	—	n.d.	—	tr.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
NO <sub>3</sub> ·	nil	—	nil	—	0·38	0·006	nil	—	n.d.	—	nil	—	n.d.	—	tr.	—
SO <sub>4</sub> ·	13·5	0·28	946·2	19·70	2·3	0·047	163	3·40	16·8	0·35	36·0	0·75	68·6	1·43	27·6	0·57
PO <sub>4</sub> ·	n.d.	—	n.d.	—	tr.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
HCO <sub>3</sub> ·	48·8	0·80	nil	—	18·7	0·31	268	4·39	9·8	0·16	39·7	0·65	29·4	0·48	103·5	1·70
CO <sub>3</sub> ·	nil	—	60·0	2·00	—	—	12	0·40	27·0	0·90	16·8	0·56	44·2	1·47	12·0	0·40
Sum of anions	2164·9	60·403	5255·6	141·63	1325·98	37·153	531	10·82	84·3	2·41	295·6	8·01	749·1	20·45	282·2	6·59
SiO <sub>2</sub> (with N/1,000 as SiO <sub>3</sub> ·)	11·0	0·36	26·0	0·86	21·9	0·74	28	0·92	40·2	1·34	37·0	1·23	14·8	0·49	66·7	2·22
Dissolved H <sub>2</sub> S	—	—	—	—	tr.	—	16	—	2·3	—	6·2	—	0·79	—	1·6*	—
Total sum of items	3536·0	—	8463·4	—	2189·4	—	806	—	180·9	—	519·9	—	1214·19	—	502·3	—
NaHCO <sub>3</sub>	nil	—	nil	—	—	—	252	—	—	—	84	—	—	—	—	—
Na <sub>2</sub> CO <sub>3</sub>	nil	—	nil	—	—	—	21	—	—	—	30	—	—	—	—	—
pH	8·25	—	8·95	—	n.d.	—	9·1	—	9·6	—	9·0	—	n.d.	—	n.d.	—
Sought but not found	—	—	Mn·, NO <sub>2</sub> ·	—	Rb, Cs (sp.)	—	NO <sub>2</sub> ·	—	—	—	Mn·	—	—	—	—	—
Date and Analyst	1947, W. Sunkel and P. Kok	—	1948, W. Sunkel and P. Kok	—	1916, M. M. Rindl	—	1948, W. Sunkel	—	1946, W. Sunkel and P. Kok	—	1947, W. Sunkel and P. Kok	—	c. 1913, P. D. Hahn	—	1944, H. S. Schoeman	—

\* From a 1938 analysis.

Of interest is the occurrence of 7.2 mgm. per litre of  $\text{Sr}^{++}$  in the water from a deep borehole near Trompsburg in the Orange Free State. It amounts, however, to only 0.09 per cent. of the total dissolved solids.

Saline residues obtained by evaporation were referred for spectrographic analysis to Dr. B. Wasserstein of the Geological Survey, whose report follows. The four waters from the Cape system and the water from the spring at Fort Beaufort deposited iron and aluminium hydroxides before the samples reached the analyst. The deposits had to be removed from the bottles by acids and thus could not be included in the water taken to dryness. Such elements as Cu, Mn, Ba, and As would be precipitated together with the hydroxides, and for this reason the spectrographic data may be incomplete.

#### VI. SPECTROGRAPHIC DATA ON RESIDUES FROM THERMAL WATERS BY B. WASSERSTEIN.

The soluble solids obtained from evaporating the waters analysed by the Division of Chemical Services were subjected to qualitative spectrochemical analysis. The results are listed in the Table on page 243, and as a quantitative guide the intensity of each element-line has been visually estimated using an arbitrary scale from zero to 10. This allows a comparison vertically, and to a lesser extent horizontally, between the elements Pb, Mo, Li, Ba and possibly Mn, as their limits of detection are similar, viz. 0.002 per cent. or 0.003 per cent. of the solid. For Al the sensitivity is much less, perhaps not better than 0.3 per cent., whereas for Sr, it is much greater, probably 0.0001 per cent.—these two elements can certainly only be compared vertically in their respective columns.

In order to be able to judge the "order of magnitude" of the more important components, mixtures were synthesised with pure sodium chloride as a base—this was the commonest major component, by far, in the waters examined here. The mixtures made contained respectively 1 per cent.; 0.1 per cent.; 0.01 per cent.; and 0.001 per cent. of the elements Pb, Mo, Li, Sr, and Ba. They were arced a number of times and the intensities noted for the different concentrations; these observations served as a basis for approximate quantitative estimation. It was found, for example, that an intensity of "3" corresponded to the presence of about 0.1 per cent. of Li, Mo, and Pb. For Ba, the same intensity denoted a slightly smaller amount but for Sr, a very much smaller amount, of the order 0.005 per cent.

Many more elements were sought than have been listed; some could not be found for reasons that cannot be elaborated here, and other omissions of results are due to possibilities of contamination; e.g. Zn was found in all the five waters from the Odendaalsrus area—no doubt derived from the galvanised lining of the boreholes. Very small amounts of Cr were found in most residues, but these results were discarded as experience has shown that chrome spatulas when used in scraping the residue from an evaporating dish, can cause contamination. In fairness to the chemists it must be stated that spectrochemical work was not envisaged. A few results on boron have been included, although at least some of this element was furnished by the glass containers.

ANALYSES OF SOUTH AFRICAN THERMAL WATERS.

Locality.	Natal Spa, Natal.		Badplaats, Transvaal.		Evangelina, Transvaal.		Tugela, Transvaal.		Paddysland, Transvaal.		Sulphur Springs, Transvaal.		Machadodorp, Transvaal.		Die Oog, Transvaal.		Riffontein, Transvaal.	
Formation.	Archaean granite.		Archaean granite.		Archaean gneiss.		Archaean gneiss.		Archaean hornblende-gneiss.		Pongola system.		Pretoria series.		Rooiberg series (felsites).		Rooiberg series.	
Temperature of water °C. ..	44·4		50·0		32·5		40—41		26		31		27·5—28·5		39·5		28·3—29·0	
Ions	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre†	N/1,000	mgm. per litre†	N/1,000	mgm. per litre	N/1,000
NH <sub>4</sub> · .. .. .	0·05	0·003	nil	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	0·1	0·006	nil	—
Li· .. .. .	n.d.	—	n.d.	—	tr.	—	nil	—	nil	—	nil	—	0·35	0·050	0·074	0·011	n.d.	—
Na· .. .. .	75·7	3·29	119·1	5·18	343·8	14·95	364·3	15·84	98·7	4·29	26·5	1·15	54·7	2·38	46·4	2·02	235·0	10·22
K· .. .. .	n.d.	—	3·7	0·092	n.d.	—	6·6	0·17	5·8	0·15	n.d.	—	2·0	0·051	0·38	0·010	6·0	0·18
Mg·· .. .. .	1·5	0·13	1·8	0·15	29·4	2·43	0·6	0·05	56·7	4·66	2·0	0·17	3·2	0·27	0·84	0·070	3·0	0·25
Ca·· .. .. .	5·7	0·29	8·0	0·40	78·8	3·94	123·7	6·18	58·6	2·93	4·7	0·23	12·8	0·64	18·6	0·93	30·1	1·51
Al·· .. .. .	} 2·5	(0·18)	n.d.	—	0·53	0·06	nil	—	nil	—	nil	—	} 1·5	(0·10)	n.d.	—	n.d.	—
Fe·· .. .. .			n.d.	—	1·4	0·05	tr.	—	tr.	—	1·2	0·043			n.d.	—	tr.	—
Mn·· .. .. .			nil	—	n.d.	—	n.d.	—	n.d.	—	nil	—			n.d.	—	nil	—
Sum of cations .. .. .	85·45	3·893	132·6	5·822	453·93	21·43	495·2	22·24	219·8	12·03	34·4	1·593	74·55	3·491	66·394	3·047	274·1	12·16
F' .. .. .	n.d.	—	10·5	0·55	3·2	0·17	0·4	0·021	4·0	0·21	nil	—	n.d.	—	5·7	0·30	8·8	0·46
Cl' .. .. .	46·0	1·30	134·9	3·80	443·0	12·49	418·0	11·79	106·0	2·99	5·0	0·14	52·2	1·49	24·8	0·70	248·5	7·01
Br' .. .. .	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	nil	—	n.d.	—
NO <sub>3</sub> ' .. .. .	nil	—	nil	—	n.d.	—	n.d.	—	n.d.	—	0·56	0·009	n.d.	—	0·01	0·0002	nil	—
SO <sub>4</sub> '' .. .. .	23·4	0·49	24·0	0·50	215·9	4·49	503·9	10·49	16·8	0·35	7·0	0·15	5·3	0·11	8·2	0·17	38·4	0·80
PO <sub>4</sub> ''' .. .. .	n.d.	—	n.d.	—	nil	—	nil	—	nil	—	nil	—	n.d.	—	nil	—	n.d.	—
HCO <sub>3</sub> ' .. .. .	—	—	33·6	0·55	191·3	3·14	27·0	0·44	506·0	8·30	—	—	54·9	0·90	109·8	1·80	237·9	3·90
CO <sub>3</sub> '' .. .. .	54·6†	1·82	18·0	0·60	—	—	—	—	—	—	39·0†	1·30	—	—	—	—	nil	—
Sum of anions .. .. .	124·0	3·61	221·0	6·00	853·4	20·29	949·3	22·741	632·8	11·85	51·56	1·599	112·5*	2·503	148·51	2·9702	533·6	12·17
SiO <sub>2</sub> (with N/1,000 as SiO <sub>3</sub> ··) .. .. .	63·2	2·11	55·0	1·83	48·2	1·61	73·0	2·43	86·0	2·87	44·0	1·47	26·7	0·89	42·0	1·40	48·2	1·61
Dissolved H <sub>2</sub> S .. .. .	n.d.	—	0·21	—	nil	—	nil	—	nil	—	nd.	—	0·67	—	nil	—	nil	—
Total sum of items .. .. .	272·65	—	408·81	—	1,355·53	—	1,517·5	—	938·6	—	129·96	—	214·42	—	256·904	—	855·9	—
NaHCO <sub>3</sub> .. .. .	—	—	—	—	n.d.	—	n.d.	—	n.d.	—	nd.	—	nd.	—	nd.	—	202	—
Na <sub>2</sub> CO <sub>3</sub> .. .. .	—	—	32	—	n.d.	—	n.d.	—	n.d.	—	—	—	—	—	—	—	nil	—
pH .. .. .	n.d.		8·95		7·15		7·85		7·45		9·1		n.d.		n.d.		7·8	
Sought but not found .. .. .	NO <sub>2</sub> '		NO <sub>2</sub> '		Cu, SO <sub>3</sub> '', B		Cu, B		Cu, B		Ba··, Sr··, NO <sub>2</sub> ', B		—		Cr, As, Br'.		NO <sub>2</sub> '	
Date and Analyst .. .. .	c. 1946, J. Gray		1948, W. Sunkel & P. Kok		1941, C. J. Liebenberg		1941, C. F. J. van der Walt		1941, C. F. J. van der Walt		1946, Messrs. McLachlan and Lazar		1913, P. D. Hahn		1939, C. F. J. van der Walt		1948, W. Sunkel and P. Kok	

† Total Carbonates expressed as CO<sub>3</sub>''. \* Includes 0·10 mgm. per litre of SH' with N/1,000=0·003. ‡ Also determined—CuO 0·016, and B 0·08 mgm. per litre.



