HYDROGEOCHEMICAL EXPLORATION AT TSUMEB

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VOLUME IA: TEXT

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PERIODIC TABLE OF THE ELEMENTS

Table of Radioactive Isotopes

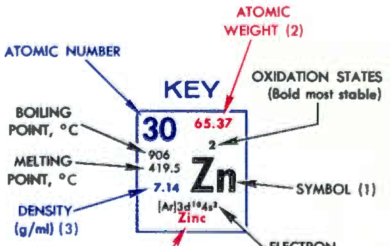
Ac	227(22y)β^-,α
Ag	110(24s)β^-,γ 111(7.5d)β^-,γ
Am	241(458 y)α,γ,e^- 242(16.0h)β^-,K,α,γ 243(8000y)α,γ
As	76(26.7h)β^-,γ 77(39h)β^-,γ
At	210(8.3h)K,α,γ 211(7.2h),Kα,γ
Au	198(2.69d)β^-,γ
Ba	131(12d)K,γ 133(7.2y)K,γ,e^-
Bi	210(5d)β^-,α
Bk	245(4.9d)K,α,γ 249(314d)β^-,α,SF
Br	82(36h)β^-,γ
C	14(5700 y)β^-
Ca	41(8×10^4y)K 45(165d)β^- 47(4.5d)β^-,γ
Cd	115(43d)β^-,γ
Ce	141(32d)β^-,γ 143(33h)β^-,γ 144(285d)β^-,γ
Cf	246(35h)α,γ,SF 249(360 y)α,γ,SF 251(800 y)γ
Cl	36(3×10^5y)β^-
Cm	243(35y),α,γ 245(9300y),α,γ 247(10^7y)
Co	58(71d),K,β^+,γ 60(5.27y)β^-,γ
Cr	51(27d),K,γ
Cs	134(2.0y)β^-,γ 135(3×10^6y)β^- 137(30y)β^-,γ
Cu	64(12.8h)K,β^-,β^+,γ
Es	253(20d)α,γ,SF 254(1y)α,SF
Eu	154(16y)β^-,γ 155(1.8y)β^-,γ
Fe	55(2.6y)K 59(45d)β^-,γ
Fm	255(20h)α
Fr	223(22m)β^-,γ,α
Ga	72(14.1h),β^-,γ
Gd	153(236d)K,γ,e^- 159(18h)β^-,γ
Ge	71(11d)K
H	3(12.3y)β^-
Hf	181(45d)β^-,γ,e^-
Hg	197(65h)K,γ,e^- 203(47d)β^-,γ,e^-
Ho	166(27.3h)β^-,γ
I	129(10^7y)β^+,γ,e 131(8.05d)β^-,γ
In	114(50d)γ
Ir	192(74.4d)β^-,γ
K	40(10^9y)β^+,K,γ 42(12.4h),β^-,γ
La	140(40.2h)β^-,γ
Lu	176(10^{10}y)β^-,K,γ 177(6.8d)β^-,γ
Md	256(90m)K,SF
Mo	99(67h)β^-,γ
Na	22(2.6y)β^+,K,γ 24(15h)β^-,γ
Nd	147(11.1d)β^-,γ
Ni	63(125y)β^- 59(8×10^4y),K
Np	237(2.2×10^6y)α,γ 239(2.33d)β^-,γ
Os	191(15d)β^-,γ,e^-
P	32(14.2d)β^-
Pa	231(34000y)α,γ
Pb	210(19.4y)β^-,γ,e^- 202(10^5y)L
Pd	103(17d)K,γ
Pm	147(2.6y)β^-
Po	210(138.4d)α,γ 209(103y)α,K,γ
Pr	143(13.8d)β^-
Pt	197(18h)β^-,γ
Pu	242(3.8×10^5y)α,SF 241(13y)β^-,α,γ 239(24300y)α,γ,SF
Ra	226(1620y)α,γ
Rb	86(18.6d)β^-,γ
Re	188(16.7h)β^-,γ 186(3.7d)β^-,γ
Rn	222(3.82d)α
Ru	103(40d)β^-,γ 97(2.9d),K,γ,e^-
S	35(88d)β^-
Sb	122(2.8d)β^-,K,β^+,γ 124(60d)β^-,γ
Sc	46(84d)β^-,γ
Se	75(120 d)K,γ
Sm	153(47h)β^-,γ 145(340d)K,γ
Sn	113(119d)K,L,γ,e^-
Sr	90(28y)β^- 89(51d)β^-,γ 85(64d)K,γ
Ta	182(115d)β^-,γ
Tb	160(73d)$\beta^-\gamma$
Tc	99(2×10^5y)β^- 97(10^6y)K
Te	127(9.3h)β^-
Th	232(1.4×10^{10}y)α,γ,SF 228(1.91y)β^-
Tl	204(3.81y)β^-,K
Tm	170(134d)β^-,γ,e^-
U	238(4.5×10^9y)α,γ,SF 234(2.5×10^5y)α,γ,SF 235(7.1×10^8y)α,γ,SF 233(1.6×10^5y)α,γ
W	185(75d)β^-
Y	90(64h)β^-,e^-
Yb	175(4.2d)β^-,γ 169(31d)K,γ,e^-
Zn	65(245d)K,β^+,γ
Zr	95(65d)β^-,γ,e^- 93(9×10^5y)β^-,γ

Naturally occurring radioactive isotopes are indicated by a blue mass number. Half lives are in parentheses where s, m, h, d and y stand for seconds, minutes, hours, days and years respectively. The symbols describing the mode of decay and resulting radiation are defined as follows:

α	alpha particle	L	L-electron capture
β^-	beta particle	SF	spontaneous fission
β^+	positron	γ	gamma ray
K	K-electron capture	e^-	internal electron conversion

GROUP IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 1.00797 1 −252.7 −259.2 0.071 **H** $1s^1$ Hydrogen																	2 4.0026 −268.9 −269.7 0.126 **He** $1s^2$ Helium
3 6.939 1 1330 180.5 0.53 **Li** $1s^2\,2s^1$ Lithium	4 9.0122 2 2770 1277 1.85 **Be** $1s^2\,2s^2$ Beryllium											5 10.811 3 — (2030) 2.34 **B** $1s^2\,2s^2\,2p^1$ Boron	6 12.01115 ±4,2 4830 3727 2.26 **C** $1s^2\,2s^2\,2p^2$ Carbon	7 14.0067 ±3,5,4,2 −195.8 −210 0.81 **N** $1s^2\,2s^2\,2p^3$ Nitrogen	8 15.9994 −2 −183 −218.8 1.14 **O** $1s^2\,2s^2\,2p^4$ Oxygen	9 18.9984 −1 −188.2 −219.6 1.505 **F** $1s^2\,2s^2\,2p^5$ Fluorine	10 20.183 −246 −248.6 1.20 **Ne** $1s^2\,2s^2\,2p^6$ Neon
11 22.9898 1 892 97.8 0.97 **Na** $[Ne]3s^1$ Sodium	12 24.312 2 1107 650 1.74 **Mg** $[Ne]3s^2$ Magnesium											13 26.9815 3 2450 660 2.70 **Al** $[Ne]3s^23p^1$ Aluminum	14 28.086 4 2680 1410 2.33 **Si** $[Ne]3s^23p^2$ Silicon	15 30.9738 ±3,5,4 280w 44.2w 1.82w **P** $[Ne]3s^23p^3$ Phosphorus	16 32.064 ±2,4,6 444.6 119.0 2.07 **S** $[Ne]3s^23p^4$ Sulfur	17 35.453 ±1,3,5,7 −34.7 −101.0 1.56 **Cl** $[Ne]3s^23p^5$ Chlorine	18 39.948 −185.8 −189.4 1.40 **Ar** $[Ne]3s^23p^6$ Argon
19 39.102 1 760 63.7 0.86 **K** $[Ar]4s^1$ Potassium	20 40.08 2 1440 838 1.55 **Ca** $[Ar]4s^2$ Calcium	21 44.956 3 2730 1539 3.0 **Sc** $[Ar]3d^14s^2$ Scandium	22 47.90 4,3 3260 1668 4.51 **Ti** $[Ar]3d^24s^2$ Titanium	23 50.942 5,4,3,2, 3450 1900 6.1 **V** $[Ar]3d^34s^2$ Vanadium	24 51.996 6,3,2 2665 1875 7.19 **Cr** $[Ar]3d^54s^1$ Chromium	25 54.938 7,6,4,2,3 2150 1245 7.43 **Mn** $[Ar]3d^54s^2$ Manganese	26 55.847 2,3 3000 1536 7.86 **Fe** $[Ar]3d^64s^2$ Iron	27 58.933 2,3 2900 1495 8.9 **Co** $[Ar]3d^74s^2$ Cobalt	28 58.71 2,3 2730 1453 8.9 **Ni** $[Ar]3d^84s^2$ Nickel	29 63.54 2,1 2595 1083 8.96 **Cu** $[Ar]3d^{10}4s^1$ Copper	30 65.37 2 906 419.5 7.14 **Zn** $[Ar]3d^{10}4s^2$ Zinc	31 69.72 3 2237 29.8 5.91 **Ga** $[Ar]3d^{10}4s^24p^1$ Gallium	32 72.59 4 2830 937.4 5.32 **Ge** $[Ar]3d^{10}4s^24p^2$ Germanium	33 74.922 ±3,5 613° 817 5.72 **As** $[Ar]3d^{10}4s^24p^3$ Arsenic	34 78.96 −2,4,6 685 217 4.79 **Se** $[Ar]3d^{10}4s^24p^4$ Selenium	35 79.909 ±1,5 58 −7.2 3.12 **Br** $[Ar]3d^{10}4s^24p^5$ Bromine	36 83.80 −152 −157.3 2.6 **Kr** $[Ar]3d^{10}4s^24p^6$ Krypton
37 85.47 1 688 38.9 1.53 **Rb** $[Kr]5s^1$ Rubidium	38 87.62 2 1380 768 2.6 **Sr** $[Kr]5s^2$ Strontium	39 88.905 3 2927 1509 4.47 **Y** $[Kr]4d^15s^2$ Yttrium	40 91.22 4 3580 1852 6.49 **Zr** $[Kr]4d^25s^2$ Zirconium	41 92.906 5,3 3300 2468 8.4 **Nb** $[Kr]4d^45s^1$ Niobium	42 95.94 6,5,4,3,2 5560 2610 10.2 **Mo** $[Kr]4d^55s^1$ Molybdenum	43 (98) 7 — 2140 11.5 **Tc** $[Kr]4d^55s^2$ Technetium	44 101.07 2,3,4,6,8 4900 2500 12.2 **Ru** $[Kr]4d^75s^1$ Ruthenium	45 102.905 2,3,4 4500 1966 12.4 **Rh** $[Kr]4d^85s^1$ Rhodium	46 106.4 2,4 3980 1552 12.0 **Pd** $[Kr]4d^{10}5s^0$ Palladium	47 107.870 1 2210 960.8 10.5 **Ag** $[Kr]4d^{10}5s^1$ Silver	48 112.40 2 765 320.9 8.65 **Cd** $[Kr]4d^{10}5s^2$ Cadmium	49 114.82 3 2000 156.2 7.31 **In** $[Kr]4d^{10}5s^25p^1$ Indium	50 118.69 4,2 2270 231.9 7.30 **Sn** $[Kr]4d^{10}5s^25p^2$ Tin	51 121.75 ±3,5 1380 630.5 6.62 **Sb** $[Kr]4d^{10}5s^25p^3$ Antimony	52 127.60 −2,4,6 989.8 449.5 6.24 **Te** $[Kr]4d^{10}5s^25p^4$ Tellurium	53 126.904 ±1,5,7 183 113.7 4.94 **I** $[Kr]4d^{10}5s^25p^5$ Iodine	54 131.30 −108.0 −111.9 3.06 **Xe** $[Kr]4d^{10}5s^25p^6$ Xenon
55 132.905 1 690 28.7 1.90 **Cs** $[Xe]6s^1$ Cesium	56 137.34 2 1640 714 3.5 **Ba** $[Xe]6s^2$ Barium	57 138.91 3 3470 920 6.17 **La** ★ $[Xe]5d^16s^2$ Lanthanum	72 178.49 4 5400 2222 13.1 **Hf** $[Xe]4f^{14}5d^26s^2$ Hafnium	73 180.948 5 5425 2996 16.6 **Ta** $[Xe]4f^{14}5d^36s^2$ Tantalum	74 183.85 6,5,4,3,2 5930 3410 19.3 **W** $[Xe]4f^{14}5d^46s^2$ Wolfram	75 186.2 7,6,4,2,−1 5900 3180 21.0 **Re** $[Xe]4f^{14}5d^56s^2$ Rhenium	76 190.2 2,3,4,6,8 5500 3000 22.6 **Os** $[Xe]\,4f^{14}5d^66s^2$ Osmium	77 192.2 2,3,4,6 5300 2454 22.5 **Ir** $[Xe]4f^{14}5d^76s^2$ Iridium	78 195.09 2,4 4530 1769 21.4 **Pt** $[Xe]\,4f^{14}\,5d^9\,6s^1$ Platinum	79 196.967 3,1 2970 1063 19.3 **Au** $[Xe]4f^{14}5d^{10}6s^1$ Gold	80 200.59 2,1 357 −38.4 13.6 **Hg** $[Xe]4f^{14}5d^{10}6s^2$ Mercury	81 204.37 3,1 1457 303 11.85 **Tl** $[Xe]4f^{14}5d^{10}6s^26p^1$ Thallium	82 207.19 4,2 1725 327.4 11.4 **Pb** $[Xe]4f^{14}5d^{10}6s^26p^2$ Lead	83 208.980 3,5 1560 271.3 9.8 **Bi** $[Xe]4f^{14}5d^{10}6s^26p^3$ Bismuth	84 (210) 2,4 — 254 (9.2) **Po** $[Xe]4f^{14}5d^{10}6s^26p^4$ Polonium	85 (210) ±1,3,5,7 — (302) — **At** $[Xe]4f^{14}5d^{10}6s^26p^5$ Astatine	86 (222) (−61.8) (−71) — **Rn** $[Xe]4f^{14}5d^{10}6s^26p^6$ Radon
87 (223) 1 — (27) — **Fr** $[Rn]7s^1$ Francium	88 (226) 2 — 700 5.0 **Ra** $[Rn]7s^2$ Radium	89 (227) 3 — 1050 — **Ac** ★★ $[Rn]6d^17s^2$ Actinium	104														

★	58 140.12 3,4 3468 795 6.67 **Ce** $[Xe]4f^25d^06s^2$ Cerium	59 140.907 3,4 3127 935 6.77 **Pr** $[Xe]\,4f^35d^06s^2$ Praseodymium	60 144.24 3 3027 1024 7.00 **Nd** $[Xe]\,4f^45d^06s^2$ Neodymium	61 (147) 3 — (1027) — **Pm** $[Xe]\,4f^55d^06s^2$ Promethium	62 150.35 3,2 1900 1072 7.54 **Sm** $[Xe]\,4f^65d^06s^2$ Samarium	63 151.96 3,2 1439 826 5.26 **Eu** $[Xe]\,4f^75d^06s^2$ Europium	64 157.25 3 3000 1312 7.89 **Gd** $[Xe]4f^75d^16s^2$ Gadolinium	65 158.924 3,4 2800 1356 8.27 **Tb** $[Xe]4f^95d^06s^2$ Terbium	66 162.50 3 2600 1407 8.54 **Dy** $[Xe]\,4f^{10}5d^06s^2$ Dysprosium	67 164.930 3 2600 1461 8.80 **Ho** $[Xe]4f^{11}5d^06s^2$ Holmium	68 167.26 3 2900 1497 9.05 **Er** $[Xe]\,4f^{12}5d^06s^2$ Erbium	69 168.934 3,2 1727 1545 9.33 **Tm** $[Xe]\,4f^{13}5d^06s^2$ Thulium	70 173.04 3,2 1427 824 6.98 **Yb** $[Xe]4f^{14}5d^06s^2$ Ytterbium	71 174.97 3 3327 1652 9.84 **Lu** $[Xe]\,4f^{14}5d^1\,6s^2$ Lutetium
★★	90 232.038 4 3850 1750 11.7 **Th** $[Rn]\,5f^0\,6d^2\,7s^2$ Thorium	91 (231) 5,4 — (1230) 15.4 **Pa** $[Rn]5f^26d^17s^2$ Protactinium	92 238.03 6,5,4,3 3818 1132 19.07 **U** $[Rn]5f^36d^17s^2$ Uranium	93 (237) 6,5,4,3 — 637 19.5 **Np** $[Rn]\,5f^4\,6d^1\,7s^2$ Neptunium	94 (242) 6,5,4,3 3235 640 — **Pu** $[Rn]5f^66d^07s^2$ Plutonium	95 (243) 6,5,4,3 — — 11.7 **Am** $[Rn]5f^76d^07s^2$ Americium	96 (247) 3 — — — **Cm** $[Rn]5f^76d^17s^2$ Curium	97 (247) 4,3 — — — **Bk** $[Rn]\,5f^8\,6d^0\,7s^2$ Berkelium	98 (249) 3 — — — **Cf** $[Rn]\,5f^{10}\,6d^0\,7s^2$ Californium	99 (254) — — — — **Es** $[Rn]\,5f^{11}\,6d^0\,7s^2$ Einsteinium	100 (253) — — — — **Fm** $[Rn]\,5f^{12}\,6d^0\,7s^2$ Fermium	101 (256) — — — — **Md** $[Rn]\,5f^{13}\,6d^0\,7s^2$ Mendelevium	102 (254) — — — — **No** $[Rn]\,5f^{14}\,6d^0\,7s^2$ Nobelium	103 (257) — — — — **Lw** $[Rn]\,5f^{14}\,6d^1\,7s^2$ Lawrencium



KEY

ATOMIC NUMBER

ATOMIC WEIGHT (2)

OXIDATION STATES (Bold most stable)

BOILING POINT, °C

MELTING POINT, °C

DENSITY (g/ml) (3)

SYMBOL (1)

ELECTRON STRUCTURE

NAME

NOTES:

(1) Black — solid.
Red — gas.
Blue — liquid.
Outline — synthetically prepared.

(2) Based upon carbon – 12. ( ) indicates most stable or best known isotope.

(3) Values for gaseous elements are for liquids at the boiling point.

