13. GEOCHEMISTRY OF THE SUBSURFACE WATERS OF THE NAMIB DESERT

The geochemistry of the subsurface waters of the Namib Desert was studied with two main objectives in mind. Firstly, the concentration and distribution of uranium in subsurface waters was investigated to determine whether it reflected the likelihood of uranium mineralization in the enclosing rocks. Secondly, an attempt was made to establish the underlying principles that govern the leaching and migration of uranium in the arid environment of the Namib Desert. Furthermore the subsurface waters form the second phase in the geochemical cycle of uranium.

Gableman (1970, p. 326) defined certain characteristics necessary for a fluid to form uranium ores. These are:

'1. Corrosiveness: It must be capable of altering rock by leaching and replacement.

2. Penetrability: It must be capable of permeating dense rocks impenetrable by fresh ground-waters.

3. Concentration: It must have a high concentration of a large variety of mineral ions and mineralizers in addition to the dominant uranium, vanadium, etc.

4. Selectivity: Its chemical character must enable it to react only to certain host rock chemical environments.'

Butler (1969, p. 85) and Gableman (1970, p. 325) are of the opinion that the ore fluids are meteoritic waters having a high concentration of dissolved salts. Isotopic studies in natural brines (Clayton et al, 1966, in Gableman, 1970) have confirmed both this and the fact that the total salinity content was derived from the rocks through which the water moved. Hellewig (1969) described the movement of subsurface waters from the Namib Desert in general and concluded that the concentration of the dissolved solids increased towards the coast. This, he pointed out, is due to the dissolution of subsurface marine salt deposits.

The mean annual rainfall in the Namib Desert is very low and over a period of 35 years it is only 17,9 mm at Swakopmund (Table 39). On the assumption that inland figures are of the same order of magnitude, recharging of the acquifers is a very slow process. In fact most of the rain is more than likely to be removed from the surface by evaporation before it has a chance to replenish the acquifers. So the system being dealt with is one of partial stagnation.

The area from which samples 1 to 29 were taken lies between the Swakop River in the south and the Khan River in the north (Fig. 41). Samples 30 and 31 were taken from boreholes HJ-1 and J-1 respectively in the Gawib River Valley (Map 1).

Geological mapping of the area was done by Jacob (1974) and the Anglo American Prospecting Co. Ltd. The latter was concerned with the evaluation of uranium ore reserves over the farms Dorstrivier 15, Nordenburg 76, Vlakteplaas 110 and Bloemhof 109. (Annual Prospecting Reports (1972, 1973) Prospecting Grant M46/3/209). Most of the concession held by Anglo American Prospecting Co. Ltd. is covered by calcrete

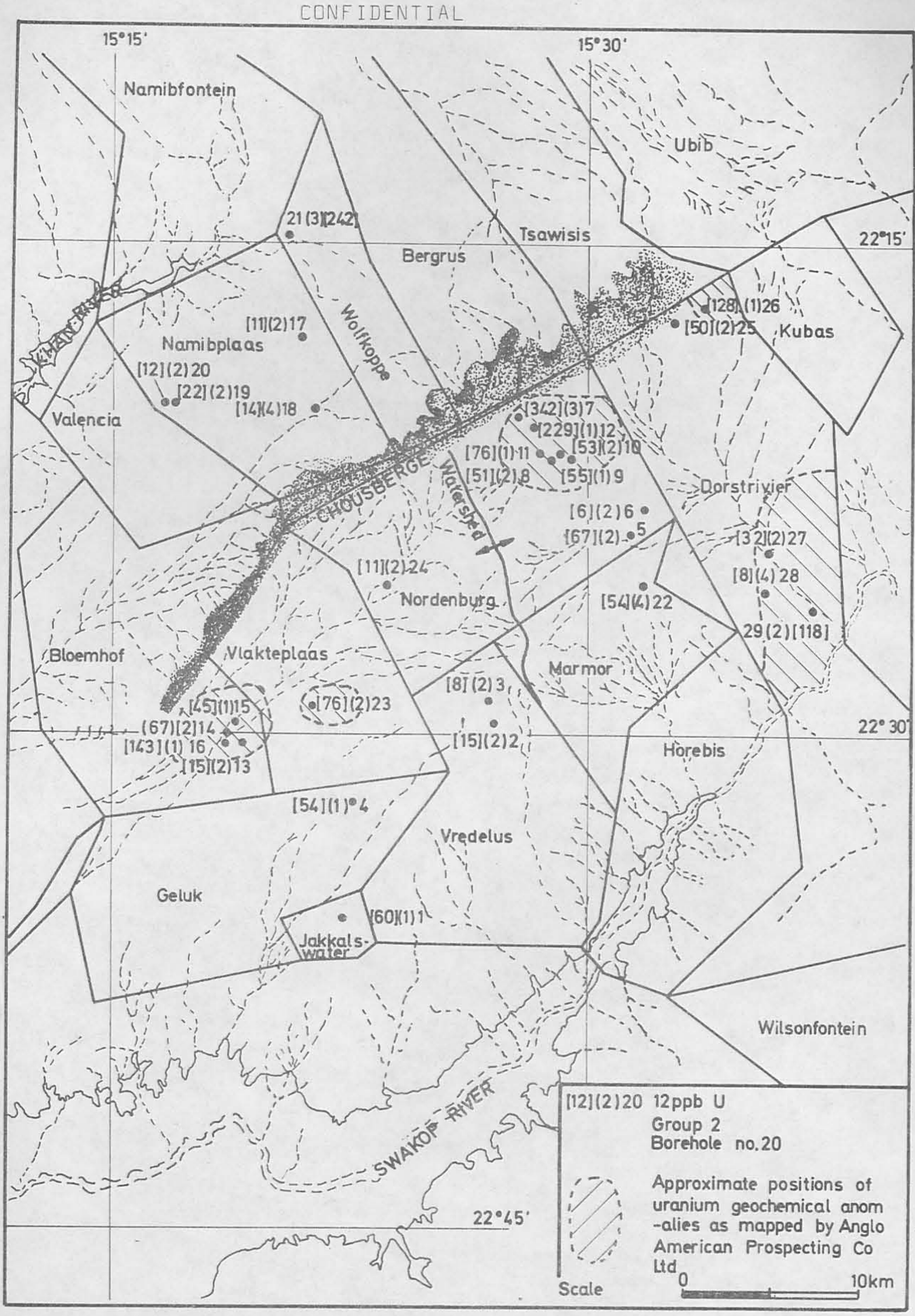

Fig. 41: The area and localities of the boreholes from which the subsurface water samples were taken. Each sample point is designated as follows: e.g. [12] (2)20 means that the sample was taken from borehole number 20, classified into Group 2, and contains 12 ppb U.

deposits, with the exception of the mountainous areas (Chuosberge) and the eroded southern portion of Dorstrivier. Surface geochemical prospecting delineated several radioactive anomalies with uranium contents above 15 ppm in calcrete on the farms Bloemhof, Vlakteplaas and the northern part of Dorstrivier. In the southern part of Dorstrivier the anomaly is mainly on granite (Gn_1).

Uranium crystallized into the minerals carnotite and soddyite, which are found together. Mineralization in the calcretes on Bloemhof and Vlakteplaas is of low grade, the highest value being 388 ppm U_3O_8. Generally the range of values for U_3O_8 lies between 5 ppm and 90 ppm, with most of it concentrated within the upper 10 m of the calcrete. Bedrock was intersected at depths between 6 m and 47 m.

The watershed of the Chuosberge dominates the main drainage system of this area (Fig. 41). It runs approximately north-east, separating rivers flowing southwards to the Swakop River from those flowing northwards to the Khan River. One minor watershed runs north-south through the farm Nordenburg and influences only the southward flowing rivers.

13.1 Analytical Results

Water samples numbers 1 to 31 were classified into four groups and are listed in Tables 15 to 18. Table 19 gives the means and range of values for all the samples.

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TABLE 15: CHEMICAL ANALYSES OF GROUP 1 SUBSURFACE WATERS FROM THE NAMIB DESERT

	1	4	9	11	12	15	16	26	31	MEAN	MINIMUM	MAXIMUM
pH	8,0	7,2	9,2	7,8	8,3	7,5	7,9	8,3	7,6	8,0	7,2	9,2
*CONDUCTIVITY	9 800	18 500	4 700	8 000	5 400	8 300	8 400	4 000	12 800	8 878	4 700	18 500
+TDS (ppm)	7 695	15 285	3 415	5 085	3 630	5 735	5 590	2 870	10 840	6 683	2 870	15 285
Na (ppm)	1 360	3 480	544	870	560	1 120	1 265	488	1 760	1 272	488	3 480
K (ppm)	50	340	26	50	44	66	112	16	94	89	16	340
Ca (ppm)	1 008	1 638	460	672	367	735	357	240	1 304	753	240	1 638
Mg (ppm)	202	269	106	236	204	137	196	135	74	173	74	269
U (ppb)	60	54	53	76	229	45	143	128	107	99	45	229
V (ppb)	58	79	26	13	4	57	54	10	65	41	4	79
Sr (ppb)	6 725	11 219	2 783	3 534	2 897	7 152	5 819	3 100	1 395	4 958	395	11 219
Ba (ppb)	346	673	137	198	160	229	589	462	488	365	137	673
SO_4 (ppm)	678	1 596	959	820	480	1 356	856	327	725	666	327	1 596
NO_3 (ppm)	165	127	5	2	82	14	23	96	9	58	2	165
SiO_2 (ppm)	15	20	10	15	25	25	40	40	25	24	10	40
F (ppm)	1,8	2,4	0,5	1,1	0,6	0,9	1,4	2,2	3,5	1,6	0,5	3,5
Cl (ppm)	3 475	7 700	1 205	2 550	1 330	2 325	2 400	910	1 600	2 611	910	7 700
CO_3 (ppm)	54	60	27	72	204	48	132	135	90	91	27	204

* Conductivity units, mho.