Locality.	Warmbaths, Transvaal.		Buffelshoek, Transvaal.		Malmesbury, C.P.		Loubad, Transvaal.		Brandvlei, C.P.		Warmwaterberg, C.P.		Olifants valley, C.P.		Zwartkops, C.P. (borehole).	
Formation.	Bushveld granite.		Bushveld granite (see p. 255).		Cape granite.		Waterberg system.		Cape system.		Table Mt. series.		Table Mt. series.		Cape system (see p. 257).	
Temp. of water °C.	51·9		30·6		32·9		32·4-33·0		64·2		45·6		50-51		54·5	
Ions	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000
NH <sub>4</sub> ·	n.d.	—	n.d.	—	n.d.	—	nil	—	nil	—	nil	—	nil	—	nil	—
Li·	n.d.	—	nil	—	n.d.	—	nil	—	nil	—	n.d.	—	n.d.	—	n.d.	—
Na·	132·5	5·76	151·6	6·59	371·3	16·15	8·2	0·36	14·5	0·63	22·3	0·79	23·0	1·00	145·8	6·30
K·	2·9	0·07	5·7	0·15	tr.	—	2·8	0·07	2·3	0·06	8·9	0·23	8·9	0·23	10·2	0·26
Mg··	1·8	0·15	4·7	0·39	3·8	0·31	5·6	0·46	1·0	0·082	6·0	0·49	6·1	0·50	16·4	1·35
Ca··	13·0	0·65	27·1	1·35	51·6	2·58	26·4	1·32	2·9	0·15	18·0	0·90	12·0	0·60	10·0	0·50
Ba··	n.d.	—	n.d.	—	n.d.	—	nil	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Al··	n.d.	—	nil	—	1·5	0·17	tr.	—	0·85	0·094	} 0·6	(0·04)	} 2·1	(0·15)	2·8	(0·31)
Fe··	n.d.	—	nil	—	0·77	0·028	tr.	—	0·14	0·005					3·2	(0·11)
Mn··	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	0·9	(0·033)	2·9	(0·11)	1·0	(0·036)
Sum of cations	150·2	6·63	189·1	8·48	428·97	19·238	43·0	2·21	21·69	1·021	56·7	2·663	55·0	2·59	189·4	8·866
F'	11·0	0·58	6·6	0·35	n.d.	—	0·49	0·03	nil	—	0·20	0·015	0·30	0·016	0·50	0·036
Cl'	85·2	2·40	138·5	3·91	561·1	15·81	3·6	0·10	16·5	0·47	37·3	1·05	37·6	1·06	237·9	6·71
Br'	n.d.	—	n.d.	—	0·91	0·011	n.d.	—	nil	—	n.d.	—	n.d.	—	nil	—
NO <sub>3</sub> '	nil	—	nil	—	n.d.	—	nil	—	nil	—	nil	—	nil	—	nil	—
SO <sub>4</sub> ''	12·1	0·25	35·1	0·73	52·2	1·09	tr.	—	2·8	0·06	10·6	0·22	12·0	0·25	33·6	0·70
PO <sub>4</sub> '''	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	0·4	0·013
HCO <sub>3</sub> '	—	—	213·5	3·50	79·7	1·31	122·0	2·00	24·2	0·40	85·4	1·40	61·0	1·00	82·4	1·36
CO <sub>3</sub> ''	102·0*	3·40	nil	—	—	—	nil	—	—	—	nil	—	nil	—	nil	—
Sum of anions	210·3	6·63	393·7	8·49	693·91	18·221	126·09	2·13	43·5	0·93	133·5	2·685	110·9	2·326	354·8	8·819
SiO <sub>2</sub> (with N/1,000 as SiO <sub>3</sub> '')	48·2	1·61	44·8	1·49	56·0	1·86	18·9	0·63	29·5	0·982	15·0	0·50	31·0	1·12	18·0	0·60
Dissolved H <sub>2</sub> S	nil	—	nil	—	7·44	—	nil	—	nil	—	nil	—	nil	—	0·53	—
Total sum of items	408·7	—	627·6	—	1186·32	—	187·99	—	94·69	—	205·2	—	196·9	—	562·73	—
NaHCO <sub>3</sub>	—	—	—	—	—	—	—	—	—	—	16·8	—	nil	—	nil	—
Na <sub>2</sub> CO <sub>3</sub>	137·8	—	93·3	—	—	—	15·9	—	9·5	—	nil	—	nil	—	nil	—
pH	8·65		7·1		n.d.		7·20		n.d.		7·5		7·35		6·95	
Sought but not found	—		—		—		NO <sub>2</sub> ', AsO <sub>4</sub> ''		NO <sub>2</sub> ', I'		—		—		—	
Date and Analyst	1940, W. Sunkel		1944, W. Sunkel		1922, J. Muller		1941, C. F. J. van der Walt		1946, J. Muller		1947, W. Sunkel and P. Kok		1947, W. Sunkel and P. Kok		1948, W. Sunkel and P. Kok	

\* Total carbonates expressed as CO<sub>3</sub>'.

Locality	J.R.I. nr. Oden- daalsrus, O.F.S. (borehole).		T.G.I. nr. Tromps- burg, O.F.S. (borehole).		Florisbad, O.F.S.		Stinkfontein, C.P.		Cradock, C.P.		Fort Beaufort, C.P.		Aliwal North, C.P.		Chipise, Transvaal.	
Formation	Ventersdorp system (lavas) (see pp. 248 & 253).		Pre-Karoo norite (see pp. 248 & 253).		Ecca series.		Beaufort series (Lower stage).		Beaufort series (Lower stage).		Beaufort series (Lower stage).		Beaufort series (Upper stage).		Karoo system (see p. 253).	
Temp. of water °C.	34		37·2		28-30		28·7		29·0-31·3		27·0-29·0		36·9		65	
Ions	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000	mgm. per litre	N/1,000
NH <sub>4</sub> ·	n.d.	—	nil	—	0·62	0·035	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Li·	n.d.	—	n.d.	—	0·69	0·099	n.d.	—	nil	—	n.d.	—	2·3	0·33	n.d.	—
Na·	1246·0	54·20	2665·3	115·88	744·1	32·35	209	9·12	49·9	2·17	163·7	7·12	344·5	14·98	140·9	6·13
K·	9·0	0·23	16·1	0·41	nil	—	3	0·08	0·6	0·015	2·2	0·051	6·2	0·16	2·2	0·06
Mg·	7·3	0·60	20·0	1·65	0·79	0·065	15	1·25	0·6	0·049	3·0	0·25	5·5	0·46	1·3	0·11
Ca·	97·8	4·88	473·2	23·66	93·4	4·66	4	0·20	3·0	0·150	11·0	0·55	83·8	4·19	6·0	0·30
Sr·	n.d.	—	7·2	0·16	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Ba·	n.d.	—	n.d.	—	0·74	0·011	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Al·	n.d.	—	n.d.	—	0·85	0·094	nil	—	nil	—	}	1·2	7·3	0·81	n.d.	—
Fe·	n.d.	—	n.d.	—	0·33	0·012	nil	—	nil	—		(0·09)	n.d.	—	1·4	0·05
Sum of cations	1360·1	59·91	3181·8	141·76	841·52	37·326	231	10·65	54·1	2·384	181·1	8·061	449·6	20·93	151·8	6·65
F·	1·0	0·053	3·6	0·19	n.d.	—	6·0	0·32	5·8	0·30	13·2	0·69	n.d.	—	n.d.	—
Cl·	2101·6	59·27	4245·8	119·74	1304·6	36·79	82	2·31	24·9	0·70	189·9	5·36	605·3	17·05	139·1	3·92
Br·	n.d.	—	nil	—	n.d.	—	n.d.	—	n.d.	—	nil	—	1·6	0·02	n.d.	—
I·	n.d.	—	n.d.	—	tr.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
NO <sub>3</sub> ·	nil	—	nil	—	0·38	0·006	nil	—	n.d.	—	nil	—	n.d.	—	tr.	—
SO <sub>4</sub> ·	13·5	0·28	946·2	19·70	2·3	0·047	163	3·40	16·8	0·35	36·0	0·75	68·6	1·43	27·6	0·57
PO <sub>4</sub> ·	n.d.	—	n.d.	—	tr.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—
HCO <sub>3</sub> ·	48·8	0·80	nil	—	18·7	0·31	268	4·39	9·8	0·16	39·7	0·65	29·4	0·48	103·5	1·70
CO <sub>3</sub> ·	nil	—	60·0	2·00	—	—	12	0·40	27·0	0·90	16·8	0·56	44·2	1·47	12·0	0·40
Sum of anions	2164·9	60·403	5255·6	141·63	1325·98	37·153	531	10·82	84·3	2·41	295·6	8·01	749·1	20·45	282·2	6·59
SiO <sub>2</sub> (with N/1,000 as SiO <sub>3</sub> ·)	11·0	0·36	26·0	0·86	21·9	0·74	28	0·92	40·2	1·34	37·0	1·23	14·8	0·49	66·7	2·22
Dissolved H <sub>2</sub> S	—	—	—	—	tr.	—	16	—	2·3	—	6·2	—	0·79	—	1·6*	—
Total sum of items	3536·0	—	8463·4	—	2189·4	—	806	—	180·9	—	519·9	—	1214·19	—	502·3	—
NaHCO <sub>3</sub>	nil	—	nil	—	—	—	252	—	—	—	84	—	—	—	—	—
Na <sub>2</sub> CO <sub>3</sub>	nil	—	nil	—	—	—	21	—	—	—	30	—	—	—	—	—
pH	8·25	—	8·95	—	n.d.	—	9·1	—	9·6	—	9·0	—	n.d.	—	n.d.	—
Sought but not found	—	—	Mn·, NO <sub>2</sub> ·	—	Rb, Cs (sp.)	—	NO <sub>2</sub> ·	—	—	—	Mn·	—	—	—	—	—
Date and Analyst	1947, W. Sunkel and P. Kok		1948, W. Sunkel and P. Kok		1916, M. M. Rindl		1948, W. Sunkel		1946, W. Sunkel and P. Kok		1947, W. Sunkel and P. Kok		c. 1913, P. D. Hahn		1944, H. S. Schoeman	

\* From a 1938 analysis.