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TABLE OF PERIODIC PROPERTIES OF THE ELEMENTS

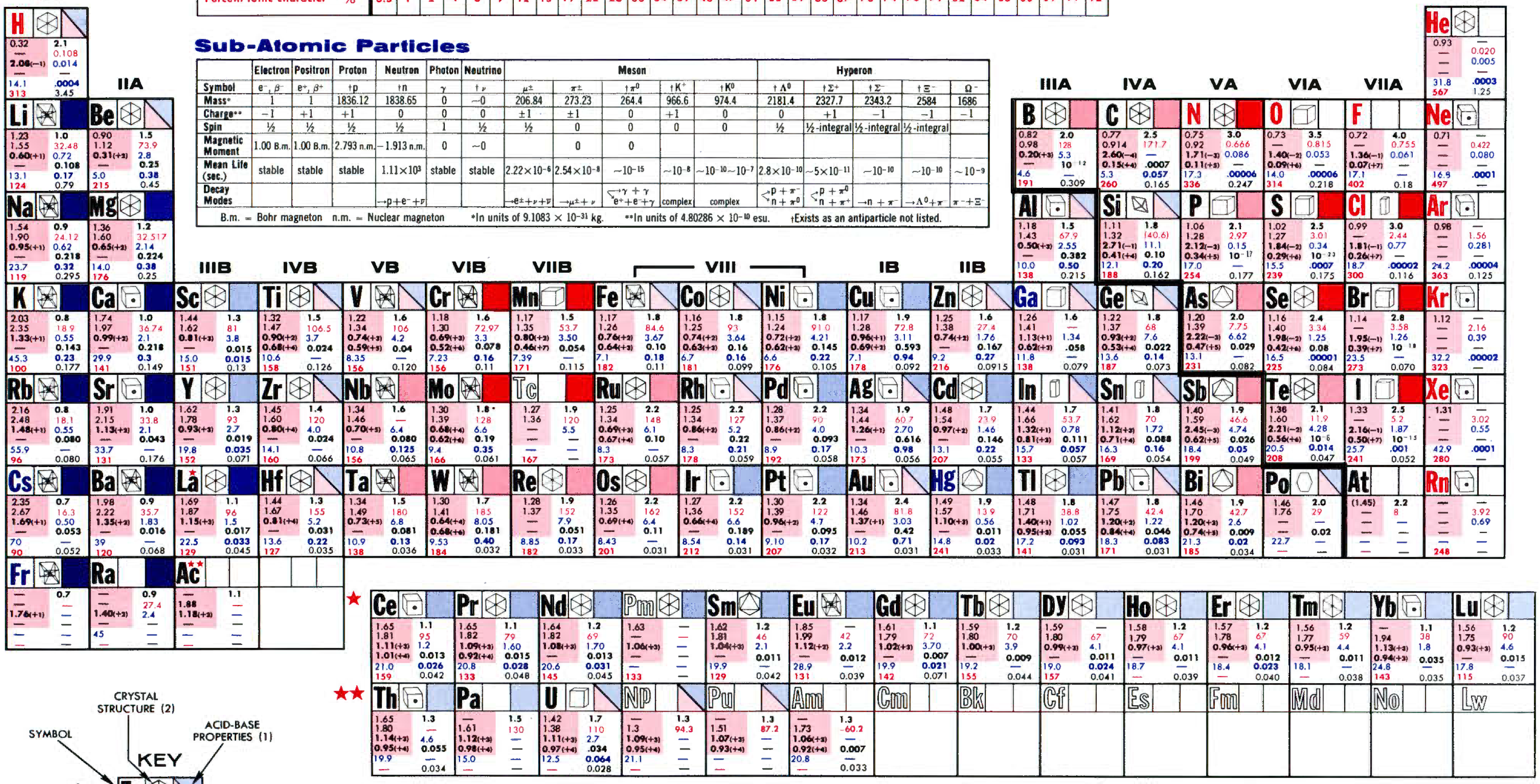
Percent Ionic Character of a Single Chemical Bond

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

Sub-Atomic Particles

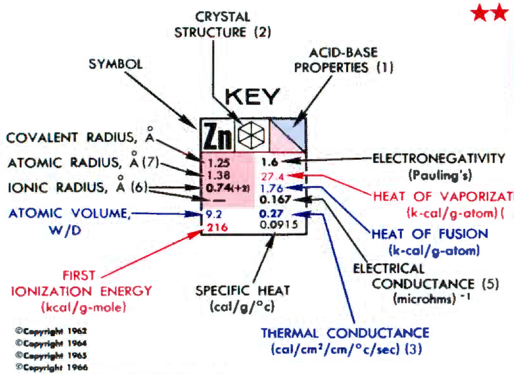
	Electron	Positron	Proton	Neutron	Photon	Neutrino	Meson					Hyperon				
Symbol	e^-, β^-	e^+, β^+	†p	†n	γ	†ν	$\mu^\pm$	$\pi^\pm$	†π^0	†K^+	†K^0	†Λ^0	†Σ^+	†Σ^-	†Ξ^-	Ω^-
Mass*	1	1	1836.12	1838.65	0	~0	206.84	273.23	264.4	966.6	974.4	2181.4	2327.7	2343.2	2584	1686
Charge**	−1	+1	+1	0	0	0	±1	±1	0	+1	0	0	+1	−1	−1	−1
Spin	½	½	½	½	1	½	½	0	0	0	0	½	½-integral	½-integral	½-integral	
Magnetic Moment	1.00 B.m.	1.00 B.m.	2.793 n.m.	−1.913 n.m.	0	~0		0	0							
Mean Life (sec.)	stable	stable	stable	1.11×10^3	stable	stable	2.22×10^{-6}	2.54×10^{-8}	$\sim10^{-15}$	$\sim10^{-8}$	$\sim10^{-10}$–10^{-7}	2.8×10^{-10}	$\sim5\times10^{-11}$	$\sim10^{-10}$	$\sim10^{-10}$	$\sim10^{-9}$
Decay Modes				$\rightarrow p+e^-+\bar{\nu}$			$\rightarrow e^\pm+\nu+\bar{\nu}$	$\rightarrow \mu^\pm+\nu$	$\rightarrow \gamma+\gamma$ $e^++e^-+\gamma$	complex	complex	$p+\pi^-$ $n+\pi^0$	$p+\pi^0$ $n+\pi^+$	$\rightarrow n+\pi^-$	$\rightarrow \Lambda^0+\pi^-$	$\pi^-+\Xi^-$

B.m. = Bohr magneton n.m. = Nuclear magneton *In units of 9.1083×10^{-31} kg. **In units of 4.80286×10^{-10} esu. †Exists as an antiparticle not listed.



GROUP IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 0.32 2.1 — 0.108 2.08(−1) 0.014 — — 14.1 .0004 313 3.45																	**He** 0.93 — — 0.020 — 0.005 — — 31.8 .0003 567 1.25
Li 1.23 1.0 1.55 32.48 0.60(+1) 0.72 — 0.108 13.1 0.17 124 0.79	**Be** 0.90 1.5 1.12 73.9 0.31(+2) 2.8 — 0.25 5.0 0.38 215 0.45											**B** 0.82 2.0 0.98 128 0.20(+3) 5.3 — 10^{-12} 4.6 — 191 0.309	**C** 0.77 2.5 0.914 171.7 2.60(−4) — 0.15(+4) .0007 5.3 0.057 260 0.165	**N** 0.75 3.0 0.92 0.666 1.71(−3) 0.086 0.11(+5) — 17.3 .00006 336 0.247	**O** 0.73 3.5 — 0.815 1.40(−2) 0.053 0.09(+6) — 14.0 .00006 314 0.218	**F** 0.72 4.0 — 0.755 1.36(−1) 0.061 0.07(+7) — 17.1 — 402 0.18	**Ne** 0.71 — — 0.422 — 0.080 — — 16.8 .0001 497 —
Na 1.54 0.9 1.90 24.12 0.95(+1) 0.62 — 0.218 23.7 0.32 119 0.295	**Mg** 1.36 1.2 1.60 32.517 0.65(+2) 2.14 — 0.224 14.0 0.38 176 0.25											**Al** 1.18 1.5 1.43 67.9 0.50(+3) 2.55 — 0.382 10.0 0.50 138 0.215	**Si** 1.11 1.8 1.32 (40.6) 2.71(−1) 11.1 0.41(+4) 0.10 12.1 0.20 188 0.162	**P** 1.06 2.1 1.28 2.97 2.12(−3) 0.15 0.34(+5) 10^{-17} 17.0 — 254 0.177	**S** 1.02 2.5 1.27 3.01 1.84(−2) 0.34 0.29(+6) 10^{-23} 15.5 .0007 239 0.175	**Cl** 0.99 3.0 — 2.44 1.81(−1) 0.77 0.26(+7) — 18.7 .00002 300 0.116	**Ar** 0.98 — — 1.56 — 0.281 — — 24.2 .00004 363 0.125
K 2.03 0.8 2.35 18.9 1.33(+1) 0.55 — 0.143 45.3 0.23 100 0.177	**Ca** 1.74 1.0 1.97 36.74 0.99(+2) 2.1 — 0.218 29.9 0.3 141 0.149	**Sc** 1.44 1.3 1.62 81 0.81(+3) 3.8 — 0.015 15.0 0.015 151 0.13	**Ti** 1.32 1.5 1.47 106.5 0.90(+2) 3.7 0.68(+4) 0.024 10.6 — 158 0.126	**V** 1.22 1.6 1.34 106 0.74(+3) 4.2 0.59(+5) 0.04 8.35 — 156 0.120	**Cr** 1.18 1.6 1.30 72.97 0.69(+3) 3.3 0.52(+6) 0.078 7.23 0.16 156 0.11	**Mn** 1.17 1.5 1.35 53.7 0.80(+2) 3.50 0.46(+7) 0.054 7.39 — 171 0.115	**Fe** 1.17 1.8 1.26 84.6 0.76(+2) 3.67 0.64(+3) 0.10 7.1 0.18 182 0.11	**Co** 1.16 1.8 1.25 93 0.74(+2) 3.64 0.63(+3) 0.16 6.7 0.16 181 0.099	**Ni** 1.15 1.8 1.24 91.0 0.72(+2) 4.21 0.62(+3) 0.145 6.6 0.22 176 0.105	**Cu** 1.17 1.9 1.28 72.8 0.96(+1) 3.11 0.69(+2) 0.593 7.1 0.94 178 0.092	**Zn** 1.25 1.6 1.38 27.4 0.74(+2) 1.76 — 0.167 9.2 0.27 216 0.0915	**Ga** 1.26 1.6 1.41 — 1.13(+1) 1.34 0.62(+3) .058 11.8 — 138 0.079	**Ge** 1.22 1.8 1.37 68 0.93(+2) 7.6 0.53(+4) 0.022 13.6 0.14 187 0.073	**As** 1.20 2.0 1.39 7.75 2.22(−3) 6.62 0.47(+5) 0.029 13.1 — 231 0.082	**Se** 1.16 2.4 1.40 3.34 1.98(−2) 1.25 0.42(+6) 0.08 16.5 .00001 225 0.084	**Br** 1.14 2.8 — 3.58 1.95(−1) 1.26 0.39(+7) 10^{-18} 23.5 — 273 0.070	**Kr** 1.12 — — 2.16 — 0.39 — — 32.2 .00002 323 —
Rb 2.16 0.8 2.48 18.1 1.48(+1) 0.55 — 0.080 55.9 — 96 0.080	**Sr** 1.91 1.0 2.15 33.8 1.13(+2) 2.1 — 0.043 33.7 — 131 0.176	**Y** 1.62 1.3 1.78 93 0.93(+3) 2.7 — 0.019 19.8 0.035 152 0.071	**Zr** 1.45 1.4 1.60 120 0.80(+4) 4.0 — 0.024 14.1 — 160 0.066	**Nb** 1.34 1.6 1.46 — 0.70(+5) 6.4 — 0.080 10.8 0.125 156 0.065	**Mo** 1.30 1.8 1.39 128 0.68(+4) 6.6 0.62(+6) 0.19 9.4 0.35 166 0.061	**Tc** 1.27 1.9 1.36 120 — 5.5 — — — — 167 —	**Ru** 1.25 2.2 1.34 148 0.69(+3) 6.1 0.67(+4) 0.10 8.3 — 173 0.057	**Rh** 1.25 2.2 1.34 127 0.86(+2) 5.2 — 0.22 8.3 0.21 178 0.059	**Pd** 1.28 2.2 1.37 90 0.86(+2) 4.0 — 0.093 8.9 0.17 192 0.058	**Ag** 1.34 1.9 1.44 60.7 1.26(+1) 2.70 — 0.616 10.3 0.98 175 0.056	**Cd** 1.48 1.7 1.54 23.9 0.97(+2) 1.46 — 0.146 13.1 0.22 207 0.055	**In** 1.44 1.7 1.66 53.7 1.32(+1) 0.78 0.81(+3) 0.111 15.7 0.057 133 0.057	**Sn** 1.41 1.8 1.62 70 1.12(+2) 1.72 0.71(+4) 0.088 16.3 0.16 169 0.054	**Sb** 1.40 1.9 1.59 46.6 2.45(−3) 4.74 0.62(+5) 0.026 18.4 0.05 199 0.049	**Te** 1.36 2.1 1.60 11.9 2.21(−2) 4.28 0.56(+6) 10^{-6} 20.5 0.014 208 0.047	**I** 1.33 2.5 — 5.2 2.16(−1) 1.87 0.50(+7) 10^{-15} 25.7 .001 241 0.052	**Xe** 1.31 — — 3.02 — 0.55 — — 42.9 .0001 280 —
Cs 2.35 0.7 2.67 16.3 1.69(+1) 0.50 — 0.053 70 — 90 0.052	**Ba** 1.98 0.9 2.22 35.7 1.35(+2) 1.83 — 0.016 39 — 120 0.068	**La**★ 1.69 1.1 1.87 96 1.15(+3) 1.5 — 0.017 22.5 0.033 129 0.045	**Hf** 1.44 1.3 1.67 155 0.81(+4) 5.2 — 0.031 13.6 0.22 127 0.035	**Ta** 1.34 1.5 1.49 180 0.73(+5) 6.8 — 0.081 10.9 0.13 138 0.036	**W** 1.30 1.7 1.41 185 0.64(+4) 8.05 0.68(+6) 0.181 9.53 0.40 184 0.032	**Re** 1.28 1.9 1.37 152 — 7.9 — 0.051 8.85 0.17 182 0.033	**Os** 1.26 2.2 1.35 162 0.69(+4) 6.4 — 0.11 8.43 — 201 0.031	**Ir** 1.27 2.2 1.36 152 0.66(+4) 6.6 — 0.189 8.54 0.14 212 0.031	**Pt** 1.30 2.2 1.39 122 0.96(+2) 4.7 — 0.095 9.10 0.17 207 0.032	**Au** 1.34 2.4 1.46 81.8 1.37(+1) 3.03 — 0.42 10.2 0.71 213 0.031	**Hg** 1.49 1.9 1.57 13.9 1.10(+2) 0.56 — 0.011 14.8 0.02 241 0.033	**Tl** 1.48 1.8 1.71 38.8 1.40(+1) 1.02 0.95(+3) 0.055 17.2 0.093 141 0.031	**Pb** 1.47 1.8 1.75 42.4 1.20(+2) 1.22 0.84(+4) 0.046 18.3 0.083 171 0.031	**Bi** 1.46 1.9 1.70 42.7 1.20(+3) 2.6 0.74(+5) 0.009 21.3 0.02 185 0.034	**Po** 1.46 2.0 1.76 29 — — — 0.02 22.7 — — —	**At** (1.45) 2.2 — 8 — — — — — — — —	**Rn** — — — 3.92 — 0.69 — — — — 248 —
Fr — 0.7 — — 1.76(+1) — — — — — — —	**Ra** — 0.9 — 27.4 1.40(+2) 2.4 — — 45 — — —	**Ac**★★ — 1.1 1.88 — 1.18(+3) — — — — — — —															

★	**Ce** 1.65 1.1 1.81 95 1.11(+3) 1.2 1.01(+4) 0.013 21.0 0.026 159 0.042	**Pr** 1.65 1.1 1.82 79 1.09(+3) 1.60 0.92(+4) 0.015 20.8 0.028 133 0.048	**Nd** 1.64 1.2 1.82 69 1.08(+3) 1.70 — 0.013 20.6 0.031 145 0.045	**Pm** 1.63 — — — 1.06(+3) — — — — — 133 —	**Sm** 1.62 1.2 1.81 46 1.04(+3) 2.1 — 0.011 19.9 — 129 0.042	**Eu** 1.85 — 1.99 42 1.12(+2) 2.2 — 0.012 28.9 — 131 0.039	**Gd** 1.61 1.1 1.79 72 1.02(+3) 3.70 — 0.007 19.9 0.021 142 0.071	**Tb** 1.59 1.2 1.80 70 1.00(+3) 3.9 — 0.009 19.2 — 155 0.044	**Dy** 1.59 — 1.80 67 0.99(+3) 4.1 — 0.011 19.0 0.024 157 0.041	**Ho** 1.58 1.2 1.79 67 0.97(+3) 4.1 — 0.011 18.7 — — 0.039	**Er** 1.57 1.2 1.78 67 0.96(+3) 4.1 — 0.012 18.4 0.023 — 0.040	**Tm** 1.56 1.2 1.77 59 0.95(+3) 4.4 — 0.011 18.1 — — 0.038	**Yb** — 1.1 1.94 38 1.13(+2) 1.8 0.94(+3) 0.035 24.8 — 143 0.035	**Lu** 1.56 1.2 1.75 90 0.93(+3) 4.6 — 0.015 17.8 — 115 0.037
★★	**Th** 1.65 1.3 1.80 — 1.14(+3) 4.6 0.95(+4) 0.055 19.9 — — 0.034	**Pa** — 1.5 1.61 130 1.12(+3) — 0.98(+4) — 15.0 — — —	**U** 1.42 1.7 1.38 110 1.11(+3) 2.7 0.97(+4) .034 12.5 0.064 — 0.028	**Np** — 1.3 1.3 94.3 1.09(+3) — 0.95(+4) — 21.1 — — —	**Pu** — 1.3 1.51 87.2 1.07(+3) — 0.93(+4) — — — — —	**Am** — 1.3 1.73 −60.2 1.06(+3) — 0.92(+4) 0.007 20.8 — — 0.033	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lw**



NOTES:

(1) For representative oxides (higher valence) of group. Oxide is acidic if color is red, basic if color is blue and amphoteric if both colors are shown. Intensity of color indicates relative strength.

(2) Cubic, face centered; cubic, body centered; diamond; cubic; hexagonal; rhombohedral; tetragonal; orthorhombic; monoclinic.

(3) At room temperature. (4) At boiling point. (5) From 0° to 20°C.

(6) Ionic (crystal) radii for coordination number 6.

(7) Metallic radii for coordination number of 12.

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SIDE 2

PREFACE

This thesis was planned as a work in two volumes - Volume 1 for the text etc. and Volume 2 for the many maps and other illustrations of A2 size. Volume 1 eventually grew so large that it became necessary to divide it into three sub-volumes:

Volume 1A:	Text
Volume 1B:	Plates and Appendices
Volume 1C:	Literature Survey and Lists of References.

Some of the maps in the thesis were prepared several years before publication, and refer to the Karroo formation. It was recently officially ruled that the spelling Karoo should be adopted. Some of the values for pressures are given in atmospheres because that was the unit of measurement in force at the time that the experimental work was undertaken. The currently-accepted S.I. unit for pressure is the Pascal.

ABSTRACT

The Precambrian Otavi dolomites in the district of Tsumeb in Namibia are host to base metal mineralization but large tracts of these rocks occupy a mature pediplain and are deeply buried by transported overburden of Kalahari age. This sandy material makes exploration for minerals very difficult. Hydrogeochemistry was considered as a possible answer to the problem of prospecting in this region but a major obstacle was the lack of an undisturbed site for orientation studies. The Tsumeb mine was therefore used as a "surrogate" orientation target and water samples collected there were analyzed for about forty elements or ions. The data were plotted on long-sections through the orebody and examined with the aid of simple statistical calculations. The Na /Cl$^-$ ratio proved to be a powerful index for identifying groups of waters with a common origin. It appeared that the most important of these groups of waters were not natural groundwaters but were being recycled. Millions of litres of water are pumped from the mine daily and a significant proportion finds its way back into the workings through seepage. This conclusion was supported by chemical data and by calculations in which the rates of pumping and recharge were balanced. Over the years the process of recycling has caused a rise in the concentrations of sodium, chloride and sulphate in the water arriving at the sumps in the mine. The other major components of these waters - Ca, Mg and HCO_3^- - are not affected to the same extent by recycling because of controls imposed by the carbonic system.