+ TDS = Total dissolved solids.

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TABLE 16: CHEMICAL ANALYSES OF GROUP 2 SUBSURFACE WATERS FROM THE NAMIB DESERT

	2	3	5	6	8	10	13	14	17	19	20	23	24	25	27	29	MEAN	MIN.	MAX.
pH	7,0	7,9	7,3	8,0	7,7	8,4	7,3	7,5	7,7	8,1	7,9	7,8	8,0	7,5	7,2	7,4	7,7	7,0	8,4
*CONDUCTIVITY	4. 880	3 100	5 300	6 100	4 550	3 400	8 300	6 700	3 280	2 250	2 550	7 170	3 150	3 600	7 050	10 000	5 086	2 250	10 000
+TDS (ppm)	3 545	2 355	3 765	4 875	3 135	2 250	5 595	4 495	2 185	1 460	1 705	5 165	1 980	2 370	4 910	7 594	3 586	1 460	7 594
Na (ppm)	353	224	508	655	386	348	1 120	870	300	298	306	826	348	330	740	1 220	552	224	1 220
K (ppm)	10	6	45	35	15	40	102	84	25	17	10	42	23	24	10	80	36	6	102
Ca (ppm)	624	397	489	638	521	158	556	441	248	118	198	651	200	290	735	651	432	118	735
Mg (ppm)	107	64	129	197	97	159	184	169	77	55	51	175	83	128	167	431	142	51	431
U (ppb)	15	8	67	6	51	53	88	67	11	22	12	76	11	50	32	118	43	6	118
V (ppb)	27	6	38	5	11	11	28	36	31	34	34	52	5	50	30	20	26	5	50
Sr (ppb)	2 634	2 746	3 803	4 397	3 047	826	6 781	5 052	1 492	1 920	1 500	5 170	4 500	3 060	7 500	23 260	4 856	826	23 260
Ba (ppb)	245	122	169	210	182	56	168	171	144	37	75	232	291	365	766	668	244	37	766
SO_4 (ppm)	295	180	638	658	425	469	720	617	197	192	245	617	279	399	617	1 192	484	180	1 192
NO_3 (ppm)	150	76	80	131	73	8	32	33	54	9	14	96	7	43	90	103	62	7	150
SiO_2 (ppm)	30	30	30	15	30	40	25	25	40	40	40	25	15	25	40	30	30	15	40
F (ppm)	1,2	0,7	1,3	0,6	0,7	0,4	1,0	1,0	0,8	1,5	1,5	1,2	0,8	1,2	1,0	1,5	1,0	0,4	1,5
Cl (ppm)	1 250	805	1 200	1 780	1 135	753	2 475	1 925	760	518	578	2 075	820	810	2 200	2 925	1 376	518	2 925
CO_3 (ppm)	105	111	183	78	156	156	171	168	147	147	159	132	78	168	168	189	145	78	189

* Conductivity units, mho.

+ TDS = Total dissolved solids

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TABLE 17: CHEMICAL ANALYSES OF GROUP 3 SUBSURFACE WATERS FROM THE NAMIB DESERT

	7	21	30	MEAN	MIN.	MAX.
pH	7,1	7,5	7,5	7,4	7,1	7,5
*CONDUCTIVITY	2 700	6 780	5 400	4 960	2 700	6 780
+TDS (ppm)	1 870	5 170	4 045	3 695	1 870	4 045
Na (ppm)	264	740	555	520	264	740
K (ppm)	20	54	42	39	20	54
Ca (ppm)	229	735	450	471	229	735
Mg (ppm)	94	161	77	81	77	161
U (ppb)	342	242	298	294	242	342
V (ppb)	16	5	18	13	5	18
Sr (ppb)	1 550	838	47 772	16 203	838	47 772
Ba (ppb)	129	207	210	182	129	210
SO_4 (ppm)	223	1 440	360	674	223	1 440
NO_3 (ppm)	52	48	2	34	2	52
SiO_2 (ppm)	40	25	10	25	10	40
F (ppm)	0,4	1,5	2,5	1,5	0,4	2,5
Cl (ppm)	515	1 600	1 600	1 238	5,5	1 600
CO_3 (ppm)	95	105	68	89	68	105

* Conductivity units, mho.

\+ TDS = Total dissolved solids.

TABLE 18: CHEMICAL ANALYSES OF GROUP 4 SUBSURFACE WATERS FROM THE NAMIB DESERT

	18	22	28	MEAN	MIN.	MAX.
pH	7,3	7,4	7,5	7,4	7,3	7,5
* CONDUCTIVITY	1 800	3 830	2 130	2 587	1 800	3 830
+ TDS (ppm)	1 130	2 375	1 355	1 620	1 130	2 375
Na (ppm)	136	200	186	174	136	200
K (ppm)	7	15	16	13	7	16
Ca (ppm)	187	397	182	255	182	395
Mg (ppm)	47	145	49	80	47	145
U (ppb)	14	15	8	12	8	15
V (ppb)	3	6	10	6	3	10
Sr (ppb)	1 472	2 392	3 430	2 431	1 472	3 430
Ba (ppb)	31	166	469	222	31	469
SO_4 (ppm)	89	339	144	191	89	339
NO_3 (ppm)	4	21	23	16	4	23
SiO_2 (ppm)	40	25	40	35	25	40
F (ppm)	0,7	0,4	0,4	0,5	0,4	0,7
Cl (ppm)	340	903	345	529	340	903
CO_3 (ppm)	210	219	204	211	204	219

* Conductivity units, mho.

\+ TDS = Total dissolved solids.

TABLE 19: MEANS AND RANGE OF CONCENTRATIONS OF IONS IN SUBSURFACE WATERS FROM THE NAMIB DESERT FOR ALL 31 SAMPLES

	MEAN	MINIMUM	MAXIMUM
pH	7,7	7,0	9,2
*CONDUCTIVITY	5 933	1 800	18 500
+TDS (ppm)	4 306	1 130	15 285
Na (ppm)	721	136	3 480
K (ppm)	49	6	340
Ca (ppm)	512	118	1 638
Mg (ppm)	142	49	431
U (ppb)	81	6	342
V (ppb)	27	3	79
Sr (ppb)	5 754	826	47 772
Ba (ppb)	271	31	766
SO_4 (ppm)	585	89	1 596
NO_3 (ppm)	54	2	165
SiO_2 (ppm)	28	10	40
F (ppm)	1,2	0,4	3,5
Cl (ppm)	1 639	340	7 700
CO_3 (ppm)	130	54	219

* Conductivity units, mho.

+ TDS = Total dissolved solids.

Analysis of samples 1 to 29 was done by the Department of Water Affairs in Windhoek according to their routine methods for water analysis. The analysis of the two samples from the Gawib River and the analyses for strontium, barium, vanadium and uranium for all samples were done at the Atomic Energy Board. Conventional atomic absorption flame procedures were used for strontium and barium, whereas the carbon rod method was used for vanadium. Uranium was analyzed using the technique of delayed neutron counting.

In Table 20 the concentrations of some trace elements in subsurface waters are given which were analyzed by Anglo American Corp. Ltd (Annual Prospecting Report (1973) Prospecting Grant M46/3/209). There is no relationship between the samples in Table 20 and those of Tables 15 to 18.

TABLE 20: TRACE ELEMENT ANALYSES OF SUBSURFACE WATERS FROM THE NAMIB DESERT. (ANNUAL PROSPECTING REPORT (1973) PROSPECTING GRANT M46/3/209

ppb	W1	W2	W3	W4	W5	W6	W7	W8	$\overline{X}$	MIN.	MAX.
U	110	110	25	55	102	51	136	55	81	25	136
Pb	34	45	19	50	78	38	31	43	42	19	78
Cu	10	11	10	16	17	19	15	17	14	10	19
Ni	22	29	11	23	32	19	15	22	22	11	32
Ag	17	10	4	18	19	24	9	9	14	4	24
Zn	24	22	11	1 000	34	35	12	12	21*	11	1 000
Cu	2	3	2	4	4	3	2	3	3	2	4

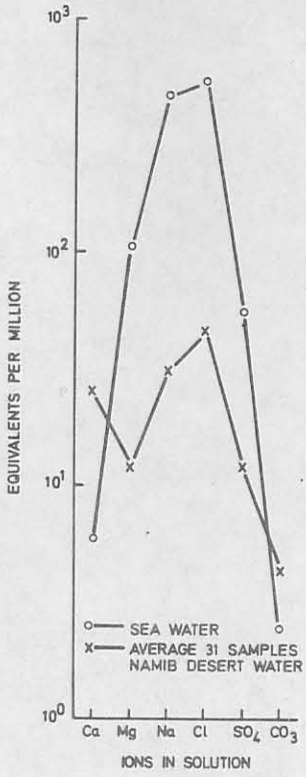
* The mean value for Zn does not include the 1 000 ppb value in sample W4.

13.2 Characteristics and Classification of the Subsurface Waters

Very wide variations in the values were found for some elements, for example potassium and uranium, where the concentrations differ by factors of about 60. Variation in the contents of carbonate and silica is less extreme and the maximum values are only a factor four greater than the minimum values. Sodium and potassium Calcium are the most abundant cations, followed by magnesium and potassium. The major anions in order of abundance are chloride, sulphate and carbonate. All the remaining ionic species are present only in trace amounts.

A convenient way to describe the composition of brines is their relationship to the composition of seawater. Fig. 42 is a Schoeller diagram representing the ions in solution in terms of their equivalents per million (Parker, 1969, p. 120). The comparisons between the concentrations of calcium, magnesium, sodium, chloride, sulphate and carbonate in seawater (Table 38) and the average values for 31 Namib Desert waters (Table 19) are shown.