The elements finally selected for examination are believed to show promise of special diagnostic significance. As a group their determination in waters is cumbersome by ordinary chemical methods and is seldom undertaken—from this aspect alone information on such elements seemed desirable. The objective was not to seek out every trace element, but rather to concentrate on such as were capable of aiding geological interpretation—with this limited purpose in view the following method was found to be satisfactory.

The dried sample was placed in the cupped hollow of a copper anode of 5.8 mm. diameter; the cathode was similar but slightly pointed. A 240 v. D.C. source was used to run the arc for 20 seconds at 5 amps. A large Hilger Littrow-type spectrograph with a setting from 2800 Å. to 5000 Å. was available; for the few boron determinations a different setting and timing were used. As far as could be judged visually, reproducible results were obtained.

Although the investigation is exploratory rather than exhaustive, the results are encouraging, especially when one is mindful of the fact of the difficulty of matching composition of underground waters with their vagaries in geological formations. On the whole the spectrographic data underline similarities and differences that are apparent from the chemical analyses. The marked presence of Mn in the Table Mountain series waters, and the paucity of this element in the others is not surprising in the light of our geological knowledge: small manganese ore bodies are known to occur in the Table Mountain series.

The identical results for the two Bushveld granite waters, although 50 miles (80 km.) apart, are what can be expected. These waters differ in respect of the selected elements from all the others with the possible exception of the Loubad one, which flows through rocks of the Waterberg system, i.e. through sediments formed partly of detritus from the Bushveld granites.

The five artesian waters from the Odendaalsrus area, viz. the boreholes V.K.1, V.K.3, J.R.1, K.1, and W.1 yield virtually identical results and this fact is in harmony with the geological data, for the waters traverse similar formations from a great depth. The boreholes are up to 10 miles apart and are a strong argument for the proposition that in respect of the selected elements, at least, similar geological environment is reflected in similar composition of associated groundwaters.

The difference in composition between waters from a deep-seated and a shallow origin is shown by the results obtained for Fort Beaufort and Kat Valley; these springs are less than a half mile apart and issue from identical rocks of the Karroo system. The difference in Li-content, and to a lesser degree in Ba, is noteworthy. That between the shallow and deep-seated waters of Stinkfontein and Kruidfontein is not quite so marked.

Many more inferences can be drawn, but it is realised that more results are necessary before the influence of the host-rocks on the composition of thermal waters, even in a restricted sense, can be recognised. At this stage it seems reasonable to assume that among the elements selected some useful diagnostic ones have been included. An interesting by-product of this investigation has been the data—fragmentary though it be—on the elements Pb and Mo, whose geochemical cycles have received very little attention. The highest concentration of these elements (Badplaats) was of the order 0.005 per cent. of the solid,

SPECTROGRAPHIC TABLE.

LOCALITY.	Solids mgm. per litre at 110°C.	4,603† Li	4,607 Sr	4,554 Ba	3,962 Al	4,031 Mn	3,903 Mo	4,058 Pb	2,498 B	Formation in which water occurs or struck.
Badplaats .. .. .	335	4	8	tr.	2	1	2	2	n.d.	Archaean granite.
Tugela .. .. .	1,518†	1	9	1	6	tr.	2	0	tr.	Archaean gneiss.
Riffontein .. .. .	794	7	6	2	1	0	1	tr.	3	Rooiberg series.
Warmbaths .. .. .	397	4	7	5	4	1	1	tr.	3	Bushveld granite.
Buffelshoek .. .. .	459	4	7	5	5	1	1	tr.	5	Bushveld granite.
Loubad .. .. .	194†	5	7	6	1	tr.	tr.	1	5	Waterberg system.
Warmwaterberg .. .. .	190	3	8	7	1	8	1	2	n.d.	Table Mountain
Olifants valley .. .. .	156	2	7	5	3	9	tr.	tr.	n.d.	series.
Gamka valley .. .. .	150	1	7	4	3	9	0	tr.	n.d.	„ „
Zwartkops†† .. .. .	543	1	8	4	2	7	0	0	n.d.	Bokkeveld series (see p. 252)
J.R.1—Jonkersrust†† ..	3,724	4	9	6	4	1	0	tr.	n.d.	Ventersdorp lavas
V.K.1—Vermeulenskraal†† ..	4,528	4	9	6	4	1	0	1	n.d.	(see pp. 248 & 253)
V.K.3—Vermeulenskraal†† ..	4,544	4	9	6	5	2	0	1	n.d.	„ „
K.1—Kaalpan†† .. .. .	3,800	3	9	5	5	1	0	tr.	n.d.	„ „
W.1—Wolvepan†† .. .. .	3,996	4	9	7	5	1	0	tr.	5	„ „
T.G.1—Trompsburg†† ..	8,570	6	9	1	1	tr.	0	0	4	Pre-Karoo norite.
Fort Beaufort .. .. .	528	6	7	1	2	0	tr.	0	n.d.	Beaufort series
Kat valley* .. .. .	1,551	0	9	5	tr.	tr.	0	0	n.d.	(Lower stage)
Stinkfontein .. .. .	754	7	6	tr.	0	1	0	1	4	„ „
Stinkfontein** .. .. .	859	5	8	tr.	1	tr.	1	1	1	„ „
Kruidfontein†† .. .. .	995	7	8	1	2	tr.	2	0	3	„ „
Kruidfontein** .. .. .	1,397	5	10	3	6	1	tr.	0	tr.	„ „

† Wave-length.

† Total sum of items determined.

†† Borehole (thermal water).

\* Cold spring.

\*\* Shallow borehole (cold water).

which is about 15 parts per 1,000 million in the water out of the Archaean granite for Pb and about 60 parts in the water at Tugela, out of the Archaean gneiss, for Mo.

The highest concentrations of Li, Sr, and Ba are of the order of 0.1 per cent. in terms of solid, as far as could be determined by the technique employed; the amounts will be found to be not much less than 0.1 per cent and certainly well below 1 per cent. when more accurate methods are employed—no greater claim to accuracy is made. The Riffontein "solid" may have a little more Li than 0.1 per cent., but the Trompsburg water will have the highest Li-content with approximately 9 parts per million. The highest Ba-content will probably be found in the Odendaalsrus waters, about half a part per million.

#### VII. SPRING GASES.

In his well-known work "Ground Water," published in 1937, C. F. Tolman states (p. 436) that spring gases consist chiefly of "carbon dioxide, hydrogen sulphide, and hydrocarbon gases." Analyses of gas from South African thermal springs and thermal artesian boreholes do not support this contention. These gases fall naturally into two distinct classes.

One is characterised by predominance of nitrogen, and the gas may be regarded as air from which a varying proportion of oxygen has been abstracted and, as a rule, small amounts of carbon dioxide added. This carbon dioxide is probably either of atmospheric origin or due to the action of acids on calcareous rocks. The small amounts of methane present at Olifants valley and Badplaats formed by the decay of organic matter in the spring pools. Springs emitting gas of this type occur in formations ranging from Archaean granite to the Devonian Table Mountain sandstone. Analyses, mostly new and previously unpublished, are given in the Table on page 245, and a few foreign ones have been added both for purposes of comparison and to show the widespread distribution.

Gases of the remaining class are marked by abundance of methane, accompanied in the Aliwal North and Florisbad springs by hydrogen. Oxygen is either absent or present in very small amounts, but nitrogen commonly constitutes a large part of the gas. Without exception the springs rise in sedimentary rocks of the Karroo system (Upper Carboniferous to Rhaetic). Boreholes in this system occasionally strike gas that invariably proves to be composed dominantly of methane. Its origin is ascribed to distillation of coal or carbonaceous shales by the Jurassic dolerite intrusions. A similar origin may be postulated for the gas in the warm and tepid springs of the Karroo. Fairly thick layers of peat have accumulated around the Aliwal North and Florisbad springs, and it seems probable that there some of the gas has formed by decay of vegetable matter.

Although sulphuretted hydrogen taints the air around many South African thermal springs the amounts are too small to be determined by the ordinary methods of analysis.

Carbon dioxide is not an important constituent of any of the gas analysed. It does, however, constitute the bulk of the gas in small, cold springs issuing from fault zones in Dwyka tillite (Permo-Carboniferous) near Bizana. Farther

## NITROGEN-RICH GASES ASSOCIATED WITH SOUTH AFRICAN AND FOREIGN THERMAL WATERS.

Locality.	Bad-plaats, Tvl.	Die Oog, Tvl.	Rif-fontein, Tvl.	Loubad, Tvl.	Warm-waterberg, C.P.	Olifants Valley, C.P.	Zwartkops, C.P. (borehole).	Buxton, England.	Banff, Canada.	Leuker, Switzerland.	Ranomafana, Madagascar.
Formation.	Archaean granite.	Rooiberg felsite.	Rooiberg series.	Waterberg system.	Table Mt. series.	Table Mt. series.	Cape system.				
O <sub>2</sub> .. ..	0.3	0.8	0.2	11	0.4	1.5	11.54	—	0.45	Nil	tr.
CO <sub>2</sub> .. ..	0.2	—	0.7	2	2.7	3.5	3.43	0.88	1.11	0.9	0.55
H <sub>2</sub> .. ..	nil	—	nil	—	nil	} 3.9	—	—	—	—	—
CH <sub>4</sub> .. ..	1.1	0.4	0.3	nil	nil		—	—	0.20	—	tr.
C <sub>2</sub> H <sub>6</sub> .. ..	nil	—	nil	—	nil		—	—	—	—	—
N <sub>2</sub> + He + A, etc.	98.4	98.8	98.8	87	96.9	91.1	85.03*	99.12	98.24	99.0	99.46
Totals ..	100.0	100.0	100.0	100	100.0	100.0	100.00	100.00	100.00	99.9	100.01
Date of analysis	1948	1939	1948	1941	1947	1947	1914	1882	c. 1918	c. 1943	c. 1926

\* N<sub>2</sub> + He + Ne = 741 p.p. million.