It was not generally possible to establish rational links between the distributions of the trace elements, the major groups of related waters and the proximity of ore. Although some trace elements tended to be more abundant in samples from the upper parts of the mine, where exposure to broken, weathered ore is greatest, the value of this association was diminished by the fact that these waters are recycled effluents that cannot be equated with the natural groundwaters that would be in contact with any undiscovered orebodies similar to the Tsumeb lode. This conclusion was reinforced by the fact that some of the trace elements were relatively abundant in waters that were comparatively saline but which had not been exposed to oxidized ore. It was concluded that it would not be possible to interpret the trace element data from the mine waters unambiguously. Nevertheless it was clear that sulphate, Cu, Pb, Zn, Hg, Cd, Se, Te and perhaps Li were being mobilized from the ore and that these were therefore all good "candidate" pathfinders. Less probable candidates were Mo, Ge, As, Na and chloride.

A second orientation study was then undertaken, using normal groundwaters from boreholes and springs on surface. Sampling was concentrated around the Tsumeb and Kombat mines as targets and waters were also obtained from background areas where dolomites were exposed. The chemical data were plotted on maps by

computer and were examined with the aid of simple statistical calculations such as the cumulative frequency distribution. Although anthropogenic effects were apparent at both mines they were not severe and it was possible to be more confident about the prospective roles of the various chemical species in hydrogeochemical exploration for ores in the Otavi dolomites. These prospective roles may be summarized as follows: undetectable or of virtually no interest: pH, temperature, phosphate, K, Ti, Fe, Li, Rb, Cs, V, Cr, Mo, Ag, Au, Cd, Hg, Tl, Ge, As, Sb, Bi, Se and Te; useful as indicators of regional hydrogeochemical features not directly related to mineralization: Si, F^-, Sr and Al; weak regional pathfinders: Ni and Co; probably good regional pathfinders: sulphate, Cu, Pb and Zn. Bicarbonate, Cl^-, Na, Ca and Mg are not pathfinders but it is useful to have these data when considering the nature and significance of the samples and the abundances in them of the trace elements. Despite the identification of a suite of pathfinders it was not feasible to establish orientation criteria such as contrast ratios.

An attempt was made to apply the findings of this orientation survey in an area to the northeast of Tsumeb, where dolomites are buried under thick sand and calcrete. An area of five thousand square kilometres was selected and all usable sources of groundwater within it were sampled. The following data were collected: total dissolved solids, pH, Ca, Mg, Na, bicarbonate, chloride, sulphate, Cu, Pb and Zn. Hydrological data suggested that the regional movement of groundwater was from the exposed dolomites into the pediplain. The hydrogeochemical data showed that during this migration the major element composition of the groundwater changed ("metamorphosed") radically. Because of this metamorphism, very severe difficulties stood in the way of applying in the sandy pediplain what had been learned in the areas of well-exposed dolomite. An attempt was therefore made to provide tighter control between the lithology of the geological profile and the hydrogeochemistry of the associated formational waters in the pediplain. This work consisted of (a) a sampling program to try to "fingerprint" specific formational waters. This proved to be impossible. (b) drilling four diamond drill holes near selected anomalies and studying the cores in detail. These revealed that the Kalahari beds were very thick (46 to >103m). In all cases the base of the overburden was far below the present water table and in some cases the overburden was underlain by unmineralized rocks other than dolomite. These results indicated that the hydrogeochemical anomalies were probably spurious and it was concluded that hydrogeochemical exploration in this kind of Kalahari terrane was not practicable.

SUMMARY

{Marchant, J.W. 1980. Hydrogeochemical exploration at Tsumeb. Ph.D. thesis, University of Cape Town. 4 volumes; 850 pages; 200 illustrations; 1200 references}

The late Precambrian Otavi dolomites in the district of Tsumeb in northern Namibia are host to important base metal mineralization, but large tracts of these rocks cannot be subjected to conventional methods of prospecting because they lie on a mature pediplain and are deeply buried by layers of superficial, transported overburden of Kalahari age (Recent to Tertiary). Hydrogeochemical exploration was considered to be a possible answer to the problem because the reactivity and mobility of groundwater favour the recognition of secondary aureoles of dispersion that would probably not be detected by other techniques. A major obstacle to any attempt to apply the hydrogeochemical method in the region was the lack of an adequate site for orientation - there being no known local deposits that are buried under a substantial layer of overburden. The Tsumeb orebody (a pipe-like Cu-Pb-Zn sulphide/oxide deposit) was therefore used as a "surrogate" orientation target, and a suite of water samples from this mine was examined with a view to identifying pathfinders. Samples were collected from a wide range of geological and hydrological settings throughout the mine. Data for the following parameters were recorded: geological and hydrological characteristics, rate of flow, air temperature, water temperature, pH, colour of total suspended solids (TSS), mass of TSS, total dissolved solids (TDS), Mg, Ca, OH^-, $CO_3^{=}$, HCO_3^-, Cl^-, F^-, $SO_4^{=}$, PO_4^{3-}, Na, K, Li, Rb, Cs, Sr, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn, Cd, Hg, Al, Tl, Si, Ge, As, Sb, Bi, Se, Te and Pb. Most of the major components were determined by wet chemical methods and most of the trace elements by atomic absorption spectrophotometry (solvent extraction, flame and flameless techniques). In addition, x-ray fluorescence spectrometry was used to make semi-quantitative estimates of the amounts of Si, Al, Mg, Ca, Ti, Mn, Fe, Cu, Pb and Zn in the TSS residues separated by filtration.

The data were plotted on computer-generated long-sections through the orebody and examined with the aid of simple statistical calculations. The interpretation proceeded in two stages: (i) the first stage was essentially a *hydrological* study aimed at the identification of characteristic bodies of related mine waters and the investigation of their origin. For this purpose Na , Cl^- and $SO_4^{=}$ were used as natural tracers. The study of the hydrology of the mine was hampered to some extent by the fact that the rock in the vicinity of the workings is heavily cementated. Nevertheless the

SUMMARY (cont.)

Na/Cl ratio proved to be a powerful index for identifying groups of waters with a common origin. The $SO_4^=$ content was not quite as diagnostic but was nonetheless valuable. Seven groups of related mine water samples were identified, which were distributed in a systematic manner through the vertical length of the mine workings, and in which the mean Na/Cl^- ratio varied from 0,6 to 1,6. It appeared that the most important of these groups of waters were not natural, pristine groundwaters but were being recycled through the mine via the surface. Millions of litres of water are pumped from the mine each day and a significant proportion finds its way back into the workings by various paths. This conclusion was supported by chemical data, by calculations in which the rates of pumping from the mine, rainfall, recharge, evaporation and disposal of wastes were balanced against one another, and to some extent by radiocarbon dating of local groundwaters. One group of recycled water enters the upper levels of the mine from directly above and is derived from industrial water discarded in the Mining Area. Another important group originates in the Slimes Dams complex some kilometres north of the town and makes its way back into the central levels of the mine (≃ 1000 m below surface) via fractures, of which a major one known as the North Break Zone is the most important. Only the most mobile species are carried through this cycle; the toxic, immobile microcomponents are fixed *en route* and are not recirculated. Over the years the process of recycling has thus caused a significant rise in the concentrations of Na, Cl^- and $SO_4^=$ in the water arriving at the sumps in the mine. The other major components of these waters - Ca, Mg and HCO_3^- - are not affected to the same extent by recycling because their concentrations are tightly controlled by the solution equilibria of the carbonic system. A computer program was written that compared the "observed" state of the carbonic system in each of the samples of mine water with the theoretical "saturated" state for that sample. The program requires data for observed pH, alkalinity, and [Ca] and allows for the effects of temperature, ionic strength and *hydrostatic pressure*, since the Tsumeb mine is about 1500 m deep and some of the pressures measured exceeded 100 atmospheres. The computation showed that [Ca], pH and $[HCO_3^-]$ in the mine waters are generally well-equilibrated and therefore cannot readily be used as natural tracers since they change in response to factors independent of the origin and movement of the different bodies of related groundwaters. The equilibrium is nevertheless *dynamic*, with continuous dissolution of dolomite and reprecipitation of calcite, and there is some evidence that the concentrations of certain

SUMMARY (cont.)

trace elements may be influenced by concomitant effects of co-precipitation or "scavenging". The incongruent solution of dolomite has lead to a disequilibrated molar Mg/Ca ratio of 1,05 (ideal value 0,8). (ii) The second stage of the interpretation was essentially *hydrogeochemical* and was aimed at constructing a picture of the interrelationships between the abovementioned major components and the minor and trace elements. It was obvious from (i) above that the groundwaters around the mine had been greatly disturbed by man and there were *prima facie* reasons for apprehending that this would be reflected in a disruption of the natural state of these relationships. This did prove to be the case and it was not generally possible to establish rational links between the distributions of the trace elements, the major groups of related waters and the proximity of ore. Lithium was the only trace element that correlated well with the groups identified on the basis of the Na/Cl^- ratio. Although some trace elements tended to be more abundant in samples from the upper parts of the mine where exposure to broken, weathered ore is greatest, the value of this association was diminished by the fact that these waters are recycled effluents that cannot be equated with the natural groundwaters that would be in contact with any undiscovered orebodies similar to the Tsumeb lode. This conclusion was reinforced by the fact that some trace elements were relatively abundant in the waters of the North Break Zone, which are comparatively saline but have not been much exposed to oxidized ore. It was concluded that it would not be possible to interpret the trace element data from the mine waters unambiguously and that one could not with confidence identify pathfinder species or establish orientation criteria such as threshold values or contrast ratios. Nevertheless it was clear from the diagrams and from statistical examination of the data that $SO_4^=$, Cu, Pb, Zn, Hg, Cd, Se, Te and perhaps Li were being mobilized from the ore on a significant scale and that these were therefore all good "candidate" pathfinders. Less probable candidates were Mo, Ge, As, Na and Cl^-.

On the basis of the above results, it was decided that a second orientation study should be undertaken, using normal groundwaters drawn from boreholes and springs on surface. This study took place in the Otavi Mountainland, which is a hilly area of well-exposed dolomites immediately south of Tsumeb. Sampling was centered around the Tsumeb and Kombat mines as targets and waters were also obtained from several background areas. The samples were analyzed for each of the chemical components that had been determined in the study of the mine waters. The data were plotted on computer-drawn, coloured maps and were examined with the aid of simple statistical calculations. The cumulative frequency distribution was used to divide the data into two classes of negative anomalies, two classes of positive anomalies and the background class. The distinction between negative anomalies and background values was useful in many cases for demonstrating regional hydrogeochemical features. The threshold values were: Grade -I, 10% of cumulative frequency; Grade -II, 20%; Grade II, 80%; Grade I, 90%. Sophisticated statistical procedures such as discriminant function analysis and cluster analysis were also utilized but they added nothing of importance to the interpretation of the results. It was useful to examine the raw data, ratios of (dissolved [element]/[TDS]), ratios of (suspended [element]/[TSS]) and summed indices such as (Cu + Pb). The following factors had to be taken into account in order to explain the observed patterns of distribution of values, to decide which of these constituted anomalies and to assess the importance of these anomalies: the individual characteristics and historical reputation in groundwater hydrogeochemical exploration of the different chemical species; contrast values and the detection limit of analysis; variations in the local value of the background concentration; the influence of the lithology of the country rocks; the correlations between TDS and TSS and the concentrations of certain species; the postulated "metallogenic zones" or primary dispersion aureoles at Tsumeb and Kombat; and the disturbance of the groundwater regimes at Tsumeb and Kombat by the activities of man. Although anthropogenic effects were apparent at both mines - manifested principally in the form of TDS and TSS anomalies and an accumulation of Na, Cl^-, Mg, PO_4^{3-}, Ti, Fe and Mn - they were not as severe as those noted in the study of the mine waters and it was possible to be more confident at this stage about the prospective roles of the various chemical species in hydrogeochemical exploration for ores in the Otavi dolomites. These prospective roles may be summarized as follows: undetectable or of virtually no interest: pH, temperature, PO_4^{3-}, K, Ti, Fe, Li, Rb, Cs, V, Cr, Mo, Ag, Au, Cd, Hg, Tl, Ge, As, Sb, Bi, Se and Te. (It is apparent from this list that the doubts entertained about the validity of performing an orientation survey with disturbed mine waters were justified); useful as indicators of general, regional hydrogeochemical features not directly related to mineralization: Si, F^-, Sr and Al; weak pathfinders: Ni and Co; probably

SUMMARY (cont.)

good pathfinders: $SO_4^=$, Cu, Pb and Zn. The remainder of the major elements form a special group. They are not good pathfinders but it is useful to have these data when considering the nature and significance of the samples and the abundances in them of the trace elements. Despite the successful identification of a suite of pathfinders, it was nevertheless significant that the anomalies at Tsumeb were generally weaker than those at Kombat. Because of this it was not realistic to establish orientation criteria such as contrast ratios, sizes of expected anomalies etc. It was clear, however, that any anomalies detected by the hydrogeochemical method would be more likely to be regional than local. Ancillary studies conducted during this orientation survey included (a) studies of the contamination of samples by borehole hardware. This was monitored by restarting pumps on boreholes that had been idle for up to 12 months, and analyzing samples collected at regular intervals for an hour or more. Contamination appeared not to be a general problem and only zinc gave trouble in certain cases. Rotary pumps are less likely to cause contamination than reciprocating pumps. (b) extensive studies of the contamination of samples by the high--density polyethylene containers in which they were stored. It was shown that this was not a problem. (c) studies of the stability of stored samples of groundwater. Trace elements appeared to be effectively stabilized for several months by acidification to pH ≈2 with HNO_3 or $HClO_4$ and freezing at -20^0 C. The major components of the groundwaters from the Tsumeb area do not require any special preservation and are very stable for at least a week. (d) studies of seasonal variations in the compositions of waters from boreholes. This was found to be slight.

It was recommended that an attempt be made to apply the findings of the second orientation survey in an area to the northeast of Tsumeb, where dolomites are buried under thick sand and calcrete. For this purpose an area of five thousand km^2 was withdrawn from pegging and all usable sources of groundwater within it were sampled. The following data were collected: TDS, pH, Ca, Mg, Na, HCO_3^-, Cl^-, $SO_4^=$, Cu, Pb and Zn. Interpretation followed lines similar to those described for the second orientation survey. Hydrological data from unpublished sources suggested that the regional movement of groundwater was from the Otavi Mountainland northwards into the pediplain. The hydrogeochemical data showed that during this migration the major element composition of the groundwater changed ("metamorphosed") radically. Because of this metamorphism, very severe difficulties stood in the way of applying in the sandy Withdrawal area what had been learned in

SUMMARY (cont.)

the areas of well-exposed dolomite. Thus: the concentrations of TDS, Na and Cl^- in the Withdrawal area were very high and variable. Only in the far south could the influence of northward-moving, dilute dolomitic waters be detected; the pH was systematically higher in the Withdrawal area; sulphate was much more abundant and correlated too well with TDS, so that attempts to define positive sulphate anomalies tended merely to outline the zones of relatively saline waters. Substituting the $SO_4^=$/TDS ratio helped but little, because the amount of sulphate rises proportionately faster than the TDS does as the groundwaters migrate northwards; the concentrations of Pb and Zn were severely suppressed relative to the dolomitic waters and many of the Cu and Zn anomalies were dubious because of a strong correlation with areas of saline water (cf. sulphate, above). In addition, many of the $SO_4^=$, Cu and Zn anomalies fell in those parts of the Withdrawal area that were thought, on the basis of aeromagnetic data, to be underlain by unfavourable rocks such as Mesozoic basalts or Archaen granites. An attempt was therefore made to minimize the need to extrapolate criteria from the orientation data to the application data, by providing tighter control between the lithology of the geological profile and the hydrogeochemistry of the associated formational waters in the Withdrawal area. This work consisted of (a) a sampling program in the east to try to "fingerprint" basaltic and granitic formational waters. This proved to be impossible, mainly because the composition of the water in the boreholes drilled into these profiles is controlled not by the impervious subcrop but by the more aquiferous Kalahari overburden; (b) drilling four diamond drill holes and studying the petrology, mineralogy and geochemistry of the cores. Two holes in the east of the Withdrawal area showed that the poorly-sorted, sandy or gravelly, calcareous Kalahari cover was deeper than had been expected; these two holes reached down to 56 and 103 m respectively and did not encounter bedrock. Both profiles (and the two penetrated by the boreholes described below) were very heavily recemented by calcrete, especially in the upper 20-40 m. It was considered impossible to pursue a program of practical hydrogeochemical exploration through this depth of overburden. There was no evidence of any secondary dispersion of base metals in the borehole cores and it was considered probable that the hydrogeochemical anomalies in the eastern portion of the Withdrawal area were spurious. A borehole sited in the northwestern corner of the Withdrawal area, upon a magnetic anomaly and a $SO_4^=$/TDS anomaly, passed through 59 m of typical Kalahari beds and into sandstone of the Mesozoic Karoo Formation. The existence of these rocks in

SUMMARY (cont.)

this part of the Withdrawal area had not been expected and this terminated the hydrogeochemical project in this region. The fourth borehole was drilled in the southwestern part of the Withdrawal area, in the hope that thinner overburden existed there, and in order to investigate a prominent zinc anomaly. The Kalahari cover was nevertheless still a daunting 46 m thick and the anomaly was specious because the drill then passed not into dolomite but into Mulden quartzites. The hydrogeochemical effort in this kind of Kalahari terrane was regarded as untenable and the withdrawal order was allowed to lapse. On the other hand, the results from the second orientation survey were held to be valid and useful for prospecting in terranes relatively free of overburden, and the hydrogeochemical methods developed in this study are currently being used by a mining group for exploration in those areas of dolomite that are not so deeply buried.

This thesis includes a very comprehensive survey of the history and literature of groundwater hydrogeochemical exploration for all types of mineral resources except petroleum.

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ABBREVIATIONS

The following abbreviations are used in this thesis. Well-known abbreviations are not included in this list.

A	alkalinity
AAS	atomic absorption spectrophotometry
APCD	ammonium pyrrolidene carbodithioate
AR	analytical (grade) reagent
ART	article
BDH	British Drug Houses
CC	correlation coefficient
CONC	concentration or concentrated
DL	detection limit (concentration)
EDTA	ethylenediaminetetraacetic acid (or its sodium salt)
FIG	figure
HCL	hollow cathode lamp
MA	methyl alkalinity
MIBK	methyl isobutyl ketone, alias 2-methyl-4-pentanone
MLC	Modified Lawrence Caldwell (diagram)
NBZ	North Break Zone (of Tsumeb mine)
PA	phenolphthalein alkalinity.
SOLN	solution
SUS	suspended
TCL	Tsumeb Corporation Limited
TDS	total dissolved solids
TH	total hardness
TMW	Tsumeb Mine water
TSS	total suspended solids
UCT	University of Cape Town
VOL	volume or volumetric
VT	Varian Techtron
WA	Withdrawal Area

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Because of the nature and the long duration of the project an unusually large number of people were involved in or associated with it. It is not feasible to record here the names of each person who assisted me and in what capacity; it must suffice to offer to all of them a general word of thanks for their contributions small and large. They include many members of the School of Earth Sciences at UCT; a large number of the staff at TCL; members of various Governmental Departments - Water Affairs, Transport (Weather Bureau, South African Airways), Geological Survey, CSIR ; the dozens of farmers who gave us every possible assistance; officials of the Tsumeb Municipality; and the members of the Computing Service at UCT.