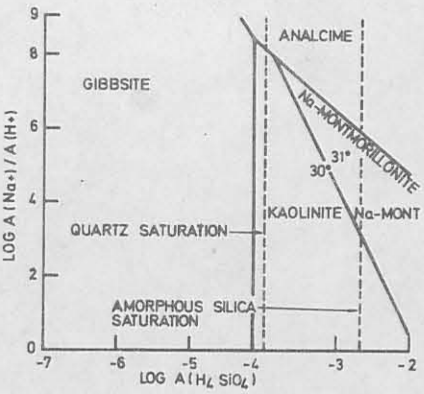
The total concentrations of the elements in the Namib Desert waters are in general lower with respect to seawater. Calcium and carbonate are, however, relatively enriched, the former being greater by a factor of approximately four. Magnesium is depleted relative to its neighbours, calcium and sodium, but this anomaly is not observed in seawater. Reasons for this were expressed by Bentor (1969, p. 84) who found that two mechanisms may apply



– Fig. 42: Schoeller diagram, comparison of the ionic distributions in subsurface waters of the Namib Desert and seawater in terms of equivalents per million ionic species.

in this situation. Firstly, magnesium is incorporated into the calcite lattice, and secondly, magnesium may be exchanged for a cation in montmorrilonite clay. The similarities between the Namib Desert brine patterns and those of certain brines in the USA (Parker, 1969, p. 119) are very striking, especially in their depletion of magnesium.

In natural brines some elements in solution do not normally exist in the purely ionic form, but as ion associa= tions or coordination complexes. The major ions, for example magnesium, form ion pairs, whereas the trace elements, for example vanadium, form coordination complexes. Truesdell and Jones (1969, p. 58) point out that magnesium is parti= cularly susceptible to the formation of ion pairs, with silica being a principal contributer, followed by carbonate and sulphate. This feature may also account for the fractionation of magnesium as shown in Fig. 42. Garrels and Thompson (1962, p. 57) determined that for seawater 87 per cent of the magnesium occurs as the free ion, 11 per cent as the $Mg-SO_4$ pair, and 1 per cent as the $Mg-HCO_3$ pair. No value for the $Mg-SiO_2$ pair was listed. In solutions supersaturated with silica, magnesium remains in solution, but in the saturation field for amorphous silica, minerals such as montmorillonite and attapulgite may develop. Fig. 43 shows the positions of samples 30 and 31 from the Langer Heinrich plotted on an activity diagram. Both



How is the activity calculated?

Fig. 43: Activity diagram for the system $Na_2O-Al_2O_3-SiO_2-H_2O$ at 25 °C at unit activity of water and 100 kPa. Adapted from Helgeson et al (1969, p. 462). Subsurface water samples 30 and 31 from the Gawib River Valley fall into the montmorillonite field.

samples fall in the montmorillonite field and below the level of amorphous silica saturation. Although this is a sodium montmorillonite, it nevertheless demonstrates the stability of montmorillonite in the calcretes of the Gawib River Valley. Hess (1966, p. 306) points out that an activity diagram (Fig. 43) strictly only applies under ideal conditions where all phases are stoichiometric and activities are equivalent to concentrations. The subsurface waters in the Namib Desert are certainly not ideal solutions and caution must be exercised in the interpretation of activity diagrams.

Mineral equilibria relationships for calcite and silica, predicted from thermodynamic considerations (Kramer, 1969), are shown in Figs. 44 and 45. On the assumption that the temperature of the subsurface waters in the Namib Desert is 20 °C (the temperature was not measured and it is therefore likely that fluctuations will occur to either side of this value) the values for samples 30 and 31, as well as the minimum and maximum values given in Table 19, have been plotted on the diagrams. All values in Fig. 44 plot well into the field saturated with calcite, indicating that the waters are saturated with respect to calcite. This is to be

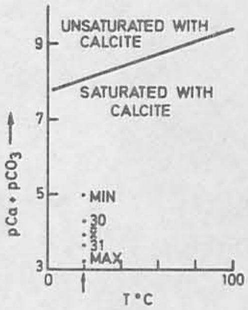


Fig. 44: Equilibrium plot for calcite or calcareous rocks as a function of temperature with respect to the subsurface brines. pCa= $-\log_{10}(Ca^{2+})$ and $pCO_3 = -\log_{10}(CO_3^{2-})$. The minimum, maximum and mean ($\bar{x}$) for all water samples are plotted. (Values taken from Table 19). Samples 30 and 31 from the Gawib River Valley are also plotted. The temperature for the subsurface water was assumed to be 20 °C.

expected in calcretes. The waters are therefore capable of precipitating calcite so that the development of calcrete is still in progress. In Fig. 45 the points tend to cluster nearer to the equilibrium line for amorphous silica. Kaolinite was not found at the Langer Heinrich. Kramer (1969, p. 48) points out that the quartz equilibrium line actually represents the kaolinite-potassium feldspar-potassium mica equilibrium. All samples fall well below this equilibrium line, indicating that these minerals are unstable under the conditions prevailing in the Namib Desert. The more stable montmorillonite is therefore the coexisting phase present, which was confirmed by X-ray diffraction.

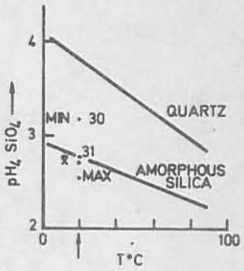


Fig. 45: Equilibrium plot for quartz and amorphous silica as a function of temperature with respect to the subsurface brines. $pH_4SiO_4 = -\log_{10}(H_4SiO_4)$. The minimum, maximum and mean ($\bar{x}$) for all water samples are plotted. (Values taken from Table 19). Samples 30 and 31 from the Gawib River Valley are also plotted. The temperature for the subsurface water was assumed to be 20 °C.

The water samples were taken over a very large area on both sides of the watershed of the Chuosberge and associated with several different rock types. For this reason they have very wide ranges in the abundances of their soluble species. Under these circumstances the probability that the samples can be grouped is very likely. Grouping was suggested from the correlation matrix of all 31 samples. Generally it can be accepted that there is a fairly good degree of correlation between uranium and carbonate, but in this matrix almost zero correlation was found. A plot of these two values (Fig. 46) showed that four groups possibly exist.

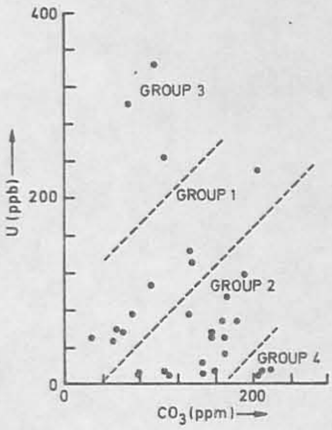


Fig. 46: Variation diagram of uranium plotted against carbonate. Four groups in the water samples are indicated. The dashed lines give the approximate group boundaries.

To test whether this classification had any merit, a multivariate discriminant analysis in a stepwise manner was performed using the computer program BMD07M (Dixon, 1967), called DISC. At each step one variable was entered into a set of discriminating variables, based on the statistical F test. For each sample a mahalanobis distance and a probability function were determined giving the likelihood of the sample fitting within the specified group. Finally a set of canonical variables was calculated in order to represent the distribution of the groups in a two-dimensional way. Furthermore, in accordance with the

[illegible]

F-tolerance limits set, elements were selected that could best discriminate between the groups.

The variables used for the discrimination were pH, total dissolved solids, sodium, potassium, calcium, magnesium, uranium, vanadium, sulphate, fluorine, chlorine and carbonate. F-values for inclusion and deletion were 2,1 and 2,0 respec=tively, from which uranium, carbonate, sodium and sulphate were the most discriminating functions for separating the groups. Canonical variables calculated for each group and their respective means are plotted in Fig. 47. A very good separation of the four groups is shown. Group 3 has the greatest variance. The probability that most samples will fall within their specified groups is generally greater than 98 per cent (Table 21).

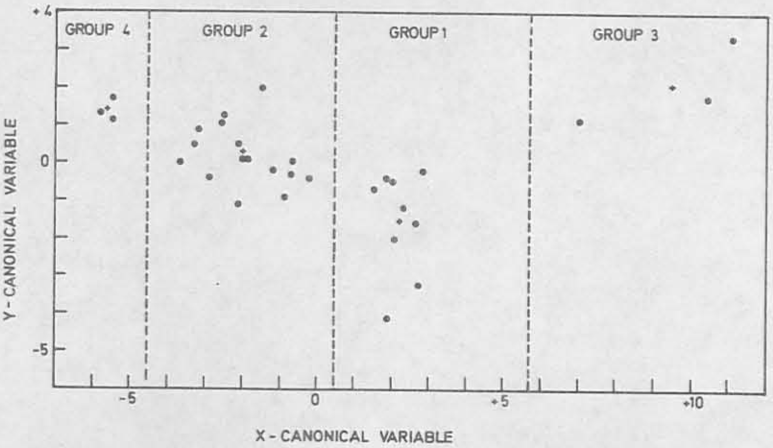


Fig. 47: A plot of the X- and Y-canonical variables derived from a multivariate discriminant analysis of the data from 31 subsurface water samples. (+ = mean).

TABLE 21: CLASSIFICATION OF THE SUBSURFACE WATERS INTO GROUPS, USING MULTIVARIATE DISCRIMINANT ANALYSIS, AND THE CALCULATED PROBABILITIES ASSOCIATED WITH EACH SAMPLE

		GROUPING BASED ON DISCRIMINANT ANALYSIS OF CHEMICAL DATA			
		GROUP 1	GROUP 2	GROUP 3	GROUP 4
INITIAL GROUPING OF THE SUBSURFACE WATERS	GROUP 1	(1) 1 (2) 1,0 31 1,0 4 1,0 9 1,0 11 1,0 12 1,0 15 1,0 16 1,0 26 1,0			
	GROUP 2	23 0,14	2 1,0 17 0,93 3 1,0 19 0,99 5 0,98 20 0,80 6 0,98 23 0,86 8 1,0 24 0,99 10 1,0 25 0,99 13 1,0 27 0,88 14 1,0 29 0,98		17 0,07 20 0,20 27 0,12
	GROUP 3			7 1,0 21 1,0 30 1,0	
	GROUP 4				18 1,0 22 1,0 28 1,0

(1) Sample number
(2) Probabilities

Group 2 has four samples with probabilities below 98 per cent. Sample 23 has a 14 per cent chance of falling into Group 1, whereas samples 17, 20 and 27 have 7 per cent, 20 per cent and 12 per cent chance respectively of falling into Group 4. These low probabilities were disregarded due to their high loadings associated with Group 2.