## COMBUSTIBLE GASES ASSOCIATED WITH SOUTH AFRICAN THERMAL WATERS.

Locality.	V.K.I., O.F.S. (bore-hole).	Florisbad, O.F.S.	Fort Beaufort, C.P.	Cradock, C.P.	Tarka Bridge, C.P. (bore-hole).	Aliwal North, C.P.	Lake Mentz, C.P. (tepid).	Grasrand nr. Graaff-Reinet, C.P. (tepid).	Vredenburg nr. Marais Siding, C.P. (tepid).	Kruitfontein nr. Edenburg, O.F.S. (tepid).	Gruisfontein nr. Devon, Tvl. (gas bore-hole).
Formation.	Ecca Series.	Ecca Series.	Beaufort Series.	Beaufort Series.	Beaufort Series.	Beaufort Series.	Dwyka Series.	Beaufort Series.	Beaufort Series.	Beaufort Series.	Ecca Series.
O <sub>2</sub> .. ..	0.4	—	—	1.1	} 0.1	3.2	tr.	0.3	1.2	—	—
CO .. ..	—	—	—	—		—	nil	nil	—	—	0.1
CO <sub>2</sub> .. ..	nil	—	—	—		—	tr.	nil	nil	—	—
H <sub>2</sub> .. ..	0.5	10.0	tr.	—	2.7	8.4	nil	nil	—	—	0.2
CH <sub>4</sub> .. ..	80.8	71.5	100	83.4	94.0	55.2	39	98.5	33.3	79	82.1
C <sub>2</sub> H <sub>6</sub> .. ..	—	—	—	—	—	—	nil	nil	—	tr.	2.1
N <sub>2</sub> + He + A, etc.	18.3	18.5	tr.	15.4	3.2	33.2	60	1.2	65.5	20	14.7
Totals	100.0	100.0	100	99.9	100.0	100.0	99	100.0	100.0	99	99.2
Date of analysis	1947	1916	1948	1946	1912	1927	1945	1945	1942	1944	1985

Analysts: Zwartkops—J. Dewar; Die Oog and Loubad—C. F. J. van der Walt; Florisbad—M. M. Rindl; Aliwal North—Messrs. Littlejohn and Whitby; Tarka Bridge—J. Moir; Remainder—Fuel Research Institute of South Africa, Pretoria.

north, at Bongwan, in the same Middle Cretaceous fault zone fairly large volumes of gas, consisting 99 per cent. of carbon dioxide, are exhaled. Gevers<sup>13</sup> concluded that the gas is not of volcanic origin but due to the action of sulphuric acid derived from the oxidation of pyrite on crystalline limestone.

### VIII. RADIOACTIVITY.

Rindl<sup>26</sup> quoted a few determinations of the radioactivity of thermal waters, presumably measured by means of electroscopes :

Locality.	Radioactivity in maché units (determined at source).	Geological formation.
Zwartkops borehole .. ..	1.35	Cape system.
Badplaats .. ..	6.5	Archaeangranite.
Machadodorp .. ..	12.3—12.8	Pretoria series.
Malmesbury .. ..	73.3	Cape granite.

The activity is due to the presence of radon, and in the case of the Malmesbury spring water it fell to between 3.5 and 3.6 maché units after only three hours.

Brandvlei scalding spring was investigated by Mr. J. Muller, Consulting Chemist, during 1946. The water showed 50 to 53 maché units, and the spring gas 450 maché units per litre. This spring rises in the Cape system, and the radon content is rather high for a water of this type.

A large sample of water from the Badplaats scalding spring was taken to dryness and the residue submitted to Dr. D. J. Simpson of the Geological Survey. Examined with beta-ray Geiger-Muller counters it showed only traces of radioactivity probably due to the 1.2 per cent. potassium present. No increase in activity was noted after the sample had been stored for two months.

### IX. SPRING DEPOSITS AND AGE OF SPRINGS.

Very few South African thermal springs have given rise to deposits. The only ones known of any importance are ochres, and ferruginous and manganese sinters, deposited by springs issuing from the Table Mountain sandstones in the belt of fold mountains along the south coast of the Cape Province. Fairly extensive deposits occur around the Caledon, Warmwaterberg, Toverwater, and Amanzi<sup>8</sup> springs. The Olifants valley and Gamka valley springs are also markedly chalybeatic, but as they issue on the banks of rivers and are thus often inundated, there has been no opportunity for sinters to accumulate.

In the deep Zwartkops borehole, near Port Elizabeth, scalding hot water was struck at depths of between 3,400 and 3,560 feet (1,036 m.—1,085 m.) in presumably Bokkeveld sediments<sup>28</sup>; the water, however, is believed to be derived mainly from the underlying Table Mountain sandstones. Ochre is deposited in the overflow channels.

Analyses show that the manganese content of these ochres and sinters increases westwards from Zwartkops to Caledon, and it is of interest to note that still nearer to Cape Town small deposits of psilomelane occur in the Table Mountain sandstone. It is possible that some of them mark the sites of extinct springs.

Ochre is also deposited by numerous cold springs rising from Table Mountain sandstone. An analysis of such an ochre from a spring in the Gamka valley has been added for comparison. The manganese content is much lower than in the thermal water deposits.

The phosphate content of all is fairly high, and an appreciable amount of barium was found in the Warmwaterberg sample.

Spring.	Caledon.	Warm-water-berg.	Zwart-kops.	Gamka Valley (cold spring).
Material analysed.	Average sample from mound.	Recently deposited ochre.	Recently deposited ochre.	Recently deposited ochre.
SiO <sub>2</sub> .. .. .	5.91	7.8	6.74	2.8
Al <sub>2</sub> O <sub>3</sub> .. .. .	2.21	n.d.	n.d.	n.d.
Fe <sub>2</sub> O <sub>3</sub> .. .. .	50.72	57.5	70.9	67.1
MnO .. .. .	—	0.55	0.50	0.16
MnO <sub>2</sub> .. .. .	27.20	8.55	1.36	nil
MgO .. .. .	n.d.	4.8	0.3	tr.
CaO .. .. .	n.d.	0.8	0.7	0.2
BaO .. .. .	n.d.	1.45	n.d.	n.d.
P <sub>2</sub> O <sub>5</sub> .. .. .	2.31	1.18	4.20	2.67
H <sub>2</sub> O + .. .. .	9.47	9.59	10.0	13.2
H <sub>2</sub> O — .. .. .	1.38	7.64	6.0	13.9
	<u>99.20</u>	<u>99.86</u>	<u>100.60</u>	<u>100.03</u>

*Analysts:* Caledon and Zwartkops—C. F. J. van der Walt; Warmwaterberg and Gamka valley—E. C. Haumann. Division of Chemical Services, Pretoria.

According to Dr. L. G. Boardman of the Geological Survey the Caledon sinter mound would weigh about 1,000,000 tons (907,000 metric tons). The one at Warmwaterberg is estimated to contain about 600,000 tons (544,000 metric tons).

Assuming that the deposition of iron and manganese is complete, and that the composition and flow of the waters have remained constant, and that there has been no erosion or solution of the deposits, the Caledon and Warmwaterberg sinters have respectively taken approximately 300,000\* and 850,000 years to accumulate. It is, of course, most unlikely that conditions remained uniform, but these figures provide a rough indication of the order of time involved. On geological grounds it is probable that hot water has issued from these springs ever since the present topography was developed during the Late Tertiary.

\* A sample of water from the Caledon spring kindly collected by the proprietors in May, 1948, was partially analysed by Mr. E. C. Haumann of the Division of Chemical Services, Pretoria. The results were :—

SiO <sub>2</sub> .. .. .	53.3	mgm. per litre	
Fe <sub>2</sub> O <sub>3</sub> .. .. .	4.1	„	(as Fe.. 2.9)
Mn <sub>2</sub> O <sub>4</sub> .. .. .	4.6	„	(as Mn.. 3.3)

On the basis of the respective manganese oxide contents, the mound is 180,000 years old; whereas when the values for ferric oxide are used the age works out at 370,000 years.



These age estimates may be compared with Meinzer's statement<sup>36</sup> that most of the thermal springs in Nevada, Utah and southern Idaho came into existence before the close of the Tertiary. The Yellowstone Park springs, on the other hand, are probably only some 20,000 years old, and those of Iceland between 10,000 and 50,000 years.<sup>36</sup>

#### X. THERMAL ARTESIAN BOREHOLES.

Several deep boreholes have struck thermal artesian water. In one, near Port Elizabeth, the water is scalding ; in another, near Trompsburg, it is hot ; in three near Odendaalsrus it is warm.

Borehole.	Latitude °S.	Longitude °E.	Depth at which thermal water struck.		Formation in which thermal water struck.	Temp. °C. at surface.	Flow.	
			Ft.	M.			Imp. galls./ 24 hrs.	Cu. metres/ 24 hrs.
Zwartkops <sup>28, 29</sup>	33° 53'	27° 37'	3,400	1,036	Bokkeveld series (?)	54.5	250,000	1,134
T.G.1* ..	30° 3'	25° 44'	4,700	1,433	Pre-Karoo norite.	37.2	24,000	109
J.R.1* ..	28° 6'	26° 44'	3,560	1,085	Ventersdorp series (pre-Cambrian) lavas	34.0	48,000	218
V.K.1* ..	28° 6'	26° 49'	2,560	780	Ventersdorp series lavas.	32.7	48,000	218
W.1* ..	28° 2'	26° 41'	—	—	" "	28.8	60,000	272

\*This information was kindly supplied by the mining companies concerned. The temperatures of the artesian waters in the Odendaalsrus area were taken by Dr.L. T. Nel of the Geological Survey.

In the Odendaalsrus area several other recently drilled holes have struck tepid water at comparable depths. Gas consisting dominantly of methane is discharged from them all ; it enters the boreholes from the Permian Eccia series, in J.R. 1, for example, at a borehole depth of 980 feet (299 m.).

The borehole at Zwartkops has been developed into one of the leading spas of the country, and the J.R. 1. and V.K. 1. waters are used locally for medicinal purposes.

Several boreholes have been drilled near thermal springs with the object of obtaining more water. On the farm Tugela, on the Limpopo river in the northern Transvaal, a borehole 65 feet (20 m.) deep, drilled in 1947, gives a flowing supply of 15,600 gallons (71 cbm.) of hot water per day. The natural spring 100 feet away has a discharge of only 2,650 gallons (12 cbm.) a day, and according to the owner its flow has not as yet been appreciably affected by the artificial release of pressure. The borehole water has a temperature of 48.9°C. whereas the maximum temperature measured in the spring was only 42.8°C. A borehole about 100 feet (30 m.) deep at Warmwaterberg flows at the rate of 31,000 gallons (141 cbm.) a day, but the water although warm is 17.7°C. cooler than that of the nearby hot spring. A supply of about 500 gallons (2 cbm.) an hour of thermal water has recently been struck in a 157 feet (48 m.) deep borehole near the Letaba hot spring.