In addition the writer would fain offer a special word of thanks to the following people whose contributions cannot be allowed to pass without a specific mention:

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FOREWORD

Much of northern Namibia is covered by a thick blanket of recent overburden, which makes exploration for minerals in this region rather difficult. This thesis describes the development and application of methods of groundwater hydrogeochemical exploration in an attempt to solve some of the practical problems posed by this obscurative overburden. These experiments took place in the district of Tsumeb. The thesis is structured as follows:

(I) Introduction
    (i) Preliminary introductory information
    (ii) A detailed statement of the exploration problem and a consideration of the hydrogeochemical method as a possible solution thereof
(II) Orientation experiments with mine waters
(III) Orientation studies and regional surveys using ordinary groundwaters

Throughout this work numbers enclosed in sloping dashes (e.g. /24/) refer to literature references listed at the end of the volume. A comprehensive survey of literature is given in a 300-page supplementary volume entitled "A review of the history and literature of groundwater hydrogeochemical exploration for ores". In order to improve the readability of the main part of the text, many sections that deal in detail with matters such as analytical methods, sampling locations, mathematical derivations, etc. have been taken out and placed in appendices.

Many sepia overlays and other illustrations that are too large for inclusion within the text will be found in an accompanying map portfolio. All of the original graphic work for this thesis was produced on sepia overlays similar to the examples included in the map portfolio. The cost of drafting work, and especially of sepia prints, is now prohibitive and to reduce costs it has, regrettably, been necessary to reproduce many of these illustrations on paper, and to use computerized graphics routines to cope with the considerable volume of drafting work involved. These graphics routines are obviously not totally flexible and the reader is asked to overlook the minor shortcomings in the artwork produced by them.

SECTION I. INTRODUCTION

Chapter I. A description of the country around the town of Tsumeb

1.1 Location/222/

The Territory of Namibia is situated on the west coast of Africa south of the equator. The region of specific interest is in the north-central portion of the Territory (maps 1 and 1a), within a radius of about 100km of the town of Tsumeb (approximately 19^0S, 18^0E).

1.2 Climate/52,74,220-1/

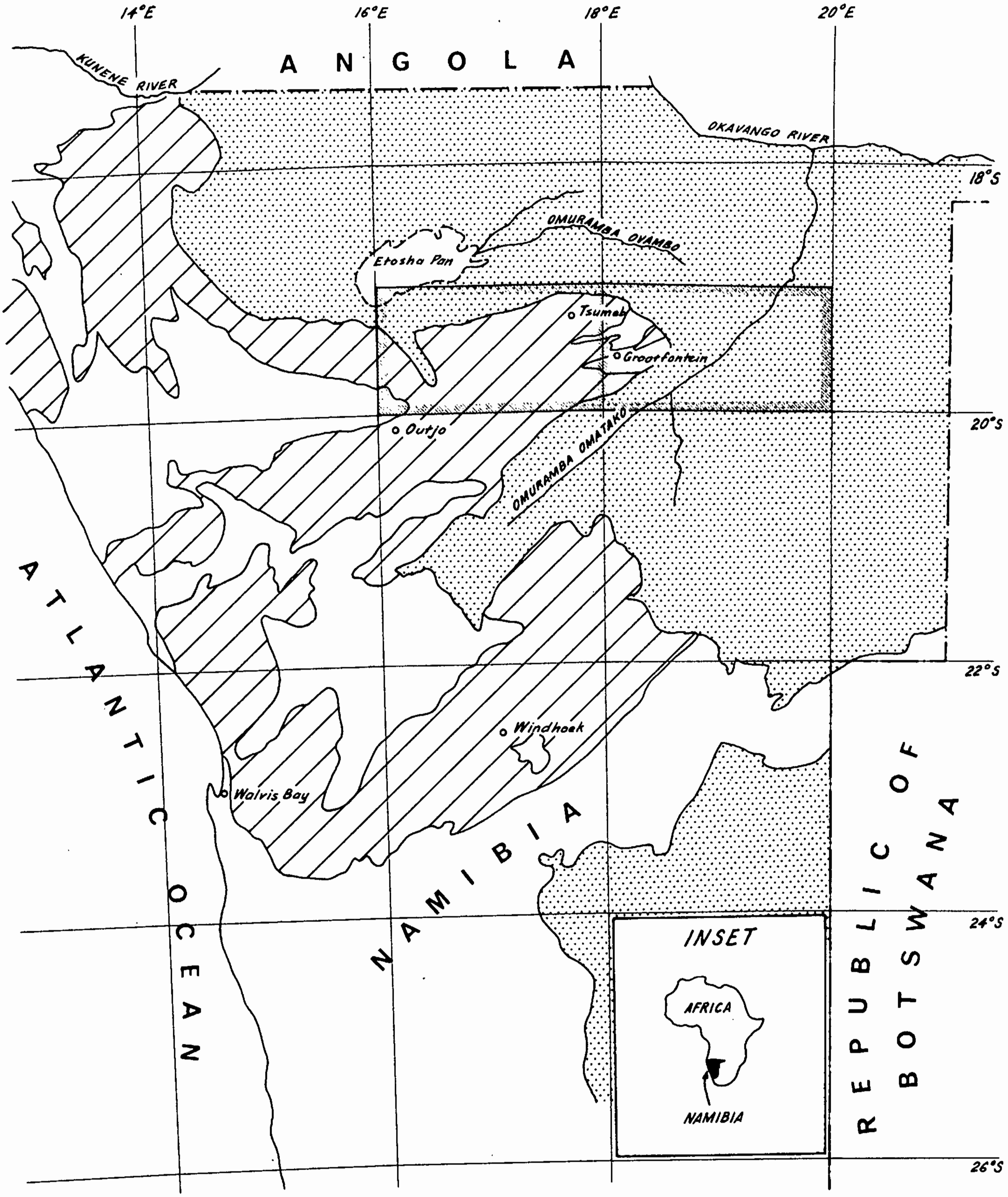
Although more than half of Namibia is within the tropics, most of the Territory is desert or semi-desert because of the influence of the cold, north-bound Benguela Current off the west coast. Rainfall improves to the north and towards the east from the coast. North-central Namibia has a warm, semi-arid climate.

The annual rainfall at Tsumeb is about 560mm, falling mainly in summer thunderstorms between November and March. Precipitation is slightly heavier in the triangular area of highlands known as the Otavi Mountainland but decreases to a mean of just under 500mm per annum in the flat areas adjacent to the mountainland. Evaporation exceeds precipitation everywhere and aridity is emphasized by the widespread development of karstic landscapes. Temperatures in summer are around 27^0C and in the dry winter they are around 15^0C.

1.3 Vegetation/32,220/(Plates 1 and 2)

Tsumeb lies within the thorn country vegetation belt of Namibia and Botswana. The typical vegetation is low thorny tree and scrub savanna, characterized by many species of *Acacia* and other common thorn species such as the Sekelbos (*Dichrostachys cineria*) and the Buffalo-thorn (*Ziziphus mucronata*). Many species of grasses grow abundantly amongst these thorny bushes and trees but open grasslands are not commonly developed except in certain of the valleys of the Otavi Mountainland.

Minor local changes in this typical pattern of vegetation, due to variations in relief, geology, soil conditions and the activities of man, are commonly seen. Some areas, especially the dolomitic hills, are fairly well-wooded and may be described as low tree savanna. Most of these trees are small or medium-sized and may be evergreen or deciduous. Well-known examples are the Mopane (*Colophospermum mopane*), Tambooti (*Spirostachys africana*) and Terminalia (*Terminalia prunoides*). Some conspicuous larger



LEGEND

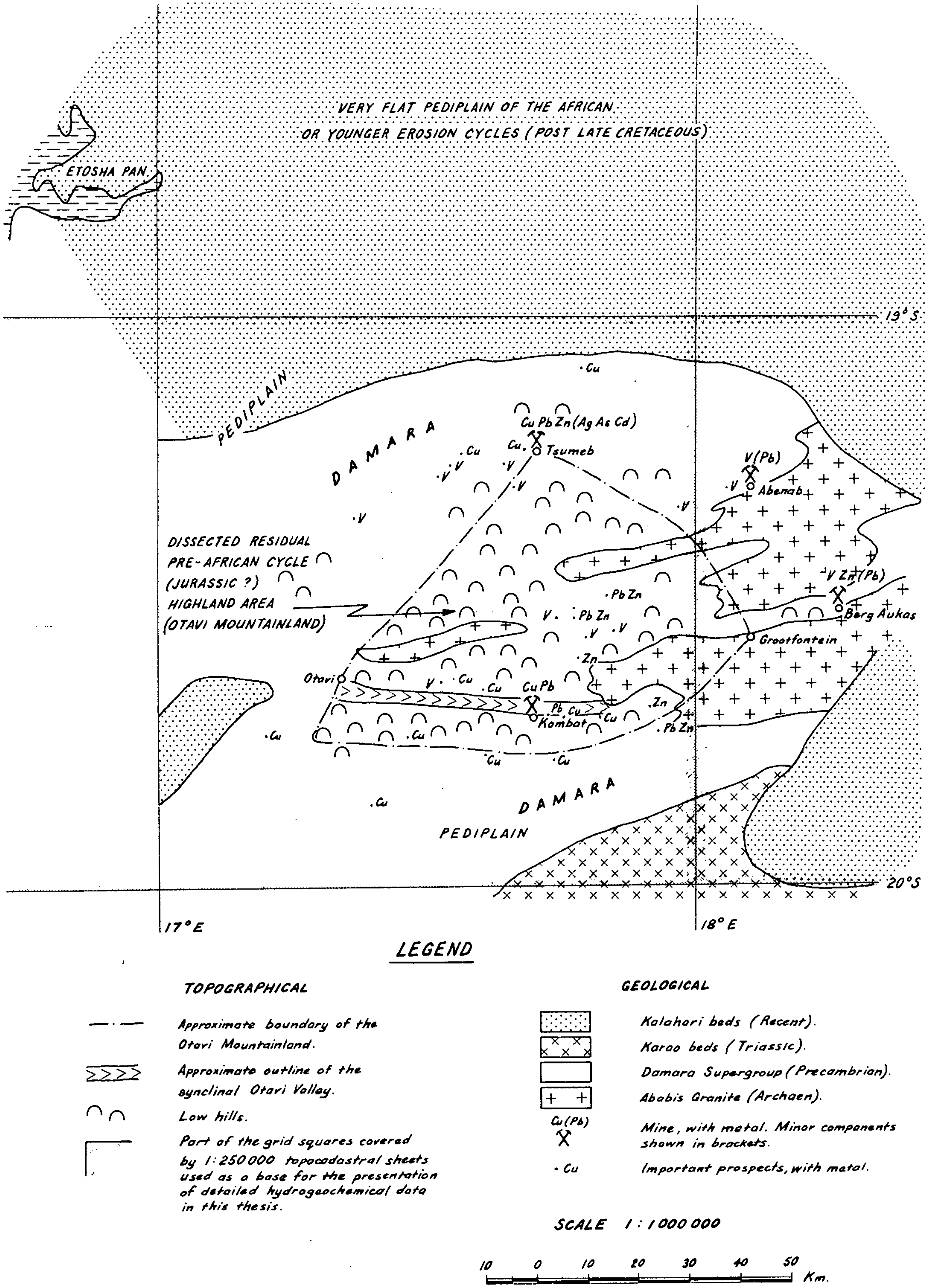
▒	*Kalahari Beds. Tertiary to Recent, Aeolian Sand etc. usually with thick Calcrete.*
▨	*Damara Supergroup. Precambrian. Mainly Dolomite in the North, well mineralised in places. Metamorphosed in the South.*
— · —	*International Boundary.*
⌜	*Grid squares covered by 1:250 000 topocadastral sheets used as a base for the presentation of detailed hydrogeochemical data in this thesis.*

SCALE 1 : 5 000 000

50 0 50 100 150 200 250 Km.

MAP OF NAMIBIA
Showing Location of Tsumeb Area
& Simplified Geology of Damara Supergroup
& overlying Kalahari Beds

Map 1.



Location Map of Area Around Tsumeb showing simplified Topography, Geology and Mineral Occurences.

Map 1A.

Table 1.4 Condensed stratigraphy of the area around Tsumeb /70,222/

Supergroup	*Series or Formation*	*Stage*	*Substage*	*Lithology*	*Max. thickness*	*Age*
	Kalahari			Sandstone,grit,marl,calcrete	300m?	Tertiary to Recent
				MAJOR UNCONFORMITY		
Karoo	(Stormberg)	Kaoko		Basaltic lava	100m?	Triassic to Lower Jurassic
		Etjo		Sandstone,quartzite	100m?	
				MAJOR UNCONFORMITY		
Damara	Mulden Series			Sandstone,quartzite,grit	700m?	More than 510 megayear,probably Late Precambrian
				DISCONFORMITY		
	Otavi Series	Tsumeb		Dolomite,minor limestone and shale	300m	
			Tillite	Tillite,conglomerate,quartzite	210m	
				DISCORDANCE		
		Abenab		Dolomite,lesser limestone,shale	1900m	
				UNCONFORMITY		
	Nosib Formation			Epidosite,schist,quartzite,arkose phyllite,minor dolomite	750m	
				MAJOR UNCONFORMITY		
Archaen Granites	Abbabis	(Outjo & Grootfontein Inliers)		Granite, augen gneiss	?	1700 megayear

trees such as the Maroelaboom (*Sclerocarya caffra*) are often quite common.

The bush *Catophractis alexandrii* occurs ubiquitously in tracts underlain by calcrete. Towards the north and east, where drainage is poorer, the conspicuous Makalani palm (*Hyphaene ventricosa*) occurs singly or in scattered groups.

1.4 Geology/52,70,222,229/(Maps 1&1a, and Map 4 in Vol. 2)

The geology of the region is relatively simple. The terrane is dominated either by the Recent Kalahari Beds (*vide infra*) or by the Outjo Facies of the Late Precambrian Damara Supergroup, a thick succession consisting mainly of dolomite and lying unconformably on the Archaen Abbabis Granite. This is probably the thickest accumulation of dolomite in the world /229,233/. Table 1.4 summarizes the geological succession. Active investigation of the Damara continues and details of subdivision, nomenclature, correlation and interpretation are not always universally agreed upon (e.g. /206,227, 234-5/) and are subject to revision.

The succession is moderately folded along open axes with a general east-west strike, tending towards northeasterly in the east. Towards the south folding becomes progressively heavier as the entire succession passes gradually into a high-grade metamorphic zone, known as the Swakop Facies of the Damara Supergroup, most of which is well south of the area of interest. The almost unmetamorphosed Outjo Facies in the Otavi-Tsumeb-Grootfontein district can be regarded as a shelf facies equivalent of the southern geosynclinal Swakop Facies.

Certain units within the Outjo Facies are well mineralized and small prospects and showings are very common. The origin of this mineralization is controversial and discussion of this topic will be deferred to section II. There are four large oxide/sulphide mines in the area /52,195-8,1165/, producing one or more of the metals Cu, Pb, Zn, V, Ag, As, Ge and Cd in varying proportions. The Tsumeb mine is particularly rich, having produced around three million tonnes of metal since 1907 from ore averaging about 5,9% copper, 7,0% zinc and 15,1% lead. Development of the pipe-like orebody continues.

It appears likely that the Damara was once wholly or extensively overlain by sedimentary rocks and/or basaltic lavas of the Mesozoic Karoo Formation. If so, the northerly portion of this cover has been largely stripped by Post-Cretaceous pediplanation, leaving outcropping remnants only, in the form of the Etjo sandstone and the Kaoka basalt in the extreme southeast of the area of interest. Boreholes have intersected more northerly outliers of Kaoko basalt totally buried beneath superficial materials- for example, an extensive lava field is known to lie under the sand some 65km east of Grootfontein, while a borehole about 25km northwest of Tsumeb passed through 25m of overburden, 60m of Kaoko basalt and penetrated a few metres into the underlying Etjo sandstone. It is likely that other unknown outliers of Karoo rocks are buried beneath the regolith north of Tsumeb.

To the north of Tsumeb and east of Grootfontein the pediplaned, tilted surface of the exposed Damara rocks disappears completely underneath a vast, flat, transgressive layer of poorly-consolidated, Recent to Tertiary terrestrial material known as the Kalahari Beds, which cover hundereds of thousands of square kilometres of south-central Africa. It is this obscurative Kalahari Formation that causes the prospecting headache, since it completely blankets the potentially mineralized Damara rocks below. The Kalahari beds in northern and northeastern Namibia are probably largely transported rather than being residual detritus that has collected *in situ*. They consist of layers of calcareous sandstone, aeolian sand, a little clay etc., which collected in a vast, shallow, continental internal drainage basin. Thick layers of calcrete (50m is not uncommon) frequently occur within or cap the beds, which reach thicknesses of 100 to 200m (and perhaps more) within 30km of Tsumeb.

Numerous general or detailed geological maps of the area are available from the Geological Survey or are in the possession of mining corporations. Aerial photographs are available from Government and private sources. ERTS imagery is also available (Fig. 3, Vol. II).

1.5 Topography/74,221/ (Plate 1)

The two principal topographic features of the Tsumeb area are the great African or post-African pediplain and the residual Otavi Mountainland of an older period. The pediplain, of post-Late Cretaceous age, is here a bevelled and extremely flat plain now standing at about 1400m above sea level and sloping slightly to the east. It confers an all-pervading, sandy flatness in the north of Namibia, truncating all formations equally where fully developed, so that in places of thick regolithic cover virtually no solid geology is visible for hundereds of kilometres on end. The detailed topography of these cyclic land surfaces is in fact quite complex. Most of the pediplain is a denudational surface of either African or post-African (dicyclic Oligocene-Miocene) age, but where the Kalahari sands encroach in the northeast the pediplain is an aggradational Recent land surface. The pediplain has few irregularities, except for isolated, low, rounded hills, which rise abruptly out of the plain. These hills are remnants of an older landscape

(Jurassic "Gondwana" cycle), which was not quite destroyed by the new pediplain. These hills are almost absent north of a line joining Tsumeb and Grootfontein, and east of Grootfontein. In the Tsumeb-Otavi-Grootfontein district the hills are always of dolomite.

The Otavi Mountainland or Highland, occupying a roughly triangular area defined by the towns of Tsumeb, Grootfontein and Otavi, is a dissected highland belonging to the same cycle of erosion as the isolated hills and representing the last coherent remnant of the old pre-African landscape. The dolomitic highland consists of interlocking, open, steep valleys and ridges, the highest of which are some 600m above the pediplain (i.e. about 2000m above sea level).

The Otavi Valley, near the southern edge of the Otavi Mountainland, is a conspicuous, open, synclinal valley running for 30km east from the town of Otavi to the Kombat mine and beyond.

Karstic features are developed both in the highland and where dolomite underlies the pediplain. Sinkholes, caves and springs are common. Examples are the large, deep sinkhole lakes at Guinas and Otjikoto, both near Tsumeb. Otjikoto Lake is some 220m in diameter and Guinas is a little larger. The Harasib cave, near Grootfontein, is at least 150m deep and contains one of the largest underground lakes in the world. Strong perennial springs occur at Otavifontein, Rietfontein, Olifantsfontein, Felsenquell and elsewhere. Springs are frequently associated with lithological contacts.

The network of surface drainage channels in the area is very poorly developed because drainage from the karst is almost entirely subterranean. There is virtually no surface runoff on a regional scale, not even from the highlands or from springs. Towards the north and east the old karstic surface of the dolomite becomes buried by the less permeable Kalahari beds and here some runoff occurs in times of flood.

The area is well triangulated and 1:250 000 and 1:50 000 topocadastral maps are available.

1.6 Pedology/74,220-1/

In general the soils of the region are typically semi-arid lithosols, being shallow, brown or reddish in colour, loose, sandy and poor in organic matter. Development of well-differentiated soil horizons is poor and layers of powdery, nodular or massive calcrete occur ubiquitously. Often there is virtually no soil layer and calcrete is exposed in decomposing sheets at the surface. At present the climate is not dry enough for the formation of shifting dunes, but occasional fossilized dunes are found banked up against the residual dolomite hills. Some variation in the type of soil occurs with changes in lithology:

A.. *Soils on dolomite*

The soils of the karstic area south and west of the main Kalahari beds are largely residual, but some old aeolian material is probably often included. The dolomite hills are generally bare or thinly covered with soil. The karstic valleys or pediplain areas are better covered but soil profiles more than 2m thick are uncommon (Plate 1). These soils are generally reddish, with varying amounts of calcrete and red clay derived from solution weathering of the carbonate bedrock. In most areas a "C" horizon of calcareous or siliceous rubble is a prominent feature of the soil profile.