The question now arises: how are these four groups distributed within the drainage patterns? Each borehole (Fig. 41) is marked with the sample number, group number (round brackets) and uranium concentration in ppb (square brackets). There seems to be no uniformity in the distribu= tion of the samples in their groups. Four boreholes situated close to each other on the farm Bloemhof are presented by Groups 1 and 2. In the north-eastern corner of Nordenburg six boreholes, also clustered together, fall within Groups 1 and 3. Northwards, across the Chuosberge, Groups 2, 3 and 4 are found. Waters within the same drainage channels also fall within different groups.

Unfortunately no information was available concerning the depth of the borehole, the quality of the casing or the frequency of the pumping, for these factors are important in evaluating the mineralizing characteristics of the water. The depth of the borehole and the quality and length of casing will determine the depth from where the sample was obtained. Ultimately these parameters may account for the discrepancies in the contents of the dissolved solids. A second possibility, although unlikely, to account for group differences within nearby boreholes is that they may be fed from different acquifers.

A very close coherence was observed between the uranium concentrations of the subsurface waters and the surface uranium geochemical anomalies (Fig. 41). Certain exceptions are the high values on Jakkalswater, Marmor and in the south-eastern corner of Nordenburg. Lack of information concerning the uranium mineralization within these areas may account for this. North of the Chuosberge only one sample has a significant uranium concentration; here again no information on mineralization was available from this area. It may therefore be inferred that there is a reasonable probability that uranium mineralization may be present in the Wolfkoppe area. Samples 13 and 28 occur within mineralized areas but have low uranium concentrations. No reason can be given for this feature which may be due to a large number of causes, some of which were enumerated above.

A second classification, although very rough, has therefore been established. Those waters with uranium concentrations above 30 ppb are generally located within zones of potentially high uranium concentration. Values below this level may be regarded as background. In the USA 5 ppb uranium is background, whereas 10 ppb uranium is anomalous (Butler, 1969, p. 85). Care must be exercised with the interpretation of the uranium concentration in water because, assuming that the values of samples 13 and 28 reflect the actual situation, deviations from ideality can nevertheless occur. Two conditions may prevail that could account for anomalously high uranium values:

(a) An uneconomical uranium source undergoing weathering. For example, sample 29 with 118 ppb uranium is situated in Red Granite gneiss terrain. Figures quoted by Anglo American Prospecting Co. Ltd gave a mean of 14,5 ppm U_3O_8 for the Red Granite gneiss in the southern sector of Dorstrivier (Annual Prospecting Report (1973) Prospecting Grant M46/3/209).

(b) Water was in contact with a potential uranium deposit at or below the water-table, for example, the calcrete uranium deposits on the farm Bloemhof.

Therefore for waters in the Namib Desert the following applies: Uranium concentrations of 30 ppb or more reflect a potentially mineralized zone nearby. Uranium concentrations less than 30 ppb generally do not indicate mineralization. However, background uranium values do not necessarily mean that potential mineralization is absent, and anomalous values (greater than 30 ppb) do not necessarily imply a uranium deposit below or nearby.

13.3 Factor Analysis

Important parameters determining the distribution of the elements in the hydrological environment have been outlined by Spencer et al (1968, p. 981), viz:

(a) Composition of the source rocks and the weathering processes that act upon them.

(b) Nature of transporting processes and mechanisms of deposition.

They further pointed out that mechanisms involved in the evolution of sediments usually occur under non-equilibrium conditions, making interpretation of the analyses all that more complicated. Furthermore it becomes increasingly more difficult when a large number of variables are considered. Twenty-five samples (Groups 1 and 2) were analyzed for 17 variables, giving a total of 425 independent parameters (Tables 15 and 16). The technique adopted was factor analysis using the computer program GEO, a modified version of that written by Cameron (1967).

The distribution of elements within a system is controlled by a set of parameters. The classical method for the interpretation of the results rested solely on the application of variation diagrams and the more elementary statistics such as regression and means. Although these methods still form the basis of interpretation, more sophisticated approaches such as factor analysis were developed to be used in conjunction with them.

Factor analysis is capable of simultaneously deriving relationships, both correlated and uncorrelated, between many variables in a large number of samples. Herbosch (1974, p. 367) states that 'in an unknown field the factor analysis operates like a creative method of exploration of hypotheses'.

The steps involved in the factor analysis were the following:

(a) Calculation of a correlation matrix between the variables using both normal and transformed data and including the means and standard deviations.

(b) Calculation of eigenvalues from which the unrotated factors were determined along with their corresponding percentage variability to explain each factor.

(c) Orthogonal rotation of the vectors yielding a varimax matrix containing the number of factors as specified by a minimum eigenvalue of 0,5.

(d) Listing of the factors' scores which determine the contribution of each sample to a factor in the vari=max matrix.

(e) Rotation of vectors forming oblique factors in the promax matrix. Herbosch (1974) notes that natural phenomena essentially follow the oblique rotation as opposed to the orthogonal.

(f) From the promax method, correlations between factors are obtained. The number of rotations is determined by the parameter of obliquity (KMIN).

(g) The factor scores for the promax are finally calculated.

Interpretations of the factor analysis data for the water samples were based upon the varimax matrix only because no further useful information could be derived from the promax rotations in this instance.

13.4 Geochemistry of Groups 1 and 2 Subsurface Waters

The waters were classified into four groups, the last two containing only three samples each. Consequently Groups 3 and 4 were not included in the geochemical interpretations by factor analysis.

Although the samples were classified into two main groups, the geochemistry of each is very similar. Discussion will initially be concerned with comparisons, and will terminate with the geochemistry of some of the elements.

The means of the variables in Group 1 (Table 15) are marginally and in some cases very much higher than those for Group 2, e.g. sodium is 1 272 ppm and 552 ppm respectively. For nitrate, silica and carbonate the reverse applies, e.g. carbonate is 91 ppm and 145 ppm respectively. Based upon log-transformed data, correlation matrices for Groups 1 and 2 are given in Table 22. Table 23 contains summaries compiled from the matrices. Only those correlations for the 99 per cent and 95 per cent confidence limits were included in Table 23.

Most variables correlate directly with the conductivity and total dissolved solids, and inversely with the pH. One of the most noteworthy features is the correlation at 99 per cent confidence limit between uranium and carbonate in both groups, which emphasizes their close coherence. In Group 2, uranium correlates with other variables, but at the 95 per cent level. Table 22 shows that uranium correlates marginally with other variables below the 95 per cent level.

Varimax matrices for Groups 1 and 2 are given in Table 24.

TABLE 22: CORRELATION MATRICES FOR LOG-TRANSFORMED DATA OF THE SUBSURFACE WATERS FROM THE NAMIB DESERT FOR GROUPS 1 AND 2.

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GROUP 1

CORRELATION MATRIX OF 9 SAMPLES

	MEAN	STD DEV	pH	Cond	TDS	Na	K	Ca	Mg	U	V	Sr	Ba	SO_4	NO_3	SiO_2	F	Cl	CO_3
pH	0.901D 00	0.510D-01	1.000	-0.829	-0.786	-0.818	-0.779	-0.658	-0.303	0.189	-0.515	-0.452	-0.609	-0.471	-0.164	-0.330	-0.616	-0.712	-0.130
Cond	0.390D 01	0.211D 00	-0.829	1.000	0.989	0.984	0.918	0.903	0.226	-0.356	0.738	0.411	0.578	0.660	0.114	-0.061	0.585	0.854	-0.171
TDS	0.376D 01	0.239D 00	-0.786	0.989	1.000	0.981	0.883	0.922	0.138	-0.368	0.759	0.360	0.603	0.618	0.168	-0.077	0.635	0.812	-0.200
Na	0.302D 01	0.277D 00	-0.818	0.984	0.981	1.000	0.928	0.855	0.229	-0.377	0.797	0.492	0.672	0.670	0.201	0.010	0.619	0.865	-0.183
K	0.178D 01	0.383D 00	-0.779	0.918	0.888	0.928	1.000	0.714	0.356	-0.203	0.638	0.507	0.563	0.719	0.141	0.076	0.398	0.841	-0.037
Ca	0.280D 01	0.280D 00	-0.656	0.903	0.922	0.855	0.714	1.000	0.043	-0.565	0.688	0.265	0.299	0.652	0.007	-0.383	0.463	0.742	-0.440
Mg	0.221D 01	0.181D 00	-0.303	0.226	0.138	0.229	0.356	0.043	1.000	0.017	-0.139	0.717	0.095	0.180	0.359	-0.020	-0.114	0.629	0.191
U	0.194D 01	0.240D 00	0.189	-0.356	-0.368	-0.377	-0.203	-0.565	0.017	1.000	-0.624	-0.468	0.070	-0.716	0.211	0.603	0.008	-0.486	0.929
V	0.145D 01	0.453D 00	-0.515	0.738	0.759	0.797	0.638	0.688	-0.139	-0.624	1.000	0.421	0.559	0.696	0.007	-0.078	0.487	0.614	-0.523
Sr	0.362D 01	0.276D 00	-0.452	0.411	0.360	0.492	0.507	0.265	0.717	-0.468	0.421	1.000	0.301	0.565	0.442	0.004	0.013	0.777	-0.237
Ba	0.250D 01	0.256D 00	-0.609	0.578	0.603	0.672	0.563	0.299	0.095	0.070	0.559	0.301	1.000	0.079	0.447	0.580	0.873	0.438	0.270
SO_4	0.289D 01	0.211D 00	-0.471	0.660	0.618	0.670	0.719	0.652	0.180	-0.716	0.696	0.565	0.079	1.000	-0.255	-0.370	-0.065	0.718	-0.634
NO_3	0.141D 01	0.683D 00	-0.164	0.114	0.168	0.201	0.141	0.007	0.359	0.211	0.007	0.442	0.447	-0.255	1.000	0.357	0.310	0.248	0.353
SiO_2	0.134D 01	0.199D 00	-0.330	-0.061	-0.077	0.010	0.076	-0.388	-0.020	0.603	-0.078	0.004	0.580	-0.370	0.357	1.000	0.407	-0.192	0.768
F	0.127D 00	0.284D 00	-0.616	0.585	0.635	0.619	0.398	0.463	-0.114	0.008	0.487	0.013	0.873	-0.065	0.310	0.407	1.000	0.320	0.201
Cl	0.333D 01	0.279D 00	-0.712	0.854	0.812	0.865	0.841	0.742	0.629	-0.486	0.614	0.777	0.438	0.718	0.248	-0.192	0.320	1.000	-0.272
CO_3	0.189D 01	0.270D 00	-0.130	-0.171	-0.200	-0.183	-0.037	-0.440	0.191	0.929	-0.523	-0.237	0.270	-0.634	0.353	0.768	0.201	-0.272	1.000