Former warm springs at Kruidfontein and Amanzi have dried up as a result of heavy pumping of boreholes in the immediate vicinity.

Boreholes only 65 to 225 feet (20-69 m.) deep at Tarka Bridge<sup>35</sup> yield warm (26°-27°C.) artesian, sulphuretted water accompanied by inflammable gas, mainly methane. The holes are of particular interest as they are tidal, although situated some 100 miles (160km.) from the sea. Here, too, weak thermal springs have been dried up.

In the Karroo many other shallow boreholes have struck sulphuretted water, which is generally tepid indicating a fairly deep-seated origin, probably from blind fissures.

#### XI. THERMAL MINE WATERS.

There are a few published records of thermal water having been struck in the deep gold mines of the Witwatersrand.

A narrow, water-bearing fissure in a dyke was intersected at a depth of 2,680 feet (817 m.) in a shaft on the Randfontein Estates mine. The water had a temperature of 25°C., which was the same as that in the main workings at this depth. On analysis the dissolved solids amounted to 134 mgm. per litre, the water being characterised by predominance of  $\text{SO}_4$  and virtual absence of  $\text{Cl}$ .<sup>27</sup> The supply of water was weak, but on the East Rand Proprietary Mines a supply of about 1,800,000 gallons (8,166 cbm.) of warm water per day was struck in a fault zone in Witwatersrand quartzites. Temperature readings at various points in the fissure system at vertical depths of between 5,261 and 6,056 feet (1,603-1,846 m.) ranged between 33.3° and 35°C., the rock temperatures being about 1°C. lower. The water was sulphuretted, containing 10 mgm. per litre of dissolved hydrogen sulphide, and at first was very soft with dissolved solids amounting to only 160 mgm. per litre. As dewatering proceeded the concentration of salts in the water increased to approximately 1 gm. per litre, but the dominant constituents remained the same, viz.  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ .<sup>1</sup>

Thermal water has also been struck in the copper mines at Messina where the country rocks are meta-quartzites and hornblende gneisses invaded by a pre-Cambrian granite<sup>31</sup>. The following information relating to the waters encountered in the deepest mine, the Harper, was kindly provided by Dr. C. M. Schweltnus, Geologist to the Company:—

Depth in Mine.		Source of Water.	Flow.		Temp. of Water °C.	Virgin Rock Temp. in Diamond Drill Holes °C.
Ft.	M.		Imp. Galls./ 24 Hrs.	Cu. Metres 24 Hrs.		
1,600	488	Hanging fissure	7,200	33	35	36.4
2,200	671	Borehole	2,400	11	37.8	40.8
2,650	808	Borehole	4,800	22	42.2	44.2
3,100	945	Footwall fissure	3,600	16	48.3	47.5

The geothermal step works out at 1°C. per 41 m.

## XII. THE RELATIONSHIP BETWEEN GEOLOGICAL FORMATION AND CHEMICAL COMPOSITION OF SOUTH AFRICAN THERMAL WATERS.\*

## (a) ARCHAEOAN GRANITES, GNEISSES, AMPHIBOLITES, ETC.

In these most ancient rocks the thermal springs are found along the Orange river in the Cape Province, in Natal, and in the eastern and northern Transvaal. Most of them are hot, and two—Badplaats and Tugela valley—are scalding. The flows range up to about 180,000 gallons (817 cbm.) a day, and as usual the strongest springs are hottest.

The three springs in the Orange river valley have not as yet been analysed. The remainder are of three types characterised by dominance of chlorides, sulphates, and carbonates, respectively. Those having NaCl as the main constituent occur in the northern Transvaal and contain on the average 1 gm. of dissolved solids per litre. Those with a high  $\text{SO}_4$  content, are Tugela in the extreme north of the Transvaal, and Lilani and Tugela valley in Natal. Soda-rich alkaline waters occur at Natal Spa, Badplaats, and Paddysland. In all save Paddysland  $\text{Ca}^{++}$  considerably exceeds  $\text{Mg}^{++}$ . Silica is a prominent constituent especially in the soda-rich alkaline waters.

It is interesting to note that Bond's<sup>2</sup> work shows that the water from shallow boreholes in the Archaeoan granites, etc. may be divided into the same three types, or, in other words, the thermal springs discharge water essentially similar in composition to the normal underground supplies in the vicinity. The only important point of difference is the ratio of  $\text{Ca}^{++}$  to  $\text{Mg}^{++}$ . In the non-thermal waters, save in Natal,  $\text{Ca}^{++}$  is subordinate to  $\text{Mg}^{++}$ , whereas in nearly all the thermal waters the reverse is the case. The exception, the spring at Paddysland in the northern Transvaal, is barely thermal, having a temperature of only 26°C. It is possible that at depth the thermal waters extract the  $\text{Ca}^{++}$  from calcium-magnesium silicates, whereas the Mg is retained as relatively insoluble hydrated silicates.

## (b) PONGOLA SYSTEM.

At Sulphur Springs near the Swaziland border the warm water apparently issues from rocks of this Proterozoic system. The analysis shows very weak mineralisation, with sodium carbonate as the main constituent. The water is quite strongly alkaline and contains a high proportion of silica.

There do not appear to be any published analyses of borehole waters from the Pongola system. A cold, sulphuretted spring issuing from Pongola quartzites was found to contain 253 mgm. per litre of dissolved solids, the predominant constituents being  $\text{NaHCO}_3$  and NaCl. Like the thermal spring its pH value is high, being 9.55.<sup>19</sup>

## (c) PRETORIA SERIES.

The warm spring at Machadodorp and those at Badfontein and De Bad farther to the north emerge from rocks of the Pretoria series of the pre-Cambrian Transvaal system. Only the Machadodorp water has been analysed. Although

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\* For representative analyses, refer to Table facing page 240.

classed by Rindl<sup>26</sup> amongst the sulphur springs the analysis shows less than 1 mgm. per litre of dissolved hydrogen sulphide. The water is not strongly mineralised, and the characteristic constituents  $\text{Cl}'$ ,  $\text{HCO}_3'$ , and  $\text{SiO}_2$  are present in almost equal quantities. The  $\text{SO}_4''$  content is low, and  $\text{Ca}''$  exceeds  $\text{Mg}''$  four times. Apart from the  $\text{Ca}'' : \text{Mg}''$  ratio the water is quite typical of that from shallow boreholes in the shale zones of the Pretoria series; in these the  $\text{Ca}'' : \text{Mg}''$  ratio is almost exactly 1 : 1.<sup>2</sup>

(d) ROOIBERG SERIES.

This pre-Cambrian series embraces both felsitic lavas and sediments. The hot waters at Die Oog and Welgevonden, which rise from a fault in the felsites, are of low concentration, the characteristic constituents being  $\text{NaHCO}_3$  and  $\text{Ca}(\text{HCO}_3)_2$ , with subordinate  $\text{NaCl}$ . The warm water issuing from a fault in Rooiberg series quartzites at Riffontein, on the other hand, is more than three times as concentrated, and  $\text{NaCl}$  is the major constituent followed by  $\text{NaHCO}_3$ . The Rooiberg series thermal waters are marked by great excess of  $\text{Ca}''$  over  $\text{Mg}''$ .

(e) BUSHVELD GRANITES.

The thermal springs at Warmbaths, Buffelshoek, Grovesbad, Goederede, and Vischgat, all in the central Transvaal, rise in Bushveld granite. In temperature they range from warm to scalding, and in flow from weak to about 160,000 gallons (726 cbm.) a day.

Only the Warmbaths and Buffelshoek waters have been analysed. Both chemically and spectrographically they are remarkably alike. Chemically they are quite typical of Bushveld granite borehole waters but are somewhat more concentrated, more siliceous, and have rather higher sodium chloride and sodium carbonate contents. The main point of difference is the  $\text{Ca}'' : \text{Mg}''$  ratio, which is about  $6\frac{1}{2} : 1$  for the thermal waters and  $2 : 1$  for the cold borehole waters.

(f) CAPE GRANITE.

The warm spring at Malmesbury rises from a fault zone in Cape granite. The water is saline, having  $\text{NaCl}$  as chief constituent. On the contrary, borehole waters are of low concentration but also marked by predominance of  $\text{NaCl}$ . In composition the thermal water is typical of that from boreholes in shales and slates of the Malmesbury series.

(g) WATERBERG SYSTEM.

This system, which in the central Transvaal is made up almost entirely of a thick succession of sandstones, may be of Late pre-Cambrian age. The warm springs at Loubad in the central Transvaal represent deep, artesian water from the basal layers of the system. The water is of low concentration, the main constituent being  $\text{Ca}(\text{HCO}_3)_2$ .  $\text{Cl}'$  is low and  $\text{SO}_4''$  virtually absent. The non-thermal waters from cold springs and boreholes in this system have essentially the same composition, but are of still lower concentration and contain proportionally more  $\text{Mg}''$ .<sup>18</sup>

## (h) CAPE SYSTEM.

In the western Cape Province the thermal springs all rise on the flanks of mountains formed by Mesozoic foldings. The aquifer is the Devonian Table Mountain sandstone, and most of the springs issue from fault planes. The flows are fairly strong, and with the exception of Gamka valley the water is hot or scalding. Analyses, however, show that save for a much lower content of  $\text{SiO}_2$  this Gamka valley warm spring and the nearby Olifants valley scalding spring discharge waters of almost identical composition.

Chemically the waters are all of low concentration, the total dissolved solids ranging from 77 mgm. per litre at Goudini to 190 mgm. per litre at Warmwaterberg. In the west, at Goudini and Brandvlei,  $\text{SiO}_2$  is the most abundant constituent followed as regards the anions by  $\text{HCO}_3'$ ,  $\text{Cl}'$ , and  $\text{SO}_4''$ . At Caledon, which is much nearer the sea,  $\text{Cl}'$  exceeds  $\text{HCO}_3'$ . At Warmwaterberg and Olifants valley  $\text{HCO}_3'$  and not  $\text{SiO}_2$  is the major constituent, whereas at Toverwater  $\text{Cl}'$  exceeds both. According to Bond<sup>2</sup> this latter would be typical of the non-thermal waters of the Table Mountain series, in which the order of abundance is  $\text{Cl}'$ ,  $\text{HCO}_3'$ ,  $\text{SiO}_2$  and  $\text{SO}_4''$ . The general predominance of  $\text{SiO}_2$  in the thermal waters is doubtless due to its greater solubility in hot water.

Several of the springs are chalybeatic and deposit hydrated oxides of iron and manganese. The variations in iron and manganese content were discussed in the section dealing with the spring deposits.