B. *Soils on the Kalahari Formation*

These very poorly developed lithosols are derived principally from material transported to the present location in the geologically recent past. These soils are generally sandier and often less well-drained than those occurring on the dolomite. Calcrete is extremely common in the soil profile and is frequently more than 10m thick. In places the calcrete becomes so thick -over 100m in some boreholes- that it can hardly be regarded as a legitimate component of a soil profile. Towards the north and east, on the pediplain, vertical drainage through the calcrete may be poor and large, flat areas become waterlogged during a good rainy season.

These Kalahari soils scarcely constitute a favourable substrate for the identification of the secondary anomalies of any older orebodies that may be buried deeply beneath them. It is *prima facie* very unlikely that the detectable dispersion halo of such an orebody will yet have permeated through to the surface layers of these thick, young, transported materials. From the point of view of geochemical exploration this is a critically important issue, which will be elaborated in Chapter 2.

C. *Soils associated with other lithologies*

Sandy, calcreted soils tend to develop on the Archaen granite. Fairly deep, sandy or slightly clayey red soils commonly form on the readily weathered, arkosic Mulden quartzite (uppermost member of the Damara Supergroup- cf. page 5). Deep, calcrete-free pockets of this soil are quarried as fill material for the Tsumeb mine.

1.7 Hydrology and hydrogeochemisty/33,52,220/

The hydrology of the region has not been studied in great detail. Namibian hydrological data are often officially classified as restricted information and few pertinent articles (e.g. /204/) have found there way into the literature. The surface hydrology of the karstic area is simple. There is virtually no surface runoff, even in summer. The ephemeral highland streams seldom run and the shallow omirimbi (plural of omuramba, a river) of the pediplain are dry except in times of very good rains. Some surface flood runoff occurs from the pediplain areas of Kalahari beds to the north and east but none of it ever reaches the sea. North of Tsumeb the water proceeds via the Omuramba Ovambo into the Etosha Pan, where it evaporates. Runoff from the pediplain east of Grootfontein makes its way northwards along the Omurambo Omatako into the Okavango River and hence to the closed inland drainage basin of the Okavango Swamp in Botswana.

Very little is known of the groundwater hydrology. In the karstic areas penetration and recharge are rapid and there appears to be a general lateral movement of groundwater outwards from the Mountainland into the pediplain to the north and northeast. The detailed shape of the surface of the water table is not simple, however, and the depth below the surface varies greatly, from zero at the eyes of springs to 100m or more. Many boreholes are thus dry or yield poorly. Other groundwater sources, in contrast, yield prolifically., For example, Otjikoto Lake can deliver (and in times of flood rapidly absorb) millions of litres of water without serious changes in the elevation of the local water table.

During good rains the water table rises quite rapidly everywhere and many intermittent springs run for a few weeks. On the other hand, recharge of water sources deep in the Tsumeb mine does not occur until a few months after the rainy season. There are, of course, cones of depression (de-watering) /1161/ around each of the major mines in the region.

The water table in the Kalahari beds of the pediplain, to the north and east, is generally deeper (mean >35m) than in the dolomitic terranes. The waterlogged surface often seen in summer is probably caused by a perched water table, because rainwater cannot readily pass through the thick layers of calcrete. The waterlogging disappears in winter.

Predictably, the waters of the region are both fairly hard and fairly neutral in pH. The concentration of dissolved solids in typical groundwater is moderately high and tends to be higher in the Kalahari beds than in the dolomites. Much further north, towards the Etosha Pan, extremely saline groundwaters are encountered. On the other hand some quite dilute waters occur in the higher parts of the Otavi Mountainland.

In all formations the dominant aqueous ions are Ca^{++}, Mg^{++}, Na^{+}, bicarbonate, sulphate and chloride. Potassium and silicon are common minor components.

1.8 Human Activities/52/

A. *Mining and prospecting*

Mention has been made of the many prospects and four important mines in the district. Milling facilities exist at Berg Aukas, Kombat and Tsumeb. Tsumeb has a large smelter /1171/ and there is a zinc fuming kiln at Berg Aukas /189/. The area is connected by rail and good surfaced roads to the south and to the coast and so a very good infrastructure exists for further mineral exploration and mining. Although prospecting has continued since the previous century, the possibility of further discoveries is still very good. The established corporations have well-consolidated mining, exploration, analytical, engineering, production and allied facilities. The largest of these local companies is Tsumeb Corporation Limited (TCL), which owns the Tsumeb and Kombat mines.

Mineral rights are vested in the Administration of the Territory and not in the owner of the land. Prospectors (individuals or corporate bodies) may peg claims or apply to the Administration for exclusive right to prospect within large areas "Withdrawn from pegging" in their favour for up to six months in the first instance, or longer if an extension is granted. On application to the Administration, interesting prospects or future mines may be protected by more costly and semi-permanent Grants or Mining Areas.

B. *Other activities*

Most of the area described is natural bushland, divided into privately owned, fenced farms of a few thousand hectares each. The chief agricultural activity is the raising of beef cattle. Perhaps 1% of the land is tilled. Tsumeb is the largest town (population about 17 000). Grootfontein and Otavi are smaller (5 000 to 10 000 people), while Berg Aukas, Kombat and Abenab are small mining villages. There are no other villages. Human population density is thus low and adverse environmental impact is minimal.

Chapter II. A statement of the exploration problem and a consideration of the hydrogeochemical method as a solution thereof

The exploration problem and its geological causes have been alluded to in the foregoing. In this section the problem and a possible approach to its solution will be examined in detail.

2.1 The problem/30,32,51,70,221/(Maps 1&1a;and Map 4&Fig.3 in Vol. 2)

The Damara dolomites are both well-mineralized and well-exposed in the Otavi Mountainland /195-8/ and are amenable to conventional exploration methods /52/. It is logical to assume that the dolomites north and northeast of the Mountainland may also be mineralized, but they are obscured by a thick layer of Kalahari beds and calcrete. The problem is how to set about a regional exploration of this tract of blanketed rocks *practically* and *economically*. In the absence of other information it is logical to start searching for ore beneath the Kalahari cover as near to exposed, mineralized dolomite as possible. Thus the area of immediate interest is an arbitrarily defined block of Kalahari terrane, northeast of Tsumeb, which abuts on and swallows the exposed, northeast-trending Damara rocks. This region has priority for three reasons: (a) it is near the Tsumeb mine (b) it lies on the line of projection of the major Okorusu-Cape Cross lineament and other northeast-trending structural lineaments, which may have played a part in controlling the location of important mineralization in the Otavi Mountainland /52,67,233/ and (c) an aeromagnetic survey has indicated a magnetic lineament and interesting magnetic features up to about 25km northeast of the town of Tsumeb.

Arbitrary northward extrapolation of known outcrop indicates that a block of something like 500 000 hectares of Kalahari terrane may reasonably be expected to be underlain by subcropping dolomite, but the area is open-ended to the north and east, because the ultimate extent of the Damara beneath the overburden is unknown. This block, very roughly speaking, comprises the northeastern and northwestern corners, respectively, of the two 2^0 topocadastral maps "Tsumeb 1916" and "Grootfontein 1918", which are depicted at a small scale in Maps 1 and 1a and at the original 1:250 000 in some of the hydrogeochemical data maps in this work (e.g. Map 4a in Vol. II). The co-ordinates of this block are about $17\frac{1}{2}^0$ to 19^0 E and $18\frac{3}{4}^0$ to $19\frac{1}{4}^0$ S.

For practical reasons, geographical limits must be placed on any prospecting venture. The experiments in applied hydrogeochemistry that are described in this thesis were confined within this half a million hectares. Throughout this work, unless otherwise stated, it is implied that all observations and conclusions apply, *imprimis*, only to this block. Half a million hectares (5 000 km^2) is a very large area in which to prospect under conditions as difficult as those encountered here, but it is negligible when compared to the total extent of the Kalahari Formation in southern Africa. The experimental area provides a not untypical example of the adverse prospecting conditions prevailing throughout the Kalahari belt and the results arising from this project may well be of some use in attempting to apply hydrogeochemical exploration techniques elsewhere in this sandy terrane.

None of the conventional prospecting techniques can be effectively used for a *regional* reconnaissance of this great 50 by 100km block. These techniques and their limitations are summarized below. Those described as "too expensive" may be useful for the detailed investigation of small, previously selected target areas:

(a) *Remote sensing*: Outcrop is virtually nil, except on the flanks of the Otavi Mountainland in the southwest. Aerial photography and satellite (ERTS) imagery /1145/ show hardly anything useful, because burial is total. An ERTS mosaic (with orientation overlay, Fig. 3) of the area of interest will be found in the map portfolio and should be compared with Map 1a on page 4. The Otavi Mountainland is clearly seen in the lower--central portion of the composite. Lake Otjikoto shows up as a small orange dot three centimetres to the west of Tsumeb. The Omuramba Ovambo and the thick blanket of Kalahari materials are clearly seen towards the north, where outcrop of older formations is nil. Note that false colour imagery was used; the dry Etosha Pan appears blue and fields of green crops under irrigation appear to be orange.

(b) *Ground mapping*: There is no outcrop.

(c) *Pitting or drilling on grid, or "wildcatting"*: This is too expensive and, in the case of deep pitting, too dangerous and impractical.

(d) *Aeromagnetics*: The material of the Tsumeb pipe does not have a distinctive magnetic susceptibility or remnant contrast. Orientation studies in the Tsumeb area /30/ have suggested that favourable structural settings may be detectable by magnetics. However, the value of the method is unknown and at best doubtful because of the lack of basement control.

(e) *Ground magnetics*: This is heir to all of the abovementioned ailments and is expensive to boot.

(f) *Airborne electromagnetics*: INPUT and similar techniques would have to be flown at line spacings of about 250m and would therefore be very expensive. The thick overburden and brackish water are serious obstacles.

(g) *Electrical methods*: I. P. orientation at Harasib in the Otavi Mountainland, in 1972 /30/, showed that unexposed sulphide mineralization is not readily detected under even a thin cover of calcrete and sand. Unambiguous interpretation of I.P. data is not possible in the presence of local calcretes, which have variable electrical properties.

(h) *Special variations* of the above geophysical methods /30/ are either not practically available, not applicable, or not justified by the available data.

(i) *Gravity*: The original gravity expression of the heavily-mined Tsumeb body is not known. The Tsumeb West Pipe (a poorly-mineralized structure somewhat similar to the Tsumeb body) causes a small negative gravity anomaly but this is not detectable on traverse grids larger than 50 by 50 metres. This technique is extremely expensive for regional work.

(j) *Radiometrics*: The ores of the Otavi Mountainland are not known to be significantly more radioactive than the country rocks. Radiation is in any case readily suppressed by overburden.

(k) *Pedogeochemical methods*: The prospects for regional soil sampling are slim /31,52/, in view of the expected small size of targets, the thick, transported overburden and potential problems of severe suppression of dispersion by calcrete, which tends to be thickest at or near the present landsurface /74,230/. The absence of any known orientation sites is an additional, very serious difficulty. The practical pedogeochemical techniques available at the present time cannot reasonably be expected to cope with this exceedingly unfavourable and intractable combination of circumstances. Elsewhere in the Kalahari belt (Jijombo, Zambia) an orientation survey /238,1168/ of mineralization buried under about 14m of old, transported sand has shown that an anomaly can be detected near the surface by careful study of the very fine fractions of the sand or soil. In the Tsumeb area, however, the overburden can be more than thrice this thickness. We do not know the limiting maximum depth of overburden with which these special techniques can cope but under the prevailing circumstances there is a *prima facie* case for pessimism. An attempt to detect small, low--contrast anomalies with these techniques would require a sampling density that is totally impractical for regional work and even then the risk of failing to detect a strongly suppressed or deeply buried secondary aureole would be unconscionably high.

(l) *Geobotany and biogeochemistry*: The possibility of the application of these methods is viewed unfavourably by geobotanists who have experience of the area /32/. Cole (1971 /1167/, in her discussion of the application of these techniques in the Kalahari, stated that "the enormous tract of country, the presence within it of different vegetation formations and associations, and the extent and nature of the surficial cover presented problems not encountered (elsewhere). Moreover, there were no known deposits over which to focus initial geobotanical work". The geobotanical method enjoyed some success only in special areas (e.g. at

Witvlei) where "bedrock lies relatively near surface" and "calcrete and Kalahari sand are less extensive than elsewhere".

(m) *Stream sediment geochemistry*: There is virtually no surface drainage system that might be sampled and in any case samples from the shallow omirimbi would be subject to the same limitations that apply to the regional soil sampling surveys discussed above.

(n) *Mercury vapour detection*: Mercury "sniffing" techniques are very unlikely to be of use because local studies /52/ have shown that the metal is relatively immobile (less mobile that copper or zinc) under local conditions.

(o) *Termitaria*: In some areas termite heaps include material that has been brought up from considerable depths and a few publications (e.g. /1194/) refer to the use of termitaria as a sampling medium in sandy terranes. Watson /1195/, in particular, demonstrated that a gold anomaly buried under Kalahari sand was reflected by the chemcial composition of the termite heaps directly above it. Joubert and his colleagues tried to apply this technique near Berg Aukas in the early 1970's /231/, but met with no success. They postulated that the local termites were not given to digging deep tunnels.

The writer worked for a year as exploration geochemist for TCL and found, as many others had done, that the problems caused by the Kalahari overburden were of more than academic interest. No practical prospecting tool existed with which to tackle the refractory areas to the north and northeast of the main Mountainland. It was known that other prospecting groups had run into similar problems in Namibia and elsewhere is southern Africa but, as far as could be ascertained, no effective solution had been found.

Some years previously the possibility of borehole hydrogeochemical prospecting had been mooted within the Geological and Analytical Departments of TCL. It was realized that the immediate advantages of this method are:

(a) a sample from relatively great depth is obtained rapidly and cheaply

(b) because water is highly mobile and reactive, the chemical composition of the sample tends to approach an equilibrium that reflects the average composition of the rock with which the water is in contact, or through which it had recently passed.

In 1968 J.A. Coope had written a memorandum on the subject /223/, but without reference to any specific region of potential application. Because of the daunting problems involved in such an undertaking, no action was taken at the time. During 1971 H.A.R. Meiring and the writer, in collaboration with Dr. Coope and later A.D. Buerger, resumed the investigation of the feasibility of such an undertaking /224-6/. By the latter part of 1971 we were convinced that the practical problems of sampling, analysis and interpretation could be overcome, and that groundwater geochemical prospecting was the best (and probably the only) potential regional exploration tool for the selection, in the Kalahari areas, of targets for detailed work. Samples would be obtained principally from deep boreholes.

In 1972 the Geological Survey-University of Cape Town Geochemical Exploration Research Unit and TCL adopted this study as a joint research project. The portion of the project described in this thesis spanned the period 1972 to about September 1975.

2.2 A description of the kind of mineralization sought and its probable location

The relevant geology has been depicted in Maps 1 and 1a (pp. 3-4) and in Map 4 in volume two. The only lithological units of real interest in terms of potential mineralization are the calcareous members of the Damara Supergroup. The known important mineral occurrences within the Damara are shown. They are generally sulphide bodies containing one or more of the metals Cu, Pb, Zn and V in quantity and sometimes lesser amounts of Cd, Ag, Ge and As. These bodies may be well oxidized if they occur at or near the surface. The age of the ore (at least at Tsumeb) is almost certainly pre-Karoo (Triassic) because in the Tsumeb mine it is cut by a kersantite dyke that is probably of this age /52/. The origin of the orebodies and the reasons for their geographical situations has for a long time been, and remains, the subject of much inquiry and debate (e.g. /45,52,65-7,233/). An example of this is the question of whether the vanadium concentrated in the Abenab and Berg Aukas ores, and elsewhere, is syngenetic (i.e. was present in the dolomites during sedimentation) or whether it was leached downwards from the Karoo basalts that once overlaid the area /1165/. However, for the present purposes it is not necessary to examine such questions of provenance etc. for each mineral occurrence. From the point of view of hydrogeochemical exploration it will suffice to examine the probable genesis of only the two major orebodies at Tsumeb and Kombat; all the others may then be attributed to similar or secondary processes of metal accumulation.

The ores at Tsumeb and Kombat are associated with dolomite breccias and a unique quartz/feldspar rock called pseudo-aplite, which resembles the Mulden quartzite. Mineralized pseudo-aplite is known elsewhere in the area, but is not universally present where ore is found. For example, it is not seen in the Berg Aukas body. There are at present three main theories of genesis:

(1) The pseudo-aplite is an intrusive igneous rock or hydrothermal precipitate and the orebody is a simple, epigenetic, hydrothermal feature. This old theory is seriously challenged nowadays.

(2) The Tsumeb pipe, and perhaps the Kombat body, represent ancient, deep, karstic caverns, which were partly filled with unconsolidated Mulden arenite and dolomitic rubble. The ore was deposited from mineralizing solutions that were either hydrothermal or else derived from leaching of the country rock (lateral secretion mechanism).

(3) The Tsumeb pipe, and perhaps the Kombat body, are the result of diapiric intrusion, through the dolomite, of originally stratiform bodies of arkosic material that now constitutes the pseudo-aplite. The ore may be syngenetic, or derived from the country rock or from hydrothermal sources.

Additional information about the ore will be given in a subsequent section dealing with the waters of the Tsumeb mine. It is sufficient at this stage to know that similar mineralized bodies may be expected to lie beneath parts of the Kalahari terrane to the north of the exposed dolomites of the Mountainland. These bodies will probably be well-oxidized in part if they occur at or near the pre-Kalahari topographic surface, because geological logs /33/ from a few randomly distributed boreholes to the north of Tsumeb show that the pre-Kalahari surface is well weathered and has karstic fissures and caves that are filled with Kalahari materials.

2.3 Hydrogeochemistry as a possible answer: A pre-orientation synthesis of available information

No previous study in the area has been directly concerned with hydrogeochemical prospecting. There are indeed no know southern African precedents to which one might turn. Sellschop and Verhagen /1062/, in their summary of the work that has been done on subterranean waters in the Kalahari areas, record no examples that are in any way related to mineral exploration. On the contrary, they (and others, e.g. /1153/) show that the work on groundwaters in the Kalahari regions has been largely hydrological and aimed at expanding resources of potable water. Nevertheless, there is a substantial volume of published work - mainly geological and some hydrological and chemical information - that provides an extensive if rather general background to this study. Some of this information has already been summarized in the foregoing pages. There are many useful papers on the geology of the area (e.g. 42,65-75,189,193-202,205,220-2,227,234-5/) but most of the available data remains unpublished. TCL records /52/ provide a great wealth of reports, surface and underground maps, aerial photographs and related materials. There is also limited hydrological and meteorological information, mainly for the vicinity of the town of Tsumeb. The analytical and geochemical departments of TCL provided chemical analyses of some local waters, as well as a great deal of information about the composition of the ores, rocks and soils of the region. (The TCL geochemical laboratory had, by 1975, produced an estimated two million analyses of soils alone. Only a few hundred results have been published /189/).

Various Government agencies (Department of Water Affairs, C.S.I.R., Geological Survey, Weather Bureau /33/) have accumulated limited additional geological, hydrological, meteorological, chemical and radiometric information in this region. Very little of this is directly relevant to this hydrogeochemical study and, because much of it is regarded as restricted information, reference to official data will be made only where it is possible to do so.