GROUP 2

CORRELATION MATRIX OF 16 SAMPLES

	MEAN	STD DEV	pH	Cond	TDS	Na	K	Ca	Mg	U	V	Sr	Ba	SO_4	NO_3	SiO_2	F	Cl	CO_3
pH	0.884D 00	0.214D-01	1.000	-0.584	-0.567	-0.426	-0.067	-0.682	-0.344	-0.339	-0.475	-0.531	-0.634	-0.369	-0.620	-0.051	-0.503	-0.558	-0.327
Cond	0.367D 01	0.194D 00	-0.584	1.000	0.993	0.934	0.606	0.858	0.891	0.584	0.159	0.814	0.675	0.899	0.614	0.274	0.124	0.991	0.232
TDS	0.351D 01	0.210D 00	-0.567	0.993	1.000	0.906	0.558	0.889	0.885	0.523	0.109	0.809	0.669	0.882	0.676	-0.284	0.107	0.986	0.183
Na	0.268D 01	0.231D 00	-0.426	0.934	0.906	1.000	0.740	0.657	0.855	0.631	0.233	0.800	0.526	0.904	0.352	0.262	0.219	0.933	0.297
K	0.141D 01	0.367D 00	-0.087	0.606	0.558	0.740	1.000	0.185	0.703	0.656	0.203	0.426	0.122	0.718	-0.037	-0.307	0.030	0.558	0.314
Ca	0.258D 01	0.253D 00	-0.682	0.858	0.889	0.657	0.185	1.000	0.634	0.279	0.052	0.698	0.718	0.651	0.880	-0.283	0.101	0.862	0.029
Mg	0.209D 01	0.242D 00	-0.344	0.891	0.885	0.855	0.703	0.634	1.000	0.618	0.057	0.712	0.615	0.937	0.433	-0.275	-0.028	0.862	0.233
U	0.147D 01	0.417D 00	-0.339	0.584	0.523	0.631	0.656	0.279	0.618	1.000	0.520	0.431	0.239	0.698	0.066	0.163	0.265	0.516	0.749
V	0.131D 01	0.348D 00	-0.475	0.159	0.109	0.233	0.203	0.052	0.057	0.520	1.000	0.042	0.036	0.135	0.100	0.479	0.695	0.104	0.695
Sr	0.355D 01	0.338D 00	-0.531	0.814	0.809	0.800	0.426	0.698	0.712	0.431	0.042	1.000	0.778	0.716	0.472	-0.388	0.384	0.836	0.119
Ba	0.226D 01	0.347D 00	-0.634	0.675	0.669	0.526	0.122	0.718	0.615	0.239	0.036	0.778	1.000	0.559	0.590	-0.338	0.185	0.685	0.011
SO_4	0.262D 01	0.243D 00	-0.369	0.899	0.882	0.904	0.718	0.651	0.937	0.698	0.135	0.716	0.559	1.000	0.383	-0.270	0.070	0.863	0.335
NO_3	0.163D 01	0.445D 00	-0.620	0.614	0.676	0.352	-0.037	0.880	0.433	0.066	0.100	0.472	0.590	0.383	1.000	-0.111	0.128	0.601	-0.001
SiO_2	0.146D 01	0.136D 00	-0.051	-0.274	-0.284	-0.262	-0.307	-0.283	-0.275	0.163	0.479	-0.388	-0.338	-0.270	-0.111	1.000	0.184	-0.311	0.659
F	-0.152D-01	0.162D 00	-0.503	0.124	0.107	0.219	0.030	0.101	-0.028	0.265	0.695	0.384	0.185	0.070	0.128	0.184	1.000	0.109	0.381
Cl	0.308D 01	0.238D 00	-0.558	0.991	0.986	0.933	0.558	0.862	0.862	0.516	0.104	0.836	0.685	0.863	0.601	-0.311	0.109	1.000	0.159
CO_3	0.215D 01	0.121D 00	-0.327	0.232	0.183	0.297	0.314	0.029	0.233	0.749	0.695	0.119	0.011	0.335	-0.001	0.659	0.381	0.159	1.000

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TABLE 23(a): SUMMARY OF THE CORRELATION MATRIX (TABLE 22) FOR THE GROUP 1 SUBSURFACE WATER

LOG TRANSFORMATION

	99%	95 %	99%	95 %
	+		-	
pH			Cond, Na	TDS, K, Cl
Conductivity	TDS, Na, K, Ca, Cl	V		
TDS	Na, K, Ca, Cl	V		
Na	K, Ca, V, Cl	Ba, SO_4		
K	Cl	Ca, SO_4		
Ca		V, Cl		
Mg		Sr		
U	CO_3			
V		SO_4		
Sr		Cl		
Ba	F			
SO_4		Cl		
NO_3				
SiO_2		CO_3		
F				
Cl				
CO_3				

CO^2

TABLE 23(b): SUMMARY OF THE CORRELATION MATRIX (TABLE 22) FOR THE GROUP 2 SUBSURFACE WATER

LOG TRANSFORMATION

	99 %	95 %	99 %	95 %
	+		−	
pH			Ca	Cond, TDS, Sr, Ba, NO_3, F, Cl
Conductivity	TDS, Na, Ca, Mg, Sr, Ba, SO_4, Cl	K, U, NO_3		
TDS	Na, Ca, Mg, Sr, Ba, SO_4 NO_3, Cl	K, U		
Na	K, Ca, Mg, Sr, SO_4, Cl	U, Ba		
K	Mg, U, SO_4	Cl		
Ca	Sr, Ba, SO_4, NO_3, Cl	Mg		
Mg	Sr, SO_4, Cl	U, Ba		
U	SO_4, CO_3	V, Cl		
V	F, CO_3			
Sr	Ba, SO_4, Cl			
Ba	Cl	NO_3, SO_4		
SO_4	Cl			
NO_3		Cl		
SiO_2	CO_3			
F				
Cl				
CO_3				

TABLE 24: VARIMAX MATRICES FOR GROUPS 1 AND 2 SUBSURFACE WATERS

SUBSURFACE WATER FROM NAMIB DESERT GROUP 1

LOG TRANSFORMATION

VARIMAX MATRIX ACCOUNTING FOR 90,7 PER CENT OF TOTAL PROBLEM VARIANCE

	FACTOR	1	2	3	4
SUM OF SQUARES		7,036	3.474	2.464	2.442
0.822	pH	0.842	0.120	0.197	-0.245
0.988	COND	-0.966	0.150	-0.109	0.142
0.965	TDS	-0.938	0.192	-0.045	0.217
0.992	Na	-0.925	0.194	-0.161	0.269
0.923	K	-0.917	0.009	-0.278	0.061
0.877	Ca	-0.847	0.395	0.045	-0.002
0.916	Mg	-0.176	-0.186	-0.910	-0.145
0.935	U	0.234	-0.932	0.100	0.051
0.890	V	-0.632	0.582	0.065	0.384
0.960	Sr	-0.264	0.333	-0.859	0.201
0.922	Ba	-0.513	-0.155	-0.059	0.795
0.855	SO_4	-0.638	0.575	-0.230	-0.255
0.731	NO_3	0.054	-0.176	-0.533	0.643
0.777	SiO_2	0.005	-0.657	-0.016	0.588
0.885	F	-0.537	-0.122	0.235	0.725
0.981	Cl	-0.760	0.276	-0.569	0.058
0.996	CO_3	0.066	-0.972	-0.069	0.204

SUBSURFACE WATER FROM NAMIB DESERT GROUP 2

LOG TRANSFORMATION

VARIMAX MATRIX ACCOUNTING FOR 89,7 PER CENT OF TOTAL PROBLEM VARIANCE

	FACTOR	1	2	3	4
SUM OF SQUARES		6.034	2.404	4.959	1.856
0.819	pH	0.111	0.215	-0.731	0.476
0.985	COND	-0.750	-0.002	0.649	-0.042
0.981	TDS	-0.705	0.024	0.695	-0.002
0.930	Na	-0.869	0.012	0.386	-0.162
0.873	K	-0.921	-0.003	-0.144	-0.062
0.956	Ca	-0.338	0.065	0.915	0.008
0.912	Mg	-0.847	0.007	0.430	0.101
0.857	U	-0.749	-0.502	0.046	-0.205
0.848	V	-0.123	-0.647	0.041	-0.642
0.866	Sr	-0.598	0.265	0.556	-0.359
0.734	Ba	-0.299	0.227	0.738	-0.221
0.932	SO_4	-0.882	-0.043	0.389	0.012
0.865	NO_3	-0.027	-0.039	0.928	0.031
0.887	SiO_2	0.301	-0.888	-0.093	-0.009
0.929	F	-0.007	-0.173	0.118	-0.941
0.960	Cl	-0.720	0.069	0.660	-0.038
0.917	CO_3	-0.338	-0.857	-0.020	-0.260

Group 1

Factor 1: 41 per cent of the variance. High negative loadings on conductivity, total dissolved solids, sodium, potassium, calcium and chloride and moderate loadings on barium, vanadium and fluoride. High positive loading on pH.