The hot water struck between depths of 3,400 and 3,560 feet (1,036-1,085 m.) in the borehole at Zwartkops is more concentrated than that from thermal springs in the Cape system, and contains proportionally less  $\text{HCO}_3'$ . The warm water from the Amanzi boreholes, also near Port Elizabeth, is even more concentrated and characterised by considerable excess of  $\text{SO}_4''$  over  $\text{Cl}'$ , fairly high  $\text{Fe}^{++}$  and  $\text{Al}^{+++}$  content, and absence of carbonates. The Zwartkops water is of mixed origin; probably Table mountain series, Bokkeveld series, and the base of the Cretaceous. The Amanzi water is also a mixed Table Mountain series and Cretaceous water.

## (i) KARROO SYSTEM.

Sediments of this system, which ranges from Upper Carboniferous to Rhaetic in age, cover the central part of the Cape Province, nearly the whole Orange Free State, and large areas in Natal and the Transvaal. It is divided into the following series:—

- Stormberg series
- Beaufort series
- Ecca series
- Dwyka series

All the thermal springs in the Karroo system are only warm and vary in strength from flows of only a few thousand gallons up to 840,600 gallons (3,813 cbm.) a day at Aliwal North. Most of them rise alongside dolerite dykes of early Jurassic age.

Only the Black Umfolosi spring in Natal actually issues at the surface from rocks of the Dwyka series, in this case tillite.

The springs in the west-central Orange Free State emerge from rocks of the Ecca series. The waters are rich in NaCl, and the total dissolved solids exceed 2 gm. per litre. Such a high salt content is not characteristic of the underground water in the Ecca series but rather of the underlying Dwyka series, through rocks of which it seems probable the thermal waters have percolated. Deep boreholes to the south of Odendaalsrus and near Trompsburg, both in the Orange Free State, have also struck thermal waters characterised by predominance of NaCl. As already mentioned the waters were struck in lavas of the pre-Cambrian Ventersdorp system and in norite of presumably Bushveld Complex age, but it is probable that much of the NaCl was derived as a result of downward percolation through the Dwyka series, which overlies these ancient rocks. This seems a reasonable supposition, for Bond's<sup>2</sup> analyses show that the waters in Ventersdorp lavas and Bushveld norite are characterised by a rather low Cl' content and are temporary hard carbonate waters.

In the central and eastern parts of the Cape Province the thermal waters in the Beaufort series sediments nearly all have NaCl as the predominant constituent, with total dissolved solids ranging from 496 mgm. per litre at Badsfontein to 754 mgm. per litre at Stinkfontein. From the analyses given by Bond<sup>2</sup> it is evident that the shallow underground waters from the Lower beds of the Beaufort series are saline, whereas a high sodium bicarbonate content characterises the waters from the Middle and Upper beds. The difference is believed by Bond to mark a transition from an estuarine to a fresh-water origin. The  $\text{NaHCO}_3$  in the upper beds is considered to be due to a higher proportion of unkaolinised feldspar<sup>2</sup>.

The thermal springs at Rooiwal and Cradock, however, have  $\text{CO}_3''$  and  $\text{HCO}_3'$  as the chief anions, accompanied by a fair amount of  $\text{SiO}_2$ .  $\text{Ca}''$  is very low but greatly exceeds  $\text{Mg}''$ . Near Rooiwal another thermal spring, Badsfontein, issuing from about the same horizon in the Middle Beaufort stage and having almost exactly the same temperature and flow, is saline. Thus it is probable that Badsfontein is a deeper-seated spring but that much of the excess heat has been lost before the water emerges at the surface. The difference in composition between the Cradock and not very far off Tarka Bridge thermal waters can be similarly explained.

The warm water at Stinkfontein, although issuing from Lower Beaufort strata, is characterised by a high  $\text{NaHCO}_3$  content and the presence of much  $\text{SO}_4''$  as well as Cl'.  $\text{Mg}''$ , present to the extent of 15 mgm. per litre, greatly exceeds  $\text{Ca}''$ ; judging by the analyses in Bond's memoir such preponderance of  $\text{Mg}''$  is most unusual in Karroo waters.

In the extreme north of the Transvaal the scalding Chipise spring issues from Upper Karroo beds overlying Archaean gneiss. According to Söhnge<sup>31</sup> the point of emergence is determined by a dolerite dyke approaching a fault and the contact of Cave sandstone with a dolerite sill. Mr. H. N. Visser who has recently resurveyed the area is, however, of opinion that the water issues at the intersection of two faults. Movements have taken place along these faults at intervals up to post-Permian time. The course of the water has not been determined, but it is probably of mixed Archaean granite, Waterberg system (where

# GEOLOGICAL STRUCTURES AT SOME SOUTH AFRICAN THERMAL SPRINGS

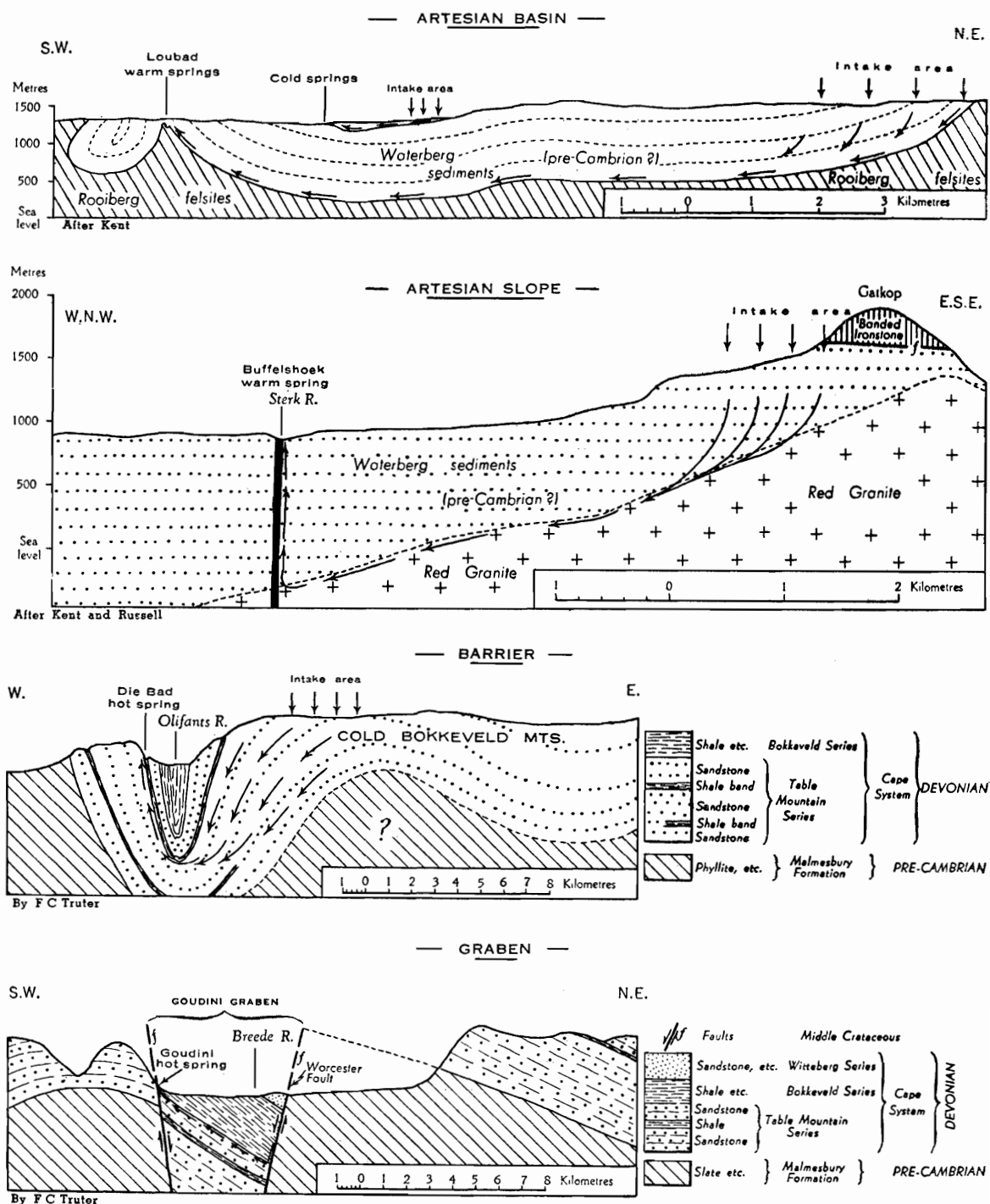


FIG. 2.

the intake area may lie), and Upper Karroo origin. It is moderately mineralised, the main constituents being NaCl and  $\text{NaHCO}_3$ . The  $\text{SiO}_2$  content is fairly high, but  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  are present in very small amounts, the former greatly exceeding the latter.

### XIII. SOURCE OF THE WATERS AND THEIR HEAT.

The youngest igneous rocks known in the Union of South Africa, the intrusions of kimberlite and melilite basalt, date back to the last stages of the Cretaceous. Admittedly the crater of the Pretoria salt-pan has generally been considered to be an extinct volcano of comparatively recent age, but the latest investigations have suggested that it is probably a meteor crater. This complete absence of Recent or Tertiary igneous activity seems to rule out eruptive rocks as a source of the heat of the South African thermal springs, or of their waters or gases. This is assuming that there are no relatively young abyssal intrusions.

It has been found possible to explain the origin of all the thermal springs that have been investigated in detail by structures permitting water of meteoric origin to descend to depth, take up earth heat, and then return to the surface at such a rate that much of this heat is retained. Some geothermal surveys have been made in South Africa, and when the temperatures at the depths to which the water is assumed to descend in such structures are calculated the results agree closely with the observed spring temperatures. Thus it is not necessary to postulate the presence of juvenile water, but the possibility cannot be ruled out that such water may contribute to the discharge of some of the springs. Connate water, on the other hand, almost certainly forms part of the thermal water flowing from the deep boreholes recently drilled in the Odendaalsrus and Trompsburg areas of the Orange Free State and may be present in some of the springs as well.

Geological sections illustrating the structures determining a few representative thermal springs are shown in Fig. 2. One of the simplest is the artesian basin around Loubad in the central Transvaal<sup>18</sup>. There rain falling on moderately high ground is believed to percolate through sandstones of the Waterberg system (late pre-Cambrian ?) until the basal shales or the impervious felsites of the Rooiberg series are reached. The water emerges from fractures next to a sharp fold that determines the south-west end of the basin. The maximum depth in the basin is about 3,600 feet (1,097 m.), and as the geothermal step is about 220 feet per 1°C. the water would be heated to a temperature of about 36°C. This agrees very well with that measured in the main orifices of the springs, viz. 31.7° to 34.1°C.