In studying the picture provided by this existing data, several important points emerged. These can be conveniently examined under a few distinct headings:

(A) *The nature of the Kalahari terrane and the problem of orientation*

It is rather important that there is no known mineralization in the Kalahari terrane that can serve as a target for conventional orientation studies (Fig. 2.3). All known mineralization is in solid dolomite with practically no overburden. Almost all of the boreholes that tap water from within the sphere of influence of these orebodies are, as a result, drilled in solid dolomite free of all but a superficial regolithic layer. Thus the waters that any orientation survey may characterize as anomalous or otherwise will all be contained in a dolomitic matrix. In contrast, the available boreholes in the Kalahari terrane almost always penetrate considerable thicknesses of calcrete and gravelly, arenaceous materials quite unlike dolomite - in fact, few of these holes reach down as far as the sub-Kalahari bedrock surface. This is a serious shortcoming, because one cannot hope to sample "dolomitic" water from beneath the buried areas. The problem is thus twofold: (a) The waters of the Kalahari beds differ chemically from the waters of the dolomitic formations and have a relatively high content of salts /52/ and (b) There is no proof that appreciable secondary hydrogeochemical dispersion from the Damara rocks into the lower Kalahari beds has occurred. Nevertheless, these Kalahari waters are the only deep samples that

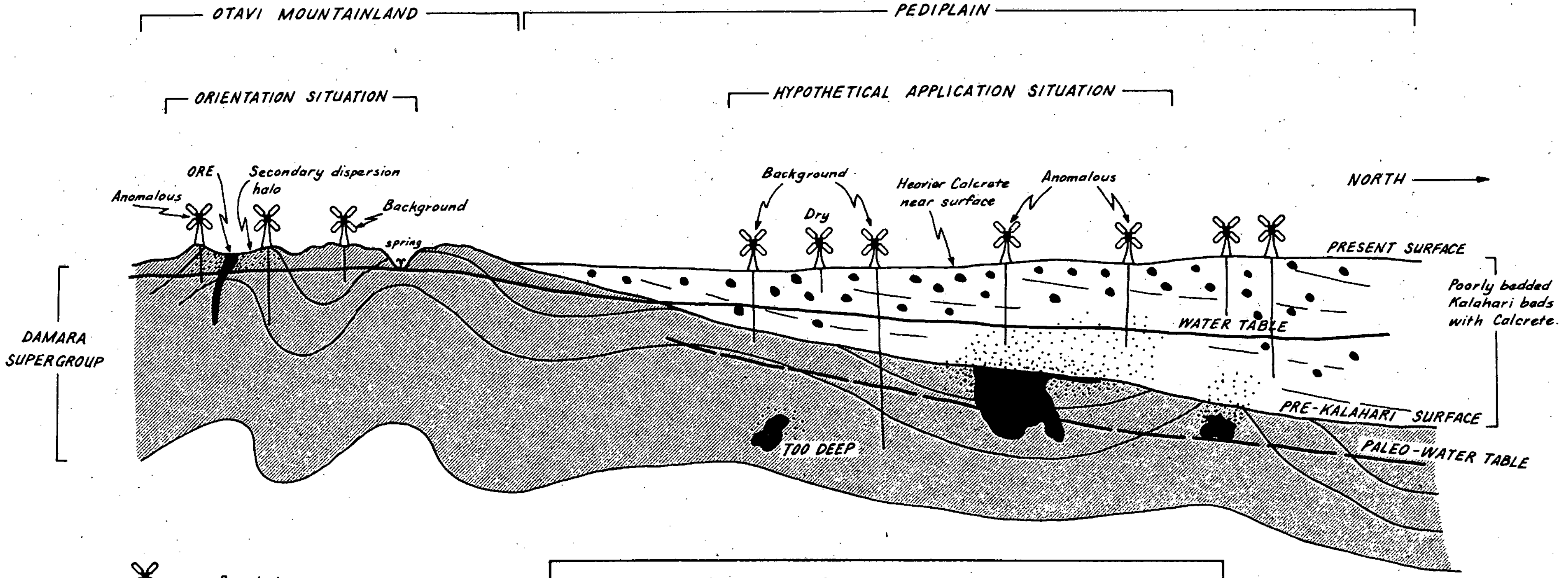


Fig 2.3

Sketch showing the relationship between the Hydrogeochemical Orientation Situation & a Hypothetical Application Situation can be collected practically. The project therefore rests on two assumptions: (i) that upward secondary migration of indicator elements, from weathered ore into the Kalahari beds, has occurred and (ii) that the influence of this secondary dispersion will still be recognizable in waters sampled from a borehole tapping only the new lithological and hydrochemical environment.

A limited number of logged water boreholes occur within the area of interest /33,52/ and they indicate that the Kalahari beds here are quite typical of the Formation as it occurs over wide areas of southern Africa /229/. Loose aeolian sand, sandstone, calcarous sandstone and calcrete are ubiquitous. Also occasionally mentioned (verbatim) in these logs are dolocrete, silty calcrete, silcrete, calcareous gritty clays, calcareous red clays, red clay, grey clay, sandy marl, calcareous silt, thin shale, arenaceous shale, silty sand, arkosic sandstone, grits, quartz grits, fine-, medium- and coarse gravel, sandy gravel with shale fragments, thin ferricreted gravels, thin layers of dolomitic pebbles and chips, quartz pebble conglomerate, scattered pebbles and rubbly calcareous conglomerate. This sort of material can be expected to be quite permeable and thus encourage significant local migration of many trace elements.

Calcrete, on the other hand, is known to be capable of strongly suppressing such dispersion under many conditions /52,855/. The mechanism of this suppression is not fully understood /232/, but carbonates have a ready ability to neutralize acidic solutions and to absorb many trace elements. An encouraging factor in the present case is that the limited data from borehole logs suggest that the heaviest calcrete is generally near the present land surface and that many boreholes penetrate through this zone to regions of lighter calcrete cementation. This phenomenon is quite typical of the Kalahari Formation elsewhere /230/.

It would be highly desirable to know more about these specific Kalahari beds and especially about the calcrete within them, but this is a difficult task /1166/. Netterberg /74-6/ has written extensively about southern African calcretes but his observations in and around the Otavi Mountainland were few and confined to surficial calcrete profiles, not deeper than about 5 metres. Since almost nothing further is known about the distribution, genesis and nature of the calcrete within these particular Kalahari beds, only very limited conclusions can be drawn from an examination of Netterberg's comprehensive comments on calcretes in general. Nevertheless this is interesting and instructive and the main points that he makes, or which can reasonably be deduced from his work, are as follows:

(1) Calcrete can be classed as pedogenic (carbonate leached from the A into the B horizon) or non-pedogenic (carbonate leached upwards by evapotranspiration from a shallow water table). Clearly, for prospecting

purposes, non-pedogenic calcretes are potentially more useful, since they are more likely to be accompanied by upward secondary dispersion.

(2) The hardpan calcretes at the present-day surface in the Grootfontein-Etosha Pan area (Fig. 3, vol. II) are non-pedogenic. This conclusion need not necessarily apply to the deeper calcretes in this region.

(3) The region between the Otavi Mountainland and the Kunene river (Angolan border) has probably had, since Late Cretaceous times, a complex history of erosion, sedimentation, cyclic climatic changes and fluctuations of the water table, with accompanying periods of formation, dissolution and reformation of calcrete. Calcretes of several ages are probably represented at various stratigraphic levels. Thus the calcrete layers encountered in deep boreholes may be pedogenic, non-pedogenic or, conceivably, not even calcrete at all but consolidated, transported calcareous sandstone. Without additional information one can only speculate as to whether pedogenic or non-pedogenic processes predominated. In an aggrading profile, such as the accumulating Kalahari beds, successive layers of pedogenic calcrete may be formed. On the other hand, if the water table in a thick succession of calcareous sediments drops slowly, a very great thickness of non-pedogenic calcretes may accumulate slowly down the profile.

(4) The exact age of the older surface calcretes here (the so-called Kalahari Limestone) is uncertain but is probably early to middle Pliocene. This calcrete may have formed as the Etosha Pan shrank westwards because its water supply was removed by river capture elsewhere. Younger calcretes are certainly present at surface, while some of the deeper calcrete may, on the other hand, be pre-Pliocene.

(5) Much of the Kalahari Limestone (*sensu stricto*) is a fossil calcrete reflecting local rainfall conditions of Pliocene times. (The main control over the formation of calcrete is climate, and calcrete forms most rapidly during waning pluvials).

This information, although valuable, unfortunately does not save us from having to make the optimistic assumption that the calcrete within the lower Kalahari beds has not generally and severely retarded local, hydrogeochemical dispersion from the underlying Damara formations. But it does suggest that such an assumption is not unwarranted, for the following two reasons:

(a) The deeper Kalahari beds and associated calcretes may be five million years old or more. This long time span favours the likelihood that significant dispersion has occurred despite the presence of the calcrete.

(b) The complex history of climatic changes and variations in the elevation of the water table increases the probability that at least some of the deep calcrete is non-pedogenic and has assisted some local dispersion.

It must be borne in mind that in certain parts of the area of interest the geological succession may be more complex than the simple combination of Damara and Kalahari rocks described above. Extrapolation of known lithological contacts (Map 1a, and Map 4, vol. II) suggests that the Kalahari may be lying directly on the Abbabis Granite in the southern portion of the pediplain, where it abuts against the Mountainland east and northeast of Grootfontein. There may be additional, isolated areas further to the north where pre-Kalahari erosion has stripped away the Damara rocks and brought the granite into direct contact with the youngest formations. The granite is not thought to be mineralized but it may have a characteristic local influence on the background hydrochemical composition of adjacent groundwaters. There is also the more serious possibility that in places a layer of Kaoko basalt may be interposed between the Damara and Kalahari rocks. Such a stratum will not only decisively suppress secondary upward migration from any ore that may be beneath it, but it is likely to leave its own characteristic chemical "fingerprint" on adjacent waters. This phenomenon of "fingerprinting" - the generation of waters of characteristic composition in the vicinity of certain specific lithological units - is of course very well known (see, for example Brooks /1179/) and unless it is recognized it can cause a great deal of confusion in hydrogeochemical surveys. Additional variations in the chemistry of local groundwaters may be caused by major differences in lithology within the Kalahari succession, or even by the influence of non-calcareous units within the Damara group (e.g. the Nosib formation).

It is impossible to predict the precise nature of the changes that may occur in the background composition of local groundwaters as a result of major changes in lithology. However, this could conceivably result in either the masking of real anomalies or the generation of spurious ones, and both of these possibilities will have to be carefully considered during interpretation of the data.

(B) *Orientation "by proxy" in the dolomitic areas*

At the start of this project it was apparent, for reasons already discussed, that some sort of "orientation by proxy" would have to take the place of a conventional orientation in the Kalahari areas. The obvious place for this was around the orebodies within the Otavi Mountainland.

The dolomite, like the calcrete, is relatively reactive and tends to retard the secondary dispersion of many trace elements, especially those mobilized at low pH. In both terranes there would be a great advantage in identifying a very mobile pathfinder element. Thus it may be apprehended that the highly mobile ions such as sulphate may be of particular importance in this sort of situation.

Because of the reactivity of carbonates, the anomalous aqueous concentrations of the metals that might be sought will generally be very small in absolute terms- probably of the order of a few micrograms per litre. This poses certain sampling and analytical problems but with care these can be overcome. An examination of the available water analyses from this region showed the following:

(a) The waters are always very hard. Calcium and magnesium habitually dominate as cations and bicarbonate as the anion. Carbonate ion is extremely rare, because the carbonic system tends to buffer the pH within the range 6,5 to 7,8. Variable amounts of sodium, potassium (Na almost always much more abundant than K), sulphate and chloride are present. These seven ions, almost without exception, constitute more than 95% of the total dissolved solids, which commonly amount to between 400 and 800 mg/l. Other reported non-metallic, minor or trace components are silicon, nitrate, nitrite, fluoride, ammonia and phosphate. The last four of these are frequently absent or present in amounts less than 1mg/l, although there are occassional nitrate-rich waters. All of this is very typical of groundwaters in dolomites /228/.

(b) Sump water pumped from the Tsumeb mine for the town water supply has a high content of sulphate (about 450 mg/l), suggesting that this ion may be a useful indicator species derived from the oxidation of sulphides.

(c) Practically nothing was known about the trace metal content of local groundwaters or of the mine water. A few available assays suggested that background values for Cu,Pb,As,Mn,Cr and Fe were likely to be well below 1mg/l. The mine sump water contains appreciable amounts of certain metals, for example copper and lead but almost all of it is in suspension rather than in solution, and is effectively removed by flocculation.

(C) *The problem of hydrological control and its consequences*

Little is known about the hydrology of either the dolomitic or Kalahari terranes and there was neither the wherewithal nor the time to rectify this shortcoming by undertaking an intensive hydrological study. Care must obviously be exercised in defining hydrochemical anomalies in the karstic mountainland. Werner /146/ stated that the hydrology of karstic terranes is often unpredictable: "...telling which way is downstream is not always easy, as demonstrated by reports showing the relation (or non--relation) of surface and subsurface drainage basins. As pointed out in several...reports, karst ground water flows often pass through ridges that form surface drainage divides. Problems of this nature...give...serious headaches...". Fortunately this problem is not likely to be serious in the pediplain, which is extremely flat and therefore hydrologically uncomplicated. Despite this advantage, we have very little understanding of the detailed picture of the flow regime in the Kalahari terrane adjacent to the Mountainland, and under these circumstances it is probably not possible to do more than identify broad, *regional* anomalies with the hydrogeochemical technique -i.e., to select anomalous sub-areas of manageable size within the vast tract of the pediplain. It should then be possible to select potential targets within these regional anomalies by application of detailed hydrogeochemistry, hydrology and geophysics, together with geological and geochemical investigations of selected drill holes.

SECTION 2. ORIENTATION STUDY OF THE HYDROGEOCHEMISTRY OF THE TSUMEB MINE

Chapter 3. Experimental

3.1 Introduction

In Section I it was shown that some sort of "orientation by proxy" would be required before an attempt could be made to apply regional hydrogeochemical exploration methods in the area of the northern pediplain. The next logical step, therefore, was a detailed study of the relationship between a typical orebody and its associated groundwaters, and the obvious place to begin this study was at the Tsumeb mine. The literature contains many examples of experiments of this nature. Suetin (1965 /1150/), for example, stated that " a comparison of results of spectral analyses of rocks....and mine waters resulted in outlining the set of element associations....which can be used in the field for hydrogeochemical prospecting....".

It was anticipated that a study of the waters of the Tsumeb mine would shed light on the following questions:

(a) What is the general major and trace element composition of the waters?

(b) Can one distinguish between waters associated with the country rock and those associated with ore? If so, are the latter waters recognizably and consistently anomalous and by what criteria? Are there any specific indicator elements or ions?

(c) To what extent can the details of the composition of the water be related to the detailed composition of the rock or ore?

(d) Under what circumstances and in what quantities are various elements released into the water, especially from the ore? What controls the residence time of the dissolved ions, their mobility and ultimate fate?

(e) To what extent are the above findings, based on the study of mine water, relevant and useful to a prospecting program utilizing groundwater drawn from surface boreholes in the Kalahari areas?

The data required for the study were obtained by collecting and analysing a suite of thirty six water samples from the mine workings. The following observations, measurements and analyses were recorded: geological setting, hydrological characteristics, rate of flow of water, air temperature, water temperature, pH, colour and concentration of total suspended solids (TSS), total dissolved solids (TDS) and the concentrations of Mg, Ca, OH^-, $CO_3^=$, HCO_3^-, Cl^-, F^-, $SO_4^=$, PO_4^{3-}, Na, K, Li, Rb, Cs, Sr, Cu, Ag, Au, Zn, Cd, Hg, V, Cr, Mo, Mn, Fe, Co, Ni, Al, Tl, Si, Ge, As, Sb, Bi, Se, Te and Pb. This is not an arbitrary list of parameters;

the basis on which they were selected is discussed in Appendix F.

A description of the Tsumeb orebody and the workings of the mine is given in Appendix E.

3.2 Selection and locations of sampling sites

The following scheme was adopted for sampling the waters of the mine:

(a) The writer went underground and noted all possible points for collecting samples of water. There were about a hundred but many were not suitable for various reasons, such as duplication, very slow rate of flow, awkward or dangerous situation, contamination etc. If a sampling point was a borehole its orientation was noted.

(b) The location and situation of these potential sampling points were examined with the aid of available diagrams (geological sections, level plans etc; examples are shown in Map 3 and Fig. 1). The location of the points with respect to the orebody, the mine workings and the major geological features was noted. The logs of identified aquiferous boreholes were scrutinized and the stereo-orientation of the hole in space was established.

(c) On the basis of this information the writer decided that a pilot study, at a sample density of about one per mine level, would give sufficient initial coverage of the mine. There are about 44 accessible levels but many, especially at shallower depths, are dry and eventually a total of thirty six representative samples was selected. It was anticipated that this would provide water samples derived from or characteristic of the following: (i) most levels of the mine (ii) all major structural and lithological features of the orebody and the surrounding country rocks (iii) all major features of the workings, such as the stopes, haulages and crosscuts (iv) all types of sampling point, such as boreholes, oreboxes and seepages (Plates 3 to 5) (v) fast flowing and slow flowing sources (vi) a selection of underground boreholes directed towards the orebody as well as some directed away from the ore and out into the country rock (vii) horizontal as well as positively and negatively inclined boreholes. The last kind are artesian.

This selection was limited by several factors: (1) The upper levels are dry. At deeper levels cementation severely restricts the flow of water into the mine at many places. (2) The ore is relatively impervious. Very little water flows in the stopes. (3) The northern side of the orebody is much wetter than the southern side, probably because the regional dip is to the south. (4) Very few drips or seepages that come directly from fissures in the rock are suitable as sampling points. A steady, coherent and relocatable flow is needed and in general seepages do not meet these requirements. (5) Some parts of the mine are dangerous or not readily accessible.

Nevertheless, the representation of (i) to (vii) above was fairly satisfactory.

(d) The 36 sampling points were numbered from 131 to 166 and tagged with galvanized iron plates with the sample number stamped into them (Plate 5). (These tags disintegrated within months;plastic tags should be used in preference).

(e) The writer originally planned to sample these flows in winter and then six months later in order to investigate seasonal fluctuations in the composition of the water. (Fix /541/, *inter alia*, has described the phenomenon of seasonal dilution of the dissolved content of waters seeping into mines). The results of the first sampling (June 1973), which are described in this section of the text, led the writer to abandon any further work with the mine waters and to proceed instead with the orientation survey of waters from surface boreholes (Section 3).

The locations and important characteristics of the 36 underground sampling points are given in Appendix A and Fig. 1A.

3.3 The collection of the samples and measurements *in situ* in the mine

The procedures for contamination-free sampling of waters and for stabilizing the samples prior to analysis are well documented /28, 45, 125, 158-62, 165, 209-12, 1001-4, 1158, 1160/ and were observed in all essential detail at all stages of sample handling. Most samples from the mine were collected in high density (linear) polyethylene bottles, of one litre capacity, and fitted with all-plastic, unlined, press-fit polyethylene closures. These containers were thoroughly tested (see Appendix J part J2) and found to be non-contaminating. Before being used the bottles were cleaned by soaking them in dilute nitric acid (1 conc. HNO_3: 4 water) for at least 3 days. Only special samples intended for mercury analysis were collected in Pyrex glass, previously rinsed with stannous chloride solution and soaked overnight in dilute perchloric acid (1 $HClO_4$: 1 water).