Factor 2: 20 per cent of the variance. High negative loadings on uranium, carbonate and silica. Moderate positive loadings on vanadium and strontium.

Factor 3: 15 per cent of the variance. High negative loadings on magnesium and strontium and moderate loadings on nitrate and chloride.

Factor 4: 15 per cent of the variance. High positive loadings on barium and fluoride and moderate loadings on nitrate and silica.

Group 2

Factor 1: 36 per cent of the variance. High negative loadings on conductivity, total dissolved solids, sodium, potassium, magnesium, uranium, sulphate and chloride, with a moderate loading on strontium.

Factor 2: 14 per cent of the variance. High negative loadings on silica and carbonate with moderate loadings on uranium and vanadium.

Factor 3: 29 per cent of the variance. High positive loadings on conductivity, total dissolved solids, calcium, barium, nitrate and chloride, with a moderate loading on strontium. High negative loading on pH.

Factor 4: 11 per cent of the variance. High negative loadings on vanadium and fluoride.

The main difference between the two groups is that in Group 1 the main constituents occur in factor 1, which includes pH, whereas in Group 2 they are divided between factors 1 and 3. Only the pH is totally located in factor 3. This all suggests that both groups have different sources for their water. In factor 2 of Group 1, uranium and silica have moderate negative loadings and vanadium has a positive loading. This suggests that due to high loadings of the same sign of uranium and silica, a uranyl silicate in place of a uranyl vanadate is likely to form in this system. In factor 2 of Group 2 moderately high negative loadings are associated with uranium, vanadium and silica. Both uranyl vanadate and uranyl silicate are the most probable stable phases. There= fore it was possible to predict from the chemistry of the subsurface waters which uranium minerals were most likely to be found. X-ray diffraction analysis of the uranium ore revealed that both carnotite (uranyl vanadate) and soddyite (uranyl silicate) are found in close association. No soddyite has so far been identified at the Langer Heinrich but is is predicted that soddyite can occur as a stable phase because sample 31 was classified into Group 1 (Table 15). pH is one of the controlling factors for the liberation of the dissolved salts from the source rocks (Feth et al, 1964) and this would account for the different signs. The activity of the H^+ ion is more vigorous for Group 1 as compared to Group 2, implied by the percentage variances of the respective factors. Carbonic acid was virtually the only source of H^+ ions formed by the reaction of carbon dioxide and water as shown in the following equations at 25 °C and 100 kPa pressure (Feth et al, 1964; Hostetler and Garrels, 1962).

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \qquad (13.1)$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad K = 10^{-6,38} \qquad (13.2)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \qquad K = 10^{-10,31} \qquad (13.3)$$

Therefore carbon dioxide enhances the reaction of water on rocks by the liberation of H^+. A direct manifestation of this is the relationship between carbonate and silica in Fig. 48 where there is a systematic relationship between the two

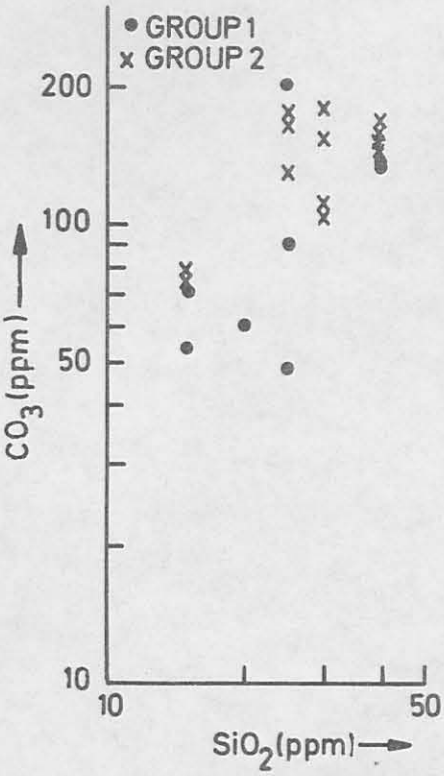


Fig. 48: Variation diagram of carbonate plotted against silica for Groups 1 and 2 sub=surface waters.

variables. Silica was obviously derived from the leaching and dissolution of the rock forming minerals. The high factor loadings with the same sign on silica and uranium do suggest a common source. When compared with Group 2, the higher reactivity of H^+ in Group 1 suggested that it behaved to a greater extent more like an open system where there is a constant replenishment of carbon dioxide from the atmosphere. A further point which added more weight to this hypothesis was that the mean total dissolved solids for Group 1 was greater than Group 2. By implication the bore=holes representing Group 1 derive their water from shallower depths than do those of Group 2. This would resolve the situation found on Bloemhof, where boreholes of both groups are within very close proximity of each other.

Szalay and Samsoni (1969) conducted a series of experiments concerning the leachability of uranium from powdered igneous rocks using 0,2 per cent sodium bicarbonate solutions. Since these aspects are important in the under=standing of uranium migration, a summary of their findings is given here.

1. The solubility of uranium in granites is much greater than in other types of igneous rocks.
2. The concentration of uranium in the water is a function of the amount of leachable uranium present in the source rocks rather than the occurrence of a hidden ore-body below.
3. Water circulating through granite detritus attains an equilibrium concentration of uranium after a period

of three to five hours. If the water is removed and replaced by a fresh solution, a new but lower equilibrium concentration is attained and indicates that the amount of leachable uranium decreases. If uranium is added to the initial solution it will asymptotically approach the original equilibrium concentration after a period of time. A decrease of uranium in solution can only be accounted for by adsorption onto grain surfaces.

The reactivity of the H^+ ion in the leaching ability of the subsurface water on rock detritus can be described in terms of the carbonate content as shown by equations (13.1), (13.2) and (13.3). Therefore the uranium concentration must be considered in terms of the pH and carbonate content.

A stepwise multivariate regression analysis was performed on both groups individually by the computer program BMDO2R (Dixon, 1967), called STEP. This program computes a sequence of multiple linear regression equations in a step=wise manner, with one variable being added at each step. The variables, carbonate and pH were regressed in terms of uranium, being the dependent variable. Log transformations of carbonate and uranium only were done, as pH was already a log function. The following function was derived from the data of Group 1 samples (Table 15).

$$\log U = -0,71 + 0,9 \log CO_3^{2-} + 0,11 \text{ pH} \qquad (13,4)$$

The uranium values calculated in terms of this equation are plotted against the original uranium values in Fig. 49. All points cluster very closely around the line of equal ratio, which demonstrates that the solubility of uranium is primarily controlled by carbonate concentration and pH.

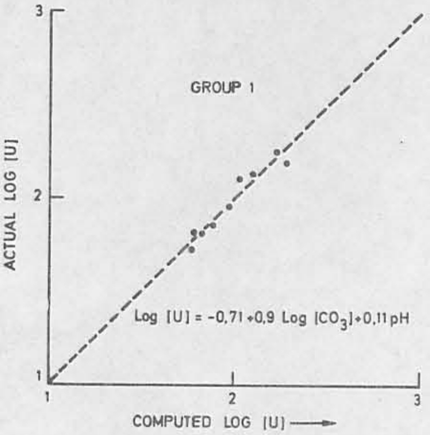


Fig. 49: Multivariate regression analysis of uranium, carbonate and pH in the subsurface water samples from Group 1.

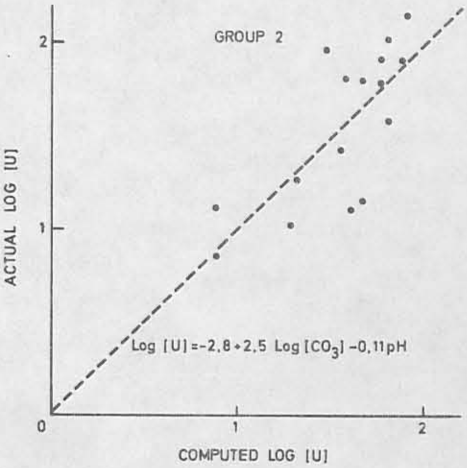


Fig. 50: Multivariate regression analysis of uranium, carbonate and pH in the subsurface water samples from Group 2.

A similar equation was derived from the data of Group 2 samples (Table 16).

$$\log U = -2{,}8 + 2{,}5 \log CO_3^{2-} - 0{,}11 \text{ pH} \qquad (13.5)$$

The plot of the computed values against the actual values (Fig. 50) shows a marked scattering of points about the equal ratio line. This implies that the uranium concentrations in Group 2 were not purely a function of pH and carbonate content, but that other influencing parameters acted upon this group and that the group was in a partially closed system with respect to carbon dioxide replenishment. Different sources of the waters for both groups are inferred, for if they were of the same source, equations (13.4) and (13.5) would have had the same coefficients. Dall'Aglio et al (1974, p. 41) derived a similar type of equation for conditions found in a part of the Italian Alps. Therefore for each system an equation may be derived that is best suited to it. The general application of one equation to describe all systems with different concentrations of uranium, carbonate and pH is therefore not possible.

13.5 Solution Geochemistry of Uranium, Vanadium and Calcium

13.5.1 Uranium

At this stage some of the theoretical aspects of the solubility of uranium in water will be studied.

Uranium in the basement rocks of the Langer Heinrich will oxidize from the (+IV) to the (+VI) state to form the uranyl cation as follows,

$$UO_2 \rightleftarrows UO_2^{2+} + 2e \qquad (13.6)$$

In the presence of carbonate ions two stable uranyl carbonate complexes will form at 25 °C and 100 kPa.