The small warm spring at Buffelshoek, also in the central Transvaal, rises from Waterberg sandstone next to a diabase dyke. The water, however, is chemically akin to that in granites, and not to that in sandstones. Geological mapping of the vicinity showed that the water in all probability percolates in Bushveld (Red) granite forming an artesian slope beneath the Waterberg sandstone until the barrier formed by the dyke is reached.<sup>20</sup> From the geological section it appears that the water would descend to a maximum depth of about 3,000 feet (915 m.), where the rock temperature would be about 31°C. In the eye of the spring the temperature is 30.5°C. It is of interest to note that chemical



and spectrographic analyses showed that the water is almost identical in composition with that issuing from a fault in Bushveld granite at Warmbaths fifty miles (80 km.) to the east-south-east.

The spring at De Bad, in the western Cape Province, is situated in a deep valley. As will be seen from the section its origin is relatively simple. Rain falling on a mountain range formed by sandstones of the Table Mountain series (Devonian) descends in a deep, fairly sharp syncline and emerges behind a barrier formed by a prominent shale band.

The hot spring at Goudini, also in the western Cape Province, rises from a mid-Cretaceous fault in the Table Mountain series. According to Dr. F. C. Truter of the Geological Survey, who investigated the area in 1938, the water probably percolates along and down the plane of the Worcester fault, which is one of the major faults of South Africa. This fault traverses mountainous country, and pressure must thus be built up in the water descending in the fracture zone. This water probably ascends in the sandstone confined between a shale band and the overlying shales of the Bokkeveld series until the plane of the Goudini fault is encountered, where the pressure is relieved. Some of the hot water may originate from rain percolating in the Goudini fault zone.

Recent detailed mapping by Mr. D. P. van Rooyen of the Geological Survey showed that both faulting and an intrusion of diabase are responsible for the emergence of hot water at Welgevonden in the north-central Transvaal. Rain water is assumed to percolate through sandstones of the Waterberg system until a diabase dyke is reached. This dyke eventually turns and follows an almost vertical fault cutting through felsites of the Rooiberg series (pre-Cambrian). The hot water rises in the fault zone alongside the dyke.

The shallower thermal artesian boreholes do not call for any special comments. The deep Zwartkops borehole was drilled in an artesian basin formed of Lower Cretaceous rocks lying unconformably on what was taken to be the Bokkeveld series.<sup>28</sup> It is less easy to account for the flowing supplies struck at great depths in the Orange Free State. Compaction of the aquifer, lavas of the Ventersdorp system around Odendaalsrus and pre-Karoo norite at Trompsburg, seems the most likely explanation.

Together the seven South African scalding springs bring to the surface approximately 150,000,000 kg. cal. of heat per 24 hours. The information regarding the temperatures and flows of the remaining thermal springs is not complete, and reliable calculations of the discharge of heat cannot be made. It is estimated that the total for all the thermal springs in South Africa is about 600,000,000 kg. cal. per 24 hours or  $5.8 \times 10^{-10}$  cal. cm.<sup>2</sup> sec. averaged over the whole surface of the country. This may be compared with Bullard's<sup>4</sup> figure of  $1.16 \times 10^{-6}$  cal. cm.<sup>2</sup> sec. for the mean heat flow in South Africa. Thus the heat brought to the surface by thermal water is only one two-thousandth part of that normally dissipated by conduction through the crust.

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## PART II. SOUTH WEST AFRICA.

## I. INTRODUCTION.

With an area of 82,292,180 hectares (317,725 sq. miles) the Territory of South West Africa is about three-quarters of the size of the Union of South Africa. In the Territory twenty-four springs are known to be thermal, and on the basis of temperature they may be classified as follows :—

Warm	...	...	...	...	8
Hot	...	...	...	...	4
Scalding	...	...	...	...	9
Temperature unknown				...	3

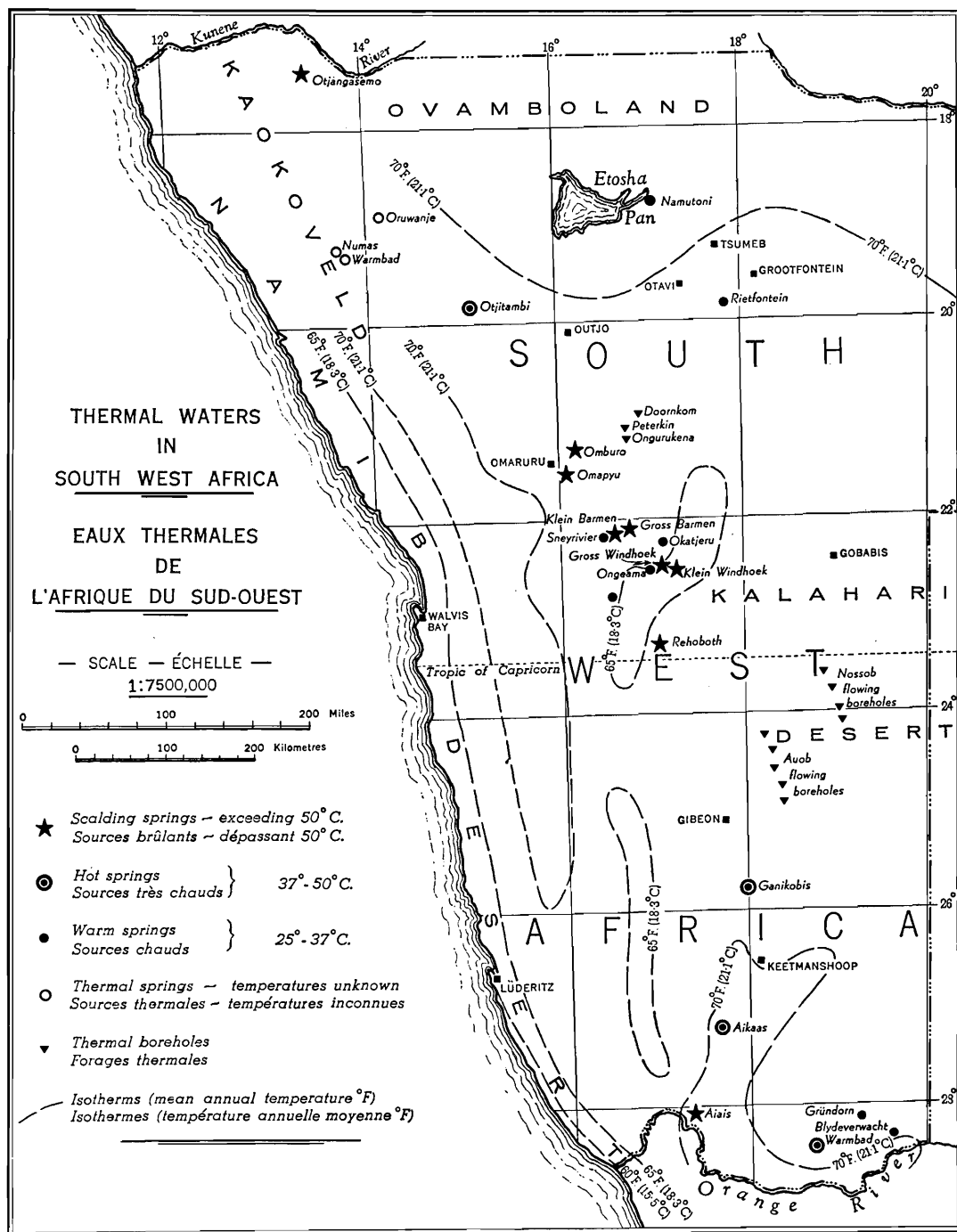
As the mean annual temperature in the mountainous tract around the capital, Windhoek, is 19°C. (66.2°F.), the same figure has been used as in the Union to divide thermal from non-thermal springs, viz. 25°C.

The positions of the various springs are shown on the map, Fig. 3, which is based on all available published information supplemented by a personal communication from Dr. H. Martin, geologist attached to the Administration of the Territory.

Relatively little is known about these thermal springs. Many of them occur in valleys in the central highlands between Rehoboth and Omaruru. On this mountainous tract, which stands some 1,500 to 2,000 metres (4,921 to 6,562 ft.) above sea-level, the rainfall is fairly high, 356 to 406 mm. (14 to 16 ins.) a year. Westwards it falls rapidly to less than 25 mm. (1 in.) in the coastal Namib desert. In the far north the coastal belt passes over from a sand desert into a fairly mountainous region known as the Kaokoveld. Here the annual rainfall is about 76 to 152 mm. (3 to 6 ins.) and there are at least four springs reputed to be thermal.<sup>6</sup> East of the Kaokoveld, in the Otavi Mountain Land, where the rainfall is about 560 mm. (22 ins.) a year, there are several fairly strong springs, only two of which, those at Rietfontein and Naumotoni, are even lukewarm. In the extreme south of the Territory, in the basins of the Orange and Fish rivers, the rainfall is very low, about the same as in the Kaokoveld; but in this arid region no less than six thermal springs are known.

## II. TEMPERATURES OF SPRINGS.

Compared with the Union a much higher percentage of the springs are scalding. Doubtless this is due, in part, to the Territory being less well-known, with the result that many lukewarm springs have not attracted any attention. Furthermore, a deep-seated spring in arid regions has a better chance of survival than a shallower one. Finally, the central highlands of South West Africa are highly faulted, and minor earthquakes show that movements still take place along several of the fault planes. By thus keeping fissures open deeper penetration of water is made possible.



The following temperature observations have been made :—

	°C.	Observer.
Gross Windhoek (Pahl spring) .. .. .	79·8	Gevers, 1931.
Omburu .. .. .	76·5	Rehbock, 1896–97.
Gross Barmen .. .. .	65	” ”
Klein Barmen .. .. .	61	” ”
Omapyu .. .. .	61	Schinz, 1885.
Aiais .. .. .	55	Range, 1906–08.
Klein Windhoek .. .. .	54·2	Gevers, 1931.
Rehoboth .. .. .	52	Rehbock, 1896–97.
Near Outjo (position unknown) .. .. .	46	Cock, 1929.
Ganikobis .. .. .	40	Range, 1906–08.
Warmbad .. .. .	37·5	Range, 1906–08.
Sneyrivier .. .. .	28	H. Martin, 1948.
Rietfontein .. .. .	27·8	Owners, 1948.