At each sampling point details such as location, orientation, nature of the sample source and any other relevant observations were noted where applicable. A numbered metal tag was attached nearby. Then, consecutively and as rapidly as possible, the *in situ* measurements were made and the sample containers filled. The following measurements were recorded at the sampling point:

(1) Air temperature (Hg thermometer)
(2) Water temperature, within the flow (Hg thermometer)
(3) pH, within the flow where possible (Pye Unicam 293 meter with Philips Call electrode)
(4) Rate of flow from the sampling point (Graduated 20 litre bucket and stopwatch

Additional information about these measurements is provided in Appendix B.

The sample container and its lid were thoroughly rinsed in the flow and then the bottle was filled by placing it directly in the running stream. Care was taken not to touch the lip of the bottle against any object or to dislodge any adjacent solid material that could have fallen into the running water. Two plastic containers were filled completely (to exclude all air) and marked for major component and wet chemical analysis. Six containers were filled to the three-quarter mark and set aside for preservation by freezing and subsequent analysis for many trace elements. The air space left in these was to allow for expansion upon freezing. A special sample for mercury was collected by running 90 ml of water directly into a 100 ml Pyrex volumetric flask already containing 10 ml of concentrated A.R. perchloric acid. The flask was immediately closed with a plastic stopper and shaken. Investigation /1-5, 7, 161, 1043/ has shown that this pre-acidification is essential in preventing a rapid loss of mercury from the sample by adsorption or volatilization. Work by the TCL Analytical Department /52/ had shown that perchloric acid was a suitable stabilizing agent.

In Appendix E mention is made of some of the practical difficulties encountered in moving between sampling points on different levels of the mine. Experience showed that the collection of six samples on three or four different levels took about six hours. Most of this time was spent moving the samples to and from the shaft stations and waiting for the cage. It proved most convenient to "sink" at De Wet shaft at midnight and to surface at about 6 a.m. when the shift changed and cages were available to travel to the bank. By 6.30 a.m. the trace element samples were in the freezer and the determination of the major components, etc. had commenced in the TCL laboratories. Since all orientation samples were personally collected and analyzed by the writer, it was not practical to process more than six samples per day. The samples were randomized as far as was possible under these somewhat difficult circumstances (see Table 3.4B, last column). A report on the transportation, storage and utilization of the samples is given in Appendix G.

3.4 Summarized analytical information and results

(A) *Introduction*

A summary is given here of the analytical procedures, important analytical parameters and results. Throughout the analytical work the emphasis has been more on precision than on absolute accuracy, since it is obviously more important to compare one sample of mine water with another rather than with some external standard. The reader will appreciate that, in a project of this kind, an attempt to establish closely the relative accuracies of analytical methods for some thirty elements - many of them present at sub-mg/l levels - would be both Herculean and ludicrous. Nevertheless, all the methods used were based on well-accepted analytical procedures and there is no *prima facie* reason to believe that the values reported here are not reasonable approximations of the real concentrations of elements in these samples.

All additional analytical information and related comments about interferences, reliability etc. will be found in Appendix B.

The analytical results for the thirty six samples of mine water are listed in the following tables in eight subdivisions:

Table 3.4B Measurements made *in situ*
3.4C Hardnesses; suspended and dissolved solids
3.4D Anions
3.4E Elements of Groups IA and IIA of the periodic table
3.4F Elements of groups IIIB to VII of the period table
3.4G Elements of groups IB and IIB of the periodic table
3.4H Elements of groups IIIA to VIA of the periodic table
3.4I Examination of TSS residues by XRFS

(Note that the nomenclature used for the groups of the Periodic Table varies (1199-1200/. The classification used throughout this thesis is that of the Periodic Table inserted on the inside of the front cover of this volume /1201/).

Each subsection of Table 3.4 comprises results, notes and summarized technical data. In order to obtain the fullest appreciation of this information the reader should also consult the relevant subsections of Appendix B, and especially B3.9 and notes 10 and 11 in B2.

(B) *Measurements made in situ (Table 3.4B)*

(i) Estimated maximum errors of measurement:

(a) Rate of flow: ± 10%
(b) Temperatures: ± $0,3^0$ C
(c) pH: ± 0,05 units

(C) *Hardnesses; suspended and dissolved solids (Table 3.4C)*

(i) General

TSS is total suspended solids, of diameter greater that 0, 45 µm
TDS is total dissolved solids, dried at 110^0 C

The colour of the suspended solids was observed on the millipore disc while wet. The colour reported in subjective, as no comparative colour chart was available. A dash indicates that the disc was colourless (white).

Hardnesses are given as $[Mg^{++}]$ and $[Ca^{++}]$. These two species account for at least 95% of the total hardness, so that the hardness values for these two cations can be taken as a close approximation of the real concentrations of dissolved calcium and magnesium.

(ii) Estimated errors of determination

(a) TSS: +0,0008 g and -0,0004 g
(b) TDS: This measurement is subject to several errors (see Appendix B). The maximum weighing error due to fluctuating mass of the nickel dish is about 0,004 g. The various samples could not all be dried for the same length of time and may have lost different amounts of water of crystalization etc. The dried TDS residues are extremely hygroscopic and may pick up several milligrams of moisture from the atmosphere within a minute or two of being removed from the oven. The amount absorbed depends on the humidity. The total uncertainty is probably about 0,010 g.

PRECISION TABLE (95% confidence)

	5%	20%	50%	dl	
TDS	-	2,0	0,4	-	g/l
Mg	48	-	-	-	mg/l
Ca	80	-	-	-	mg/l

(The use of the precision table may be explained by the following example: At values of TDS around 2,0 g/l, about 95 out of one hundred analyses of

TABLE 3.4B

Measurements made *in situ*

sample number	source	Flow (l/min.)	Air T. (°C)	Water T. (°C)	pH	mine level[1]
131	B	7,5	29,0	29,5	6,88	34
132	B	6,0	29,0	29,5	6,92	34
133	B	83,1	29,0	35,3	6,75	34
134	B	2,4	28,5	29,0	6,92	35
135	B	127,1	28,5	34,5	6,84	35
136	B	29,7	34,0	37,0	6,90	37
137	B	24,9	28,5	34,0	6,80	27
138	B	37,7	24,0	34,0	6,80	28
139	D	5[2]	28,0	32,5[3]	6,60[3]	30
140	B	4,3	27,0	29	6,4	28
141	B	13,5	27,0	33,2	6,9	27
142	B	264,0	31,0	34,0	6,4	30
143	B	5,6	22,4	26,4	6,65	22
144	B	1,8	30	34	6,6[4]	42
145	0	22,4	24,0	29,8	6,65	24
146	B	78,2	26,0	33,0	6,7	26
147	B	3,6	29,3	28,4	7,0	24
148	B	18[2]	26,3	31,6	7,1	26
149	B	4,8	29,9	37,7	6,45	44
150	B	- [5]	28,0	33,0	7,5	38
151	B	1,3	29	34	6,65	41
152	B	1,8	26,8	37,8	6,7	45
153	B	38,6	27,8	39,8	6,65	44
154	0	20,8	23,9	20,7	7,2	10
155	0	8,9	25,0	30,1	7,4	16
156	B	12,0	25,8	29	6,75	32
157	B	11,1	22,0	28,8	6,90	31
158	B	1,5	27,0	31,8	7,15	31
159	B	108,0	21,8	31,2	6,9	32
160	0	5,0	24,5	30	8,2	20
161	W	33,3	23,5	24,2	7,22	12
162	B	1,2	25,5	26,0	8,3	16
163	F	1[2]	19	19	8,3[4]	6
164	B	90,0	25,5	35,1	6,8	35
165	B	1,8	29,2	27,9	6,93	33
166	B	2,7	23,9	26,0	7,08	33

(1) Mine levels are about 30 m apart. (2) Visual estimate; situation too awkward to allow measurement of rate of flow. (3) Measured in dam; mean of two readings at either end: Temp. = 32,0 and 33,0 degrees, pH = 6,60 and 6,60. (4) Measured in a bucket; situation was too awkward to permit a direct reading. (5) The rate of flow was extreme - too high to measure with a bucket.

The following symbols are used for the types of source: B = borehole; D = dam; 0 = orebox; F = fissure; W = walled-up drive

TABLE 3.4C

Hardnesses; suspended and dissolved solids

Sample number	Colour of TSS	TSS g/l	TDS g/l	Mg mg/l	Ca mg/l
131	grey	0,0004	1,30	99	138
132	pale yellow	0,0010	1,70	86	162
133	-	0,0000	1,15	76	124
134	dark brown	0,0536	1,40	91	130
135	grey	0,0064	1,20	82	137
136	grey and brown	0,0034	1,45	96	142
137	-	0,0008	2,02	115	189
138	-	0,0002	1,44	95	154
139	-	0,0002	0,88	72	116
140	pale yellow	0,0010	1,56	114	153
141	-	0,0000	1,56	89	158
142	-	0,0004	1,64	91	158
143	grey	0,0008	1,68	88	179
144	very pale yellow	0,0000	0,90	80	123
145	-	0,0004	1,30	94	142
146	-	0,0002	1,88	94	177
147	-	0,0000	1,22	88	137
148	pale yellow	0,0008	2,04	115	186
149	very pale yellow	0,0006	0,56	65	102
150	pale yellow	0,0008	1,22	92	141
151	brown	0,0006	0,96	84	126
152	-	0,0000	0,60	65	104
153	pale yellow	0,0000	0,52	61	102
154	pale yellow grey	0,0014	0,94	102	155
155	pale grey	0,0010	1,86	147	263
156	-	0,0000	1,26	90	149
157	very pale yellow	0,0000	1,88	107	194
158	-	0,0006	1,84	97	185
159	-	0,0004	1,44	95	164
160	-	0,0002	1,40	156	144
161	-	0.0000	1,10	115	136
162	-	0,0000	0,52	70	107
163	-	0,0000	1,06	73	92
164	-	0,0000	1,18	74	122
165	grey	0,0002	1,72	99	146
166	very pale yellow	0,0002	1,34	98	167

the same sample will lie within 20% of the mean of the analyses. See Appendix B2, notes 10 and 11 for details).

(D) *Anions (Table 3.4D)*

(i) General

The values for hydroxide, carbonate and bicarbonate are calculated from equations given in Appendix B. Where P alkalinity is zero (as is the case in 35 out of the 36 samples) the concentrations of free hydroxide and carbonate ions are negligible and all carbonic components are present as bicarbonate (see also Appendix I).

(ii) Estimated errors of determination

There is no titration error in the determination of a zero P value. The Tsumeb mine waters (TMW) are not complex and probably obey theoretical carbonate equilibria closely. Therefore the hydroxide and carbonate ions are effectively absent in all samples except number 145. This sample had a relatively low M alkalinity and its pH was 6,65, which suggests that the P value determined was not real but was caused by some unidentified interference.

(a) Bicarbonate: A titration error of 0,1 ml corresponds to an error of 6 mg/l. This error is negligible compared to a maximum possible error of about 10% owing to departure from the ideal carbonate equilibria /23/; see Appendix I for details.

(b) Chloride: A titration error of 0,1 ml corresponds to an error of 3 mg/l. Variations due to interferences are equivalent to an uncertainty of about 3 mg/l as well.

(c) Fluoride: The concentration of fluoride is read on a logarithmic scale. At concentrations below about 0,4 mg/l the reproducibility is about 2 scale units, which corresponds to an error of 0,008 mg/l. For concentrations above 0,4 mg/l the corresponding errors are 5 scale units and 0,02 mg/l. At concentrations near the lowest end of the scale (equivalent to about 0,038 mg/l) lack of equilibration becomes a problem. The uncertainty here is about 0,04 mg/l, which for a reading of about 0,12 mg/l F^- means a precision of no better than about 33%.

(d) Sulphate: A weighing error of 1 mg is equivalent to 4 mg/l of sulphate. If the effects of co-precipitation and other errors are included then the total uncertainty is about 10 mg/l.

(e) Phosphate: The concentration of phosphate is near the detection limit

TABLE 3.4D

Anions

Sample	OH^-	$CO_3^{=}$	HCO_3^-	Cl^-	F^-	$SO_4^{=}$	PO_4^{3-}
131	0	0	537	148	0,13	352	0,023
132	0	0	375	224	0,50	505	0,036
133	0	0	531	103	0,34	194	0,032
134	0	0	531	143	0,19	320	0,054
135	0	0	543	139	0,26	287	0,045
136	0	0	546	137	0,21	350	0,077
137	0	0	433	294	0,26	717	0,045
138	0	0	473	232	0,26	455	0,054
139	0	0	529	44	0,62	104	0,050
140	0	0	387	109	1,58	650	0,099
141	0	0	477	212	0,33	422	0,059
142	0	0	482	237	0,41	436	0,122
143	0	0	487	164	0,20	553	0,311
144	0	0	556	77	0,10	216	0,117
145	0	21	295	54	1,62	444	0,117
146	0	0	466	256	0,27	611	0,104
147	0	0	537	93	0,27	217	0,108
148	0	0	428	285	0,27	712	0,171
149	0	0	573	9	0,12	21	0,203
150	0	0	536	137	0,12	330	0,198
151	0	0	561	86	0,13	204	0,203
152	0	0	558	36	0,12	52	0,207
153	0	0	565	6	0,12	26	0,158
154	0	0	192	130	0,77	631	0,230
155	0	0	207	100	1,46	1056	0,126
156	0	0	538	147	0,13	343	0,167
157	0	0	482	234	0,15	638	0,081
158	0	0	363	258	0,43	656	0,077
159	0	0	543	173	0,18	457	0,059
160	0	0	305	103	2,55	748	0,144
161	0	0	190	134	0,79	638	0,063
162	0	0	603	3	0,46	42	0,072
163	0	0	170	153	0,68	433	0,099
164	0	0	555	89	0,64	230	0,189
165	0	0	519	182	0,25	477	0,099
166	0	0	192	218	0,15	709	0,108

All values are in mg/l

in many cases. The possibility of contamination must also be noted, since much phosphate is used in the laboratory where this work was done. The uncertainty of measurement of absorbance is about 0,003, which is equivalent to 0,014 mg/l phosphate. This is less than the estimated blank error of 0,02 mg/l.

PRECISION TABLE (95% confidence)

	5%	10%	50%	100%	dl	
Cl^-	120	60	12	6	3	mg/l
F^-			see text			
$SO_4^=$	200	100	20	-	-	mg/l
PO_4^{3-}	0,4	0,2	0,04	0,02	0,02	mg/l

(E) *Elements of Groups IA and IIA (Table 3.4E)*

(i) General

Neither rubidium nor caesium was detectable in any sample. No attempt was made to concentrate these elements prior to analysis.

(ii) Estimated errors of determination

PRECISION TABLE (95% confidence)

	5%	10%	50%	100%	dl	
Na	40	21	4	2	-	mg/l
K	42	20	4	2	-	mg/l
Li	50	24	5	2,5	-	µg/l
Sr	204	99	-	-	-	µg/l

(F) *Elements of Groups IIIB to VIII (Table 3.4F)*

(i) Estimated errors of determination

TABLE 3.4E

Elements of Groups IA and IIA

Sample	Na mg/l	K mg/l	Li µg/l	Rb µg/l	Cs µg/l	Sr µg/l
131	139	11	11	<15	<15	213
132	150	15	10	<15	<15	288
133	97	6	8	<15	<15	200
134	129	10	8	<15	<15	188
135	116	8	6	<15	<15	200
136	126	9	10	<15	<15	225
137	176	11	12	<15	<15	263
138	143	8	9	<15	<15	188
139	47	7	8	<15	<15	188
140	124	35	12	<15	<15	350
141	142	9	10	<15	<15	150
142	146	8	9	<15	<15	175
143	140	12	20	<15	<15	375
144	83	7	7	<15	<15	338
145	62	7	44	<15	<15	350
146	161	10	12	<15	<15	200
147	100	9	15	<15	<15	263
148	172	12	13	<15	<15	263
149	16	6	5	<15	<15	225
150	119	10	10	<15	<15	263
151	88	9	8	<15	<15	300
152	28	6	4	<15	<15	275
153	19	5	4	<15	<15	300
154	109	15	29	<15	<15	263
155	94	18	45	<15	<15	363
156	126	10	13	<15	<15	350
157	163	13	18	<15	<15	463
158	166	17	15	<15	<15	400
159	140	12	16	<15	<15	363
160	95	17	46	<15	<15	400
161	115	15	27	<15	<15	225
162	3	1	8	<15	<15	163
163	138	11	34	<15	<15	175
164	53	3	6	<15	<15	213
165	155	11	13	<15	<15	325
166	165	29	10	<15	<15	375

TABLE 3.4F

Elements of Groups IIIB to VIII

Sample	V	Cr	Mo	Mn	Fe	Co	Ni
131	<10	3	<10	<28	<30	2,6	<2,2
132	<10	6	30	169	<30	25,3	4,7
133	<10	3	<10	<28	<30	<1,5	<2,2
134	<10	6	<10	141	50	5,6	3,3
135	<10	5	<10	56	<30	<1,5	4,4
136	<10	6	<10	338	67	13,2	<2,2
137	<10	3	<10	<28	<30	<1,5	<2,2
138	<10	6	<10	<28	<30	<1,5	<2,2
139	<10	3	<10	<28	<30	<1,5	<2,2
140	<10	2	33	<28	<30	<1,5	<2,2
141	<10	3	<10	<28	<30	<1,5	<2,2
142	<10	<1	<10	<28	<30	<1,5	<2,2
143	<10	5	<10	<28	<30	<1,5	<2,2
144	<10	6	<10	28	<30	1,9	<2,2
145	<10	4	22	<28	33	<1,5	2,2
146	<10	6	<10	<28	<30	2,4	2,2
147	<10	6	<10	<28	<30	<1,5	<2,2
148	<10	4	<10	<28	<30	<1,5	<2,2
149	<10	6	<10	<28	<30	<1,5	<2,2
150	<10	7	<10	<28	<30	8,2	5,0
151	<10	6	<10	<28	<30	<1,5	<2,2
152	<10	8	10	<28	<30	<1,5	<2,2
153	<10	9	<10	<28	<30	<1,5	<2,2
154	<10	8	<10	<28	<30	<1,5	<2,2
155	<10	8	<10	<28	<30	1,8	<2,2
156	<10	3	<10	<28	<30	<1,5	<2,2
157	<10	8	<10	591	<30	23,8	<2,2
158	<10	3	<10	<28	<30	2,1	<2,2
159	<10	3	<10	56	<30	5,0	<2,2
160	<10	2	<10	<28	<30	<1,5	3,3
161	<10	11	10	<28	<30	<1,5	<2,2
162	<10	7	<10	<28	<30	<1,5	<2,2
163	<10	89	<10	<28	<30	<1,5	<2,2
164	<10	14	<10	<28	<30	<1,5	<2,2
165	<10	2	<10	56	<30	<1,5	<2,2
166	<10	4	<10	113	<30	<1,5	<2,2

All values in µg/l

PRECISION TABLE (95% confidence)

	5%	10%	50%	100%	dl	
Cr	40	20	4	2	1	
Mo	-	-	20	10	10	
Mn	-	280	56	28	28	
Fe	-	-	80	42	30	(all µg/l)
Co	-	30	5,9	3,2	1,5	
Ni	-	-	5,9	3	2,2	

(G) *Elements of groups IB and IIB (Table 3.4G)*

(i) General

The detection limit for the determination of zinc by carbon rod AAS is much lower than 20 micrograms per litre but this was taken as a conservative minimum because of the high and variable blank value for this metal in this analytical run. In subsequent determinations (see Appendix B4) the zinc blank was reduced to much lower concentrations.

(ii) Estimated errors of determination

PRECISION TABLE (95% confidence)

	5%	10%	50%	100%	dl	(all values in µg/l)
Cu	-	145	28	15	10	
Zn	90	45	-	-	20	(see text)
Cd	2	1	0,2	0,1	-	
Hg	5	3	0,5	0,3	0,06	

(H) *Elements of Groups IIIA to VIA (Table 3.4H)*

(i) General

(a) Arsenic: The detection limit concentration for arsenic depends on the degree of variability of the arsenic blank (Appendix B3). The blank varies with the quality of the reagents used, especially the granules of zinc metal.

(b) Bismuth: The detection limit for some samples was improved by doubling the sample aliquot.

(ii) Estimated errors of determination

PRECISION TABLE (95% confidence)

	5%	10%	50%	100%	dl	
Si	-	2,9	0,62	0,3	-	(mg/l; others in µg/l)
Ge	140	80	17	8	3	
As	154	70	15	7	see text	
Se	290	152	40	21	-	
Te	-	160	40	19	10	
Pb	45	20	5,5	2,5	-	

(I) *Semiquantitative examination by XRFS of TSS residues (Table 3.4I)*

(i) General

The data are semiquantitative and precision figures are meaningless.

TABLE 3.4G

Elements of Groups IB and IIB

Sample	Cu	Ag	Au	Zn	Cd	Hg
131	<10	<9	<100	50	1,1	0,1
132	10	<9	<100	20	2,4	0,3
133	10	<9	<100	114	0,5	0,6
134	<10	<9	<100	36	1,4	1,3
135	<10	<9	<100	50	0,8	2,3
136	<10	<9	<100	86	0,7	0,8
137	40	<9	<100	50	1,5	3,8
138	<10	<9	<100	20	4,6	2,7
139	<10	<9	<100	57	0,4	0,1
140	89	<9	<100	186	11,0	0,5
141	20	<9	<100	57	1,7	2,7
142	<10	<9	<100	43	1,2	2,7
143	<10	<9	<100	29	0,9	0,1
144	<10	<9	<100	43	0,8	0,7
145	44	<9	<100	229	14,0	0,1
146	18	<9	<100	<20	1,5	0,9
147	<10	<9	<100	<20	0,7	0,1
148	10	<9	<100	29	1,5	2,1
149	11	<9	<100	<20	0,4	0,5
150	<10	<9	<100	<20	0,7	0,4
151	<10	<9	<100	<20	0,4	0,4
152	<10	<9	<100	<20	0,1	0,3
153	<10	<9	<100	36	0,9	0,2
154	10	<9	100	1800	320	0,06
155	45	<9	<100	7938	810	<0,06
156	<10	<9	<100	43	0,9	0,2
157	<10	<9	<100	20	1,0	1,5
158	50	<9	<100	<20	3,9	0,7
159	<10	<9	<100	<20	1,0	0,2
160	50	<9	<100	71	17,0	0,1
161	91	<9	<100	292	100	0,06
162	<10	<9	<100	<20	2,6	0,3
163	10	<9	<100	29	1,0	0,06
164	<10	<9	<100	29	0,6	<0,06
165	70	<9	<100	678	3,5	0,06
166	30	<9	<100	242	25	0,06

All values in µg/l

TABLE 3.4H

Elements of Groups IIIA to VIA

Sample	Al	Tl	Si	Ge	As	Sb	Bi	Se	Te	Pb
131	<20	<2,0	1,5	57	1	<20	<20	218	48	6,4
132	<20	<2,0	2,3	70	150	25	<20	195	90	18,6
133	<20	<2,0	1,5	37	5	<20	<20	95	37	16,3
134	<20	<2,0	1,7	7	12	<20	<20	80	62	94
135	<20	<2,0	2,0	47	8	<20	<20	75	56	10,1
136	<20	<2,0	2,0	90	4	<20	<20	112	49	4,5
137	<20	<2,0	1,7	80	12	<20	<10	239	143	20,0
138	<20	<2,0	1,3	13	10	<20	<10	240	67	12,1
139	<20	<2,0	1,0	<3	<4	<20	<10	35	<10	2,4
140	<20	<2,0	2,3	7	79	<20	<10	65	44	30,9
141	<20	<2,0	1,3	<3	18	<20	<10	104	87	10,8
142	<20	<2,0	1,3	13	9	<20	<10	241	70	9,7
143	<20	<2,0	1,7	40	27	<20	<10	118	47	24,5
144	<20	<2,0	1,7	13	<1	<20	<10	85	15	18,3
145	<20	<2,0	1,3	<3	91	<20	<10	45	15	22,7
146	<20	<2,0	1,7	3	<4	<20	<10	152	62	18,4
147	<20	<2,0	1,3	<3	12	<20	<10	50	17	11,3
148	<20	<2,0	1,3	33	17	<20	<10	168	48	10,4
149	<20	<2,0	2,7	60	9	<20	<10	20	<10	26,9
150	<20	<2,0	2,0	64	10	<20	<10	158	37	4,8
151	<20	<2,0	2,3	55	<2	<20	<10	125	21	1,9
152	<20	<2,0	1,7	57	140	<20	<10	65	<10	1,6
153	<20	<2,0	20	27	23	<20	<10	19	<10	2,2
154	<20	<2,0	1,7	30	17	<20	<10	115	40	15,9
155	<20	<2,0	1,0	37	4	<20	<10	210	46	77
156	<20	<2,0	2,0	<3	<4	<20	<10	185	33	4,6
157	<20	<2,0	1,3	37	24	<20	<10	390	60	7,6
158	<20	<2,0	1,3	27	36	<20	<10	303	77	14,6
159	<20	<2,0	1,3	13	<4	<20	<10	278	35	5,5
160	<20	<2,0	2,3	97	114	<20	<10	188	33	23,0
161	<20	<2,0	1,0	30	26	<20	<10	240	21	13,3
162	<20	<2,0	1,3	10	24	<20	<10	5	<10	24,2
163	<20	<2,0	2,0	27	<4	<20	<10	244	40	5,8
164	<20	<2,0	1,3	<3	<4	<20	<10	105	19	42
165	<20	<2,0	1,7	20	24	<20	<10	248	66	26,1
166	<20	<2,0	1,0	70	12	<20	<10	490	60	17,1

Values for Si in mg/l. All other values in µg/l

TABLE 3.41

Semiquantitative examination by XRFS of TSS residues

Sample	Si	Al	Mg	Ca	Ti	Mn	Fe	Cu	Pb	Zn
blank	0	0	0	1*	0	0	0	0	0	0
132	1	0	?	1	0	0	1	?	1	1
134	3	3	2	3	1	1	3	2	2	2
135	1	1	1	3	?	?	1	1	1	1
136	1	1	1	3	?	0	1	0	1	1
140	1	2	1	1	?	0	1	0	0	0
141	0	0	0	1	0	0	1	0	0	0
146	?	0	0	1	0	0	1	0	0	0
148	1	1	1	-	-	-	-	-	-	-
150	1	0	?	1	0	0	1	0	0	0
151	?	?	0	1	?	0	1	0	0	0
153	1	1	?	1	?	0	1	0	0	0
154	1	1	1	2	?	0	1	0	0	1
155	1	1	1	1	?	0	1	?	?	1
156	1	1	0	-	-	-	-	-	-	-
157	1	1	0	-	-	-	-	-	-	-
158	1	1	?	-	-	-	-	-	-	-
163	?	1	0	-	-	-	-	-	-	-

* = Very small peak, much smaller than any sample Ca peak.

\- = no data. 0 = no visible peak. ? = probable small peak.

1 = up to 1/3 of full scale deflection.

2 = 1/3 to 2/3 full scale deflection.

3 = more than 2/3 full scale deflection.

Chapter 4. Interpretation of the Tsumeb mine water data

4.1 Introduction

The interpretation of chemical data obtained from the analysis of mine waters is potentially complex because of the need to correlate several chemical and physical parameters in a fluid more or less free to move in and, to some extent, react with a three-dimensional rock matrix of variable mineralogical composition. The principles involved have been known for a long time (e.g. Lane, 1914 /1163/ and Hodge, 1915 /1164) but there is nevertheless no set method of tackling the problem (see Appendix D).

In a static hydrological situation, where negligible movement of water occurs, the chemical composition of groundwater can change only by reaction with the rock material of the aquifer. Rock may be dissolved into the water or formed from the water through precipitation reactions or allied processes, such precipitates being defined as part of the rock material. In an ideal, static system such as this it is relatively easy to monitor reactions between the rock and the water. However, few bodies of groundwater are static. In particular, observation of the extent to which the Tsumeb mine is continuously dewatered by pumping and, also, of the flow of water into the mine via boreholes and fissures on many levels leaves little doubt that the hydrological regime of the mine is highly dynamic.

In a dynamic hydrological situation the composition of any body of groundwater, in addition to being subject to water-rock interaction, may also be changed by mixing with waters of differing chemistry. This mixing may be purely physical or it may involve mutual chemical interaction. Under these conditions the interpretation of the chemical data becomes much more complex because it may not be possible to separate the effects produced by wall rock reactions from those due to mixing.

In the study of the waters of the Tsumeb mine it would be very useful to be able to separate these two effects somehow in order to examine them independently; in this instance the principle concern is with the water-rock reactions, because the aim of the orientation study is to learn something practically useful about the characteristics of groundwater/ore systems. What is needed therefore is a *hydrogeochemical* model of the orebody and its associated waters, which takes cognizance of both hydrological and chemical factors. If discrete bodies of water can be recognized and the mode of mixing of different masses of water can be understood, then attention can be concentrated on the interpretation of the geochemical data in terms of water-rock reactions occurring within any given body of water.

One of the fundamentals of the science of hydrology is the tracing and delineation of flows of groundwater /295-305,309/. Sometimes tracers such as fluorescent dyes, radioisotopes, spores, micro-organisms etc. are used for this purpose /305-8,310-19,322-3/. Tracer studies of this type were considered to be beyond the scope of this orientation survey. The practical problems involved would have been considerable. It is not at all certain that tracing techniques would have worked in the Tsumeb mine, because there is an overwhelming tendency for groundwater to flow into but not out of the deeper developments. It is difficult to imagine how one might introduce tracers homogeneously into selected bodies of groundwater near the mine, unless by large-scale pumping via underground boreholes below the water table or fissures above the cone of dewatering. Moreover, despite the fact that some dyes (e.g. Uranin /306/) are regarded as harmless, the mine sumps are the source of Tsumeb's drinking water and the ill-considered introduction of tracers into groundwaters that gravitate towards these sumps would be highly anti-social. Some sophisticated geophysical and electrolytical techniques (e.g. /325-9/) are also available for tracing the flow of groundwater but these were likewise considered to be beyond the scope of the project.

The alternative in a situation such as this is to try to use one of the chemical components or other properties of the groundwaters as a natural tracer /306,320,324,330,490/, rather than adding some artificial tracer to the system. Properties such as pH and temperature are clearly unsuitable in the Tsumeb mine and so the prospective natural tracer must needs be a chemical species. An ideal natural tracer would pass the following three tests:

(i) It should be well concentrated in the water, so that small additions or losses of the species will have only a minor effect on the abundance of the ion in solution. Trace elements are thus unsuitable and only the major components can be considered as candidates. In Tsumeb Mine water (TMW) these are sulphate, chloride, bicarbonate, calcium, magnesium and sodium.

(ii)The tracer should be practically unaffected by adsorption/precipitation reactions with the wall rock or *in aqua*. Only sodium, chloride and sulphate are suitable in this case, because under the conditions prevailing in TMW these are the only three ions that will not precipitate in significant amounts.(The solubility of gypsum is not exceeded in any sample). The other three ions mentioned above are components of the carbonic system (Appendix I) and they may interact freely with the carbonate country rocks.

(iii) The concentration of the natural tracer should be practically unaffected by dissolution reactions. That is it should not be possible for large masses of the species to enter the water during its movement through the mine and adjacent ore and country rocks. No natural component in TMW passes this test. Sulphate can be added as a result of the oxidation of sulphidic minerals and both chloride and sodium may enter the water as a result of cementation operations. Sodium may also be derived from the decomposition of feldspar in the pseudo-aplite of the orebody (Appendix E).

Although there is no ideal natural tracer for TMW, sulphate, sodium and chloride are the best approximations. (This is true in general and not only for the Tsumeb mine; see the following references for examples of the use of sulphate /330/, sodium /147/ and chloride /1155-7/ as natural tracers). In the following subsections (4.2 to 4.4) the distribution of these three ions in the mine water samples will be examined in an attempt to construct a *hydrological* model of the mine and its groundwaters. This construction is conveniently undertaken in two separate steps, as follows, although the concepts are of course not independent of each other:
(1) The identification of bodies of related waters (subsection 4.2)
(2) Establishing the origin of these groups of related waters (subsection 4.3). This step must necessarily include a consideration of the extent to which these waters may have been altered by unnatural or "anthropogenic" influences, since there is a mass of *prima facie* evidence that suggests that these influences have been very important (Appendix H).

Using this *hydrological* model and the remaining geochemical data, a *hydrogeochemical* model will be developed in which consideration can be given equally to hydrological factors and wall rock reactions (subsections 4.5 to 4.7). Within the framework of this model an attempt will be made to reach some understanding of the *practically useful* aspects of the natural interactions that take place between groundwater, carbonate country rock and sulphidic ore.

Naturally, where chemical composition is being used to study hydrology and vice versa, it is difficult in practice to separate the logical derivation of a "hydrological" model from that of a "hydrogeochemical" model. The two concepts and the sets of data for the separate "models" will be mingled whenever this is advantageous.

The interpretative diagrams for this Chapter are Maps 2 & 3 and Figs. 1, 1a, 1b,....1y. Some of these are in this volume and the rest are in Vol. II. The most fundamental of these is Fig. 1, a geological long section (1:5000) through the Tsuemb orebody. Fig. 1a is a translucent overlay, at the same scale, which shows the locations at which the orientation samples were collected. Figs. 1b, 1c, 1d etc. are translucent overlays or paper prints showing the concentrations of the most important chemical species determined in the mine waters, together with some additional data such as pH and rate of flow at the sampling points.

In constructing this series of overlays the writer had to contend with the problem of representing spatial information in two dimensions. It was felt that no oblique projection could portray the location in space of the sample points and boreholes without ambiguity. Therefore all the data necessary to describe the locations have been presented in two separate, but complementary, two-dimensional sections normal to each other (Fig. 1a). From these the reader can construct an accurate and unambiguous mental picture of the location of any sampling point and the spatial orientation of any borehole, and can to some extent orientate these features relative to the solid geology of the orebody and country rocks, and to the mine workings. Additional technical information about the location of the sampling points and the trigonometrical relationships involved in the construction of the variants of Fig. 1 can be found in Appendices A and C.

4.2 Identification of bodies of related Tsumeb mine waters. The use of sodium, chloride and sulphate as natural tracers

The inter-relationship between the different groups or types of waters occurring in and around the Tsumeb pipe are illustrated by the data in Figs. 1 and 1a and the overlays for sulphate, chloride, sodium, Na/Cl^- and $SO_4^=/Cl^-$, and rate of flow (Figs. 1b, 1c, 1e, 1f, 1k and 1j respectively).

The writer will attempt to show that the key to the understanding of the hydrology of the mine waters is the relationship between the concentrations of the sodium and chloride ions. If a simple grouping of the samples is made according to Na/Cl^- ratio and depth below the surface (Table 4.2), then a remarkably ordered pattern of sample properties emerges, from which there are few deviations. The locations of these groups with respect to the mine workings is shown in Fig. 1f, in which they are identified by coloured symbols. The three colours selected and the order in which they are used have no special significance; they are merely added to show more clearly which samples are grouped together.

The names that have been given to the various groups are arbitrary but hopefully descriptive. The tempting but potentially confusing terms "footwall waters" and "hanging wall waters" have been avoided, because the pipe is sinuous and the footwall is sometimes on the south side and sometimes on the north. The properties of the different groups of waters are described below in order of increasing depth below the surface.

TABLE 4.2: Samples of Tsumeb mine water grouped according to sodium/chloride ratio and depth below surface

Group	Sample	$SO_4^=$	Cl^-	Na	Na/Cl^-	$SO_4^=/Cl^-$	Flow
IA	163	433	158	138	0,90	2,83	1
	154	631	130	109	0,84	4,85	21
Stope	161	638	134	115	0,86	4,76	33
waters	155	1056	100	94	0,94	10,56	9
	160	748	103	95	0,92	7,26	5
	143	553	164	140	0,85	3,95	6
IB	162	42	3	3	1,00	14,00	1
IIA	145	444	54	62	1,15	8,22	22
Shallow	147	217	93	100	1,08	1,37	3
sodium	139	104	44	47	1,07	2,36	5
waters	140	560	109	124	1,14	5,96	4
IIB	137	717	294	176	0,60	2,44	25
	148	712	285	172	0,60	2,50	18
	166	709	218	165	0,76	3,25	3
	146	611	256	161	0,63	2,39	78
North	158	656	258	166	0,64	2,54	2
Break	157	638	234	163	0,70	2,73	11
chloride	132	505	224	150	0,67	2,25	6
waters	138	455	232	143	0,62	1,96	38
	142	436	237	146	0,62	1,84	264
	141	422	212	142	0,67	1,99	13
	164	230	89	53	0,60	2,58	90
IIC	159	457	173	140	0,81	2,64	108
	165	477	182	155	0,85	2,62	2
	156	343	147	126	0,86	2,33	12
	131	352	148	138	0,93	2,38	8
Intermediate	134	320	143	129	0,90	2,24	2
waters	136	350	137	126	0,92	2,55	30
	150	330	137	119	0,87	2,41	extreme
	135	287	139	116	0,84	2,07	127
	133	194	103	97	0,94	1,88	83
IID	144	216	77	83	1,08	2,81	2
	151	204	86	88	1,02	2,37	1
IIE	149	21	9	16	1,78	2,33	5
	153	26	6	10	1,67	4,33	39
IIF	152	52	36	28	0,78	1,44	2

IB = Upper dilute waters. *IID* = Deep sodium waters.
IIE = Deep dilute waters. *IIF* = Deep chloride waters.
Concentrations of ions are in milligrams per litre. Flow rate in l/min.

(A) *GROUP I. UPPER LEVEL WATERS*

The seven samples collected above the apex of the cone of dewatering (about 23 level) are classified as Upper Level Waters. These form what will be termed a *coherent* group of adjacent samples. The word coherent is used here to describe a collection of neighbouring samples that can be readily recognized as forming a distinctive, non-random subpattern within the overall pattern of distribution of the surrounding samples.

(1) *Group IA. Stope waters (Samples 163, 154, 161, 155, 160 & 143)*

(a) Some statistical properties of this group are as follows:

Group IA	$SO_4^=$	Cl^-	Na^+	Na/Cl^-	$SO_4^=/Cl^-$
$\bar{x}$	677	131	115	0,89	5,70
σ	213	26	20	0,041	2,79
$\%\sigma$	31,5	19,7	17,5	4,6	49,0

n = 6

(In this table and similar tables in the following pages $\bar{x}$ is the mean of all x_n, σ is the standard deviation, $\%\sigma$ is $100\sigma/x$; i.e. the coefficient of variation (COV) expressed as a percentage, and n is the number of samples. The concentrations of sulphate, sodium and chloride are always expressed in milligrams per litre).

The waters of Group IA are generally sulphate-rich and have relatively high concentrations of sodium and chloride. The concentration of sulphate is distinctly more variable than those of the other two ions. The COV is slightly lower for sodium than for chloride and this may well be due to the fact that the precision in the determination of the former ion is somewhat better than it is for the latter (Appendix B and p. 35). The Na/Cl^- ratio is remarkably steady in view of the general decrease in [Na] and $[Cl^-]$ with depth. On the other hand the sulphate/chloride ratio is very variable; the concentration of sulphate - and consequently the value of the ratio - first increases and