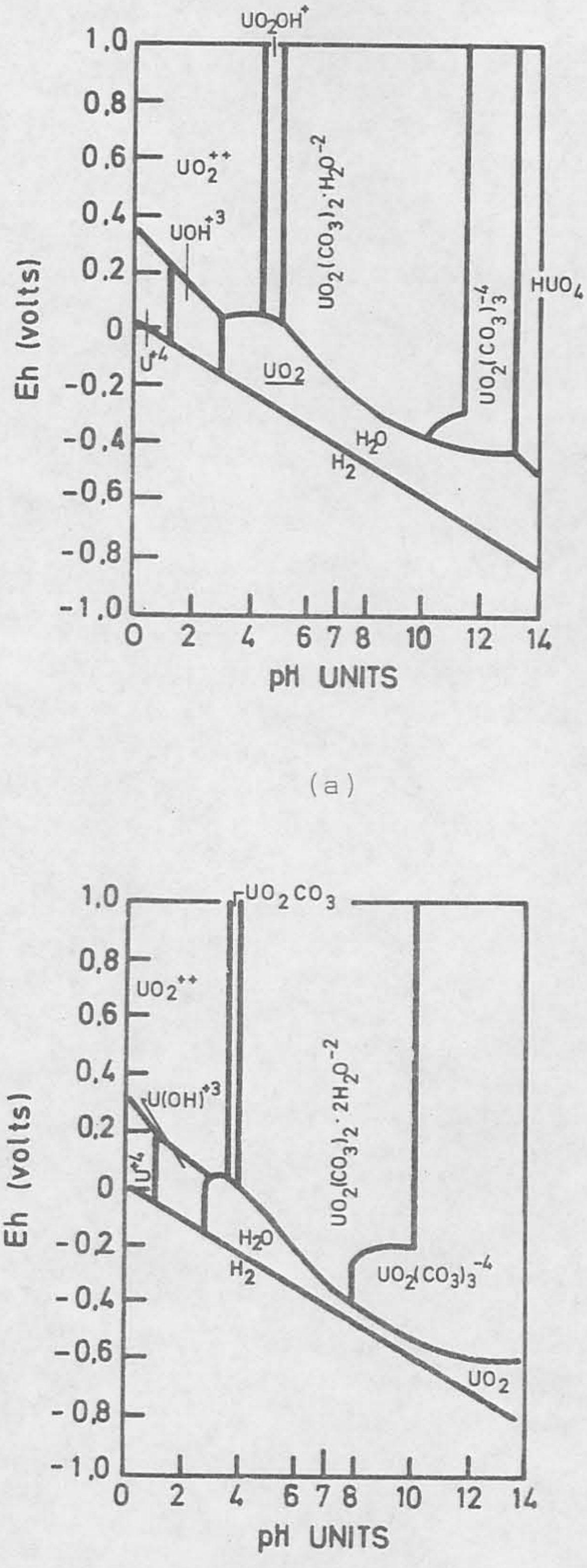
$$UO_2^{2+} + 2CO_3^{2-} + 2H_2O \rightleftarrows UO_2(CO_3)_2 \cdot 2H_2O^{2-} \quad K = 10^{-20,4} \qquad (13.7)$$

$$UO_2^{2+} + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{4-} \quad K = 10^{-24,2} \qquad (13.8)$$

The uranyl dicarbonate complex (UDC)(equation 13.7) and the uranyl tricarbonate complex (UTC)(equation 13.8) are the soluble and stable ions in alkaline solution. The equili= brium constants, K, demonstrate that the stability of the uranyl carbonate complexes is greater at higher carbonate concentrations (Hostetler and Garrels, 1962). The partial pressure of carbon dioxide (P_{CO_2}) has a marked effect on the stabilities of both UDC and UTC. At a higher P_{CO_2}, UDC is converted to UTC.

$$UO_2(CO_3)_2 \cdot 2H_2O_2^{2-} + CO_2 \rightleftarrows UO_2(CO_3)_3^{4-} + 2H_2O \qquad (13.9)$$

The stabilities of UDC and UTC are shown in Figs. 51(a) and (b) in terms of Eh, pH and P_{CO_2}. (Hostetler and Garrels, 1962, p. 146-147). Comparing these figures, it is noted that the fields of UDC and UTC are increased when $P_{CO_2} = 10^{-1}$, which happens at the expense of the other phases. If the P_{CO_2} decreases to $10^{-3,8}$ then all the UTC disproportionates in the reverse direction of equation (13,9) and its field in Fig. 51(a) will disappear completely.



(a)

(b)

Fig. 51: Aqueous equilibrium diagrams of the system $U-O_2-H_2O-CO_2$ at 25 °C and 100 kPa.
(a) $\Sigma CO_2 = 10^{-3}$
(b) $\Sigma CO_2 = 10^{-1}$
(Hostetler and Garrels, 1962, p. 146-147).

To make meaningful use of Eh-pH diagrams, the range of values that should be considered must be within the limits as determined by nature. The stability of aqueous solutions is limited by the dissociation of water. According to Hansuld (1966), these conditions seldom occur in nature when determined from actual field measurements. Sato (1960) took a considerable number of Eh-pH readings from natural waters of different sources and found that they occupied a restricted area to which he referred as the zone of weathering. This zone falls in the carnotite field in Fig. 52.

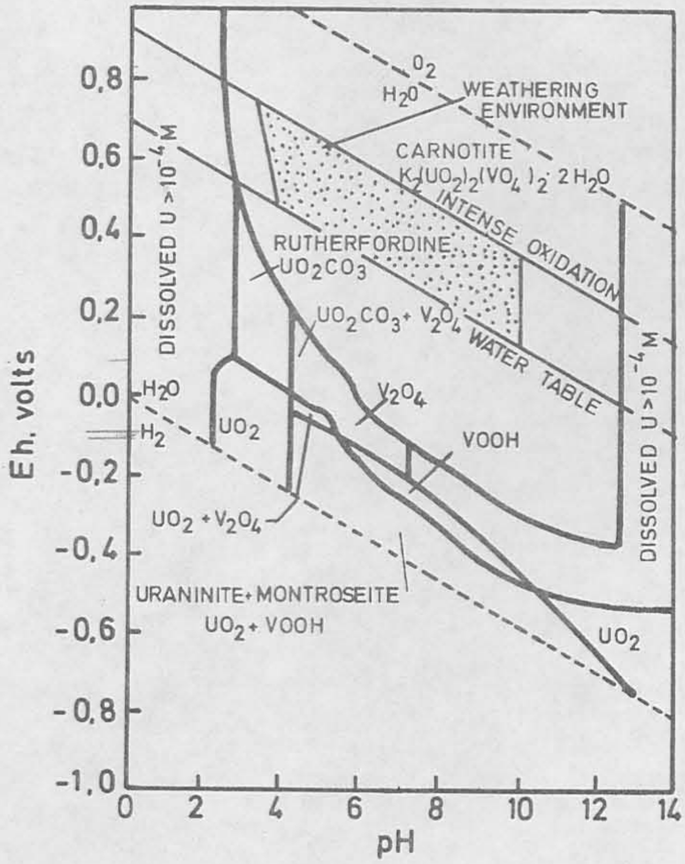


Fig. 52: The zone of weathering superimposed on an Eh-pH diagram. It occupies an area in the carnotite stability field.

Uranyl ions are precipitated from solution after disproportionation of the UDC complex (the reverse of equation 13.7), by vanadate ions with the vanadium in the (+V) state according to the following equation:

$$2K^{+} + 2UO_2^{2+} + 2H_2VO_4^{-} + 3H_2O \rightleftarrows K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O + 4H^{+} \qquad (13.10)$$

Consideration should now be given to the state of the water-table under the Bloedkoppie Flats and the Gawib River sediments, i.e. whether it is perennial or ephemeral. Boreholes sunk into the sediments of the Gawib River Valley revealed that there is a definite water-table that exists all year round. Borehole HJ-2, located on the Bloedkoppie Flats and drilled to a depth of 30 m, did not intersect water at all. The upper 9 m were uranium-rich calcrete, which indicates that water was once present but has now gone, and the remainder was barren granite (Table 27). This would suggest that the water in the Gawib River Valley is perennial, whereas under the Bloedkoppie Flats it is ephemeral, forming only after heavy rainfall.

Distinction must be made between the reactivities of both ephemeral and perennial ground-water. The former, within its lifespan, will be constantly replenished with air and carbon dioxide from the atmosphere and overlying sediments and would vigorously react with the minerals during the period of contact. Perennial water, due to lack of recharge, would not be as aggressive because of the exhaustion of its supplies of carbon dioxide.

It is therefore considered that the uranium in the basement rocks was mobilized largely by ephemeral subsurface water which had an increased supply of carbon dioxide.

The implication is, for the successful dissolution of uranium in large enough quantities to form an ore-deposit of the Langer Heinrich type, a partial dynamic system must be postulated which is dependent on ephemeral water re=plenishment. Under stagnant conditions no deposit of any magnitude would form. An ephemeral water-table is one that is constantly moving until it no longer exists or until the residual water becomes stagnant. After heavy rainfall the water percolates down to the deepest levels possible, where a water-table will form and the level will rise if the supply is of sufficient magnitude. Upon cessation of the supply the water-level will start to drop, largely by down-gradient migration. The model is schematically drawn in Fig. 53.

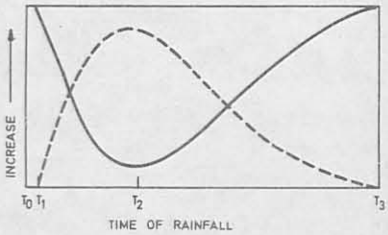


Fig. 53: Schematic diagram showing the thickness of sediment above an ephemeral water-table (——) and the leaching ability of water in relation to the time of rainfall (----).

T_0 = Time at which no water-table exists or the existing water is stagnant, i.e. a period of no rainfall. Sediment thickness above water-table at maximum and leaching ability of the water at zero.

T_1 = Time at which rain falls.

T_2 = Time at which maximum depth of water-table occurs, i.e. sediment thickness above water-table is at a minimum and leaching ability of water at a maximum. This is followed by a cessation in water supply and a reduction of leaching ability.

T_3 = Time at which the water-table ceases to exist or becomes stagnant, i.e. sediment thickness above water-table at maximum and leaching ability reduced to zero. This is equivalent to T_0 for the next ephemeral cycle.

If this cyclic model is compounded, sufficient uranium will be leached and transported to its final place of deposition, which may be a considerable distance from the source.

13.5.2 Vanadium

The association of vanadium with fluorine in factor 4 of Groups 1 and 2 (Fig. 54) hints that there is a relation=ship between them. A fluoro-vanadate coordination complex may possibly form under these conditions. Griffith and Wickins (1968) have reported the existence of a vanadium-fluorine complex of the type $(VO_2F_4)^{3-}$.

13.5.3 Calcium

The solubility of calcium in aqueous solutions is enhanced by the concentration of the alkali metals.

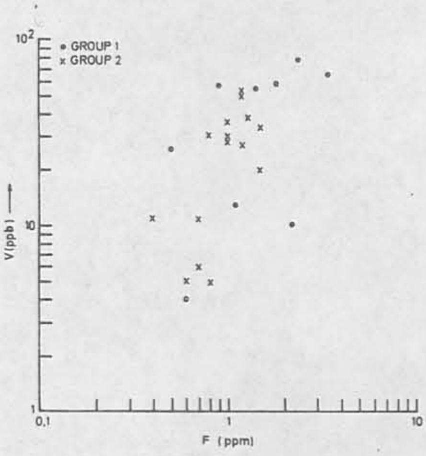


Fig. 54: Variation diagram of vanadium plotted against fluorine for the subsurface water samples from Groups 1 and 2.

(Netterberg, 1969(b), p. 230). Fig. 55 is a plot of calcium against sodium which shows a positive relationship between the two elements and confirms Netterberg's findings. This relationship is important with regard to the precipitation of calcite from the subsurface waters, for the higher the concentration of the alkali metals the greater the solubility of calcium and therefore the inhibition to some degree of the precipitation of calcite. Furthermore Netterberg (1971, p. 9) has the following to say with regard to the solubility of calcium carbonate in natural waters.

> '... an increase in water content, CO_2 content, and pressure and a decrease in temperature favour the solution of carbonate, while an increase in temperature and a decrease in water content, CO_2 content, and pressure favour the precipitation of carbonate.'

Fig. 56 reveals that water with a vapour phase has a higher calcium concentration than water with no vapour phase.

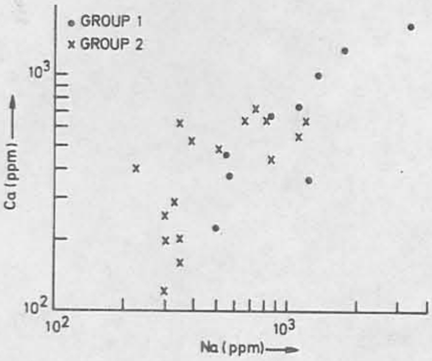


Fig. 55: Variation diagram of calcium plotted against sodium for the subsurface waters from Groups 1 and 2.

This suggests that the greater the distance of a point above the water-table in a sediment (i.e. closer to the surface), the lower the partial pressure of carbon dioxide and water vapour content. The result is a lowering of the calcium concentration in the water by the precipitation of calcite.

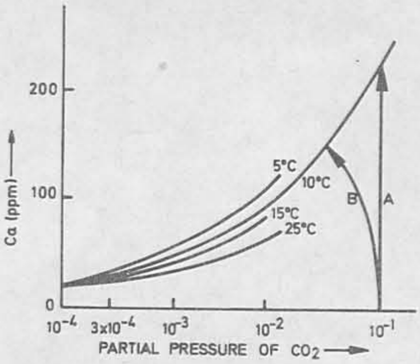


Fig. 56: Change in composition of carbonated water during equilibration with calcite at various temperatures in the presence (A) and in the absence (B) of a vapour phase. (Ostle and Ball, 1973, p. 175).

13.6 Source of Ions in Solution

Soluble contents of the subsurface waters of the Namib Desert were derived from several sources.

Feth et al (1964, p. 41) outlined the reaction of carbon dioxide and water on andesine feldspar:

$$6Na_{0,66}\ Ca_{0,33}\ Al_{1,33}\ Si_{2,66}\ O_8 + 6CO_2 + 18H_2O \rightarrow$$
$$3Na_{0,66}\ Al_{2,66}\ Si_{3,33}\ O_{10}(OH)_2 + 2Ca^{2+} + 2Na^+ + 6H_4SiO_4 + 6HCO_3^- \qquad (13,11)$$

From this reaction a multitude of ions (and montmorillonite) are formed. Disintegration of feldspar therefore probably constitutes the main source of these ions. Carbon dioxide, needed to initiate the reaction, is mainly of atmospheric origin. A small amount of chloride, sulphate, nitrate and fluoride have been derived from the weathering of biotite and amphiboles.

The second most important source of ions are the fogs. Analyses of the fogs are given in Table 38 and the salt crust from the Langer Heinrich in Table 2.

13.7 Geochemistry of Other Metallic Elements in the Subsurface Waters

Table 20 lists the results of analyses on eight samples of subsurface water taken from boreholes on the Dorstrivier concession of Anglo American Prospecting Co. Ltd. Unfortunately these boreholes do not coincide with those listed in Tables 15 to 18. Therefore a comprehensive geochemical analysis cannot be done because no values for the major constituents are available. Nevertheless it may be useful to see how the elements behave in saline water and especially their relationship, if any, to uranium.

Krauskopf (1956) considered the type of ionic species in solution for some of the elements in seawater. As we are dealing in this case with a brine, although somewhat different from seawater, it is accepted that the metal species in solution will be similar. Below is a list of the most likely species that may occur in solution.

Element	Ionic Species
U	$UO_2(CO_3)_2 \cdot 2H_2O^{2-}$
Pb	$PbCl^+$, Pb^{2+}
Cu	Cu^{2+}, $CuCl^+$
Ni	Ni^{2+}
Ag	$AgCl_2^-$
Zn	Zn^{2+}
Co	$CoCl^+$.

Table 25 gives the correlation coefficients of the samples. Significant correlations at the 95 per cent confi= dence limits are found between lead, nickel and cobalt. Correlations slightly below the 95 per cent level occur between lead and silver, nickel and silver, and zinc and cobalt. No significant correlation between uranium and any element is found.

The varimax matrix of the factor analysis after log transformation yields two factors which account for 78 per cent of the total variability. Factor 1 with 44 per cent of the variability has high positive loadings on lead, copper, silver, zinc and cobalt. Factor 2, with the remaining 34 per cent variability, has high negative loadings on uranium, lead and nickel and to a lesser extent silver.

TABLE 25: CORRELATION MATRIX OF THE LOG TRANSFORMED DATA OF TRACE ELEMENT CONCENTRATIONS IN THE SUBSURFACE WATERS OF THE NAMIB DESERT

TRACE ELEMENTS IN SWA WATER LOG TRANSFORMATION

CORRELATION MATRIX OF 8 SAMPLES

	MEAN	STD DEV	U	Pb	Cu	Ni	Ag	Zn	CO
U	0.185D 01	0.247D 00	1.000	0.478	0.028	0.560	0.404	-0.077	0.011
Pb	0.159D 01	0.177D 00	0.478	1.000	0.561	0.921	0.694	0.424	0.854
Cu	0.115D 01	0.113D 00	0.028	0.561	1.000	0.275	0.541	0.293	0.628
Ni	0.131D 01	0.150D 00	0.560	0.921	0.275	1.000	0.648	0.329	0.724
Ag	0.108D 01	0.253D 00	0.404	0.694	0.541	0.648	1.000	0.531	0.560
Zn	0.150D 01	0.639D 00	-0.077	0.424	0.293	0.329	0.531	1.000	0.642
CO	0.442D 00	0.128D 00	0.011	0.854	0.628	0.724	0.560	0.642	1.000

Small o

Satisfactory interpretations of the results at this stage are not possible until further research is done in this direction.

13.8 Summary

The study of the distribution of ionic species in the subsurface waters of the Namib Desert provided an insight into the physico-chemical processes involved during epigenesis of the calcretes. The waters have a high degree of calcite saturation, implying that the formation of calcrete is still taking place. Montmorillonite and not kaolinite is the stable clay. Only Groups 1 and 2 were used in the geochemical interpretations, as too few samples were available from Groups 3 and 4. It was possible to predict from the chemistries of Groups 1 and 2 which uranium minerals were most likely to be found. Group 1 had soddyite (uranyl silicate) as the stable phase and Group 2 had both soddyite and carnotite (uranyl vanadate) as the stable phases. X-ray diffraction analysis confirmed the presence of these coexisting minerals.

The uranium distribution was described in terms of pH and carbonate content by multivariate regression analysis, and equations were derived from Groups 1 and 2. The straight line plots of the equations demonstrated the dependency of the uranium concentration of the pH and the concentration of carbonate in the water. The solution geochemistry of uranium, vanadium and calcium is discussed which included the mechanisms of dissolution and transport of the ions in solution.

From the prospecting aspect, uranium concentrations of 30 ppb or more reflect potential mineralization nearby. Uranium concentrations less than 30 ppb generally do not indicate mineralization. However, background uranium values do not necessarily mean that mineralization is absent and values greater than 30 ppb do not necessarily imply a uranium deposit in the vicinity.

Soluble contents of the waters were derived from, firstly, the reaction between carbon dioxide and feldspars, and secondly, the dissolved contents of the onshore fogs.