### III. DISCHARGES OF SPRINGS.

At Gross Windhoek scalding hot water formerly emerged at six main springs and a number of minor ones, all strung out over a length of  $1\frac{1}{2}$  km. along a fault fissure. The hottest, the Pahl spring, had a discharge of about 400 cbm. (88,200 galls.) a day in 1923<sup>3</sup>. As the supply was insufficient for the growing needs of the town, which depended solely on the thermal springs, several boreholes were sunk, and as a result of the increased withdrawal of water all the former natural springs have dried up. In 1931, according to Gevers<sup>3</sup>, the combined yield of all these boreholes was 2,499–2,817 cbm. (550,900–621,000 galls.) a day. At Klein Windhoek, 3 km. to the east, the natural springs have also become extinct as a result of the tapping of the supply by numerous boreholes.

According to Dr. H. Martin the Gross Barmen spring yields about 720 cbm. (159,000 galls.) of water a day. At the other end of the Territory the warm spring at Blydeverwacht was estimated by Haughton and Frommurze<sup>4</sup> to have a discharge of about 180 cbm. (40,000 galls.) a day. Apparently the only other that has been gauged is the lukewarm one at Rietfontein, which, according to the owners, the Rietfontein Co-operative Creamery, Ltd., yields about 2,140 cbm. (472,000 galls.) per day.

### IV. GEOLOGY OF THE SPRINGS.

As far as is known most of the thermal springs, and especially the hotter ones, rise in fault or fracture zones. The Windhoek springs, for example, rise in almost vertical fissures associated with volcanicity possibly of Cretaceous age. The lukewarm ones at Okatjeru and Ongeama (Okanjama) also lie on associated breccia-filled fissures.<sup>3</sup> Gross Barmen emerges at the north end of a fault that passes southwards into the Khomas Highlands.

The lukewarm Rietfontein spring, on the other hand, issues at the contact of the Otavi limestones (pre-Cambrian) and Archaean schists.

According to Dr. Martin the Sneyrivier and Ganikobis springs rise alongside dykes. At Sneyrivier the country rock is Archaean granite, whereas at Ganikobis it is the basal sediments of the Dwyka series (Carboniferous-Permian).

Blydeverwacht is a barrier spring, the barrier being a reef of amphibolite cutting across sheared gneisses<sup>4</sup>.

## V. THERMAL BOREHOLES.

Warm water has been struck in many of the boreholes in the artesian areas to the north-east of Gibeon. The main aquifer, a fairly thick sandstone in the Permian Ecce series, is struck at depths of between 43 and 166 m. (140 to 545 ft.). The strongest hole yielded 4,083 cbm. a day (900,140 galls.) The temperatures of the water taken at two boreholes in the Auob area were 32°C. and 33.7°C.<sup>2</sup>

Boreholes recently drilled in north-south trending fault zones north-east of Omaruru have also struck warm water. The following particulars were obtained through Dr. Martin :—

Borehole.	Depth.		Water-level from surface.		Yield/24 hrs.		Temp. °C.
	m.	ft.	m.	ft.	cbm.	galls.	
Doornkom	81	265	33	108	>327	>72,000	35—40
Peterkin	83	274	32	106	>390	>86,000	35

It should be noted that in South West Africa water in shallow boreholes generally has rather a high temperature, about 23° to 25° C., for during the day the barren rocks and soil acquire a far higher temperature than the air.

## VI. COMPOSITION OF THE THERMAL WATERS.

Analyses of only the thermal waters at Windhoek<sup>3</sup>, Gross Barmen,<sup>5</sup> Warmbad<sup>5</sup>, and a spring near Outjo<sup>1</sup> have been published. The first two rise from Archaean schists, Warmbad from granite-invaded gneisses, while the exact locality of the Outjo district spring is not known. According to Cock<sup>1</sup> it also rises in granite. It may be Otjitambi.

In his paper on the Windhoek springs Gevers<sup>3</sup> included several analyses. The most complete of these are included in the following Table. They are of water from the Pahl spring borehole and from the Jan Jonker boreholes, 2 km. south of the Pahl spring, but on the same fissure.

The analyses have all been recalculated on an ionic basis.

The Windhoek and Gross Barmen springs are only weakly mineralised, whereas Outjo and Warmbad are saline. Compared with the thermal waters in the Union the most striking feature is the high potassium content, particularly at Gross Barmen and the Jan Jonker boreholes, where potassium exceeds sodium. Assuming the accuracy of the analyses this is doubtless due to the higher proportion of potassium in the Old granites and schists of South West Africa<sup>5</sup>

Sulphate is also high in the analysed waters and at Windhoek is far more prominent than chloride. The pH values were not determined, but for the sake of uniformity all the carbonate has been recalculated as bicarbonate. This is a particularly important item in the Windhoek waters, but owing to the deposition of calcium carbonate in the Pahl borehole pipes the analysis is not truly representative of the fissure water. As is to be expected in very hot waters containing alkali bicarbonate or carbonate the silica content is high. To maintain a balance between cations and anions it has had to be calculated as SiO<sub>3</sub>" in the Windhoek waters.

# ANALYSES OF SOUTH WEST AFRICAN THERMAL WATERS.

IONS.	WINDHOEK. Pahl spring borehole.		WINDHOEK. Jan Jonker boreholes.		GROSS BARMEN.		OUTJO DISTRICT. (Position unknown).		WARMBAD.	
	mgm. per litre.	N/1,000	mgm. per litre.	N/1,000	mgm. per litre.	N/1,000	mgm. per litre.	N/1,000	mgm. per litre.	N/1,000
NH <sub>4</sub> · .. ..	nil	—	nil	—	tr.	—	—	—	—	—
Na· .. ..	212·2	9·23	58·6	2·55	132·2	5·75	293·5	12·77	550·3	23·93
K· .. ..	101·3	2·59	76·4	1·95	134·2	3·43	155·4	3·98	9·6	0·25
Mg· .. ..	12·1	1·01	40·4	3·37	2·64	0·22	86·9	7·15	5·5	0·46
Ca· .. ..	17·9	0·89	90·1	4·50	37·9	1·89	69·2	3·46	163·6	8·18
Al· + Fe· .. ..	tr.	—	tr.	—	—	—	—	—	0·9	?
Sum of cations ..	343·5	13·72	265·5	12·37	306·94	11·29	605·0	27·36	729·9	32·82
Cl' .. ..	63·0	1·78	42·0	1·18	127·9	3·61	543·2	15·32	709·6	20·01
NO <sub>3</sub> ' .. ..	nil	—	nil	—	—	—	nil	—	tr.	—
SO <sub>4</sub> ' .. ..	176·4	3·67	141·6	2·95	373·8	7·78	411·4	8·57	546·6	11·38
HCO <sub>3</sub> ' .. ..	224·6	3·68	241·2	3·95	n.d.	—	211·1	3·46	857·7	1·41
SiO <sub>3</sub> ' .. ..	177·2	4·66	151·9	4·00	n.d.	—	—	—	—	—
Sum of anions ..	441·2	13·79	576·7	12·08	501·7	11·39	1,165·7	27·35	2,113·9	32·80
H <sub>2</sub> SiO <sub>3</sub> .. ..	—	—	—	—	n.d.	—	44·0 (‘silicates’)	—	109·2	—
Dissolved H <sub>2</sub> S ..	present	—	present	—	4·25	—	n.d.	—	n.d.	—
Total sum of items determined ..	784·7	—	842·2	—	812·89	—	1,814·7	—	2,223·1	—
Items sought but not found ..	—	—	—	—	—	—	NO <sub>2</sub> ', PO <sub>4</sub> '', HBO <sub>3</sub> '	—	—	—
Date and analyst	1926, Versuchs & Lehranstalt für Brauerei, Berlin			1911, C. Grimme			1929, G. Cock		1914, W. Versfeld	
Temperature of water °C. ..	79·8		33—35		65		46		37·5	

Tests made in 1931 by Gevers<sup>3</sup> with a calibrated electroscope showed that the scalding waters of Windhoek are only slightly radioactive. The cooler water from the Jan Jonker and other boreholes is much more radioactive, the highest value obtained being 12·23 Maché units at the borehole of the South West Breweries, Ltd.

An evaporate of a sample of water from the Aiais spring was submitted to Mr. R. F. Bouwer of the Geological Survey for determination of its radioactivity. No signs of radioactivity were, however, detected.

#### VII. SPRING DEPOSITS.

At Windhoek there has been extensive deposition of calcareous tufa, the layer at Gross Windhoek having a maximum thickness of 2½ to 3 m. Recently deposited material in the pipes at the Pahl borehole has the following composition:

CaCO <sub>3</sub>	..	..	..	..	98·24
CaSO <sub>4</sub>	..	..	..	..	0·41
BaSO <sub>4</sub>	..	..	..	..	0·38
Fe <sub>2</sub> O <sub>3</sub>	..	..	..	..	0·80
MgO	..	..	..	..	tr.
Insoluble	..	..	..	..	tr.
					<hr/>
					99·83
					<hr/>

*Analyst*: J. P. van der Westhuyzen.

#### VIII. SOURCE OF THE WATERS AND THEIR HEAT.

The Windhoek springs rise from almost vertical fault fissures along which, in possibly Cretaceous times, there was volcanic activity. Although the fissures are of volcanic origin, Gevers<sup>3</sup> regarded the water as almost certainly meteoric. Rain falling on the mountains just south of the Windhoek valley and some 700 to 800 m. (2,296 to 2,624 ft.) higher is believed to get into the fissures by percolating along a bed or beds of permeable quartzites that are interleaved with garnet-biotite schists. These beds dip northwards towards the springs, first steeply and then at about 20° to 25°, and the uppermost quartzite would lie about 2,000 to 3,000 m. below Windhoek. No geothermal measurements have been made in the Territory, and Gevers assumed the geothermal step to be about 33 m. per 1°C. In Southern Rhodesia, however, measurements at the Globe and Phoenix Mine gave average values of 67·5 m. and 65·3 m. per 1°C. for magnesian schists and Archaean granite respectively.<sup>7</sup> On the other hand the considerably lower step of 41 m. per 1°C. has been found in the copper mines at Messina in the Northern Transvaal. If the value at Windhoek is assumed to be 40 m. per 1°C., the water would have to descend to about 2,500 m. (8,202 ft.) to attain a temperature of 80°C. This is in agreement with the calculated depth of the assumed aquifer. As volcanism took place along the fault fissures it may quite safely be assumed that they penetrate to a great depth, and it seems likely that even at fairly great depths they are sufficiently open to permit percolation of water.



Even though there may have been post-Mesozoic volcanicity in the Territory, it is extremely probable that all the thermal springs are of meteoric origin, the water becoming heated as a result of the normal geothermal gradient supplemented, perhaps, by frictional heat developed by the slight movements that still take place along several of the spring faults.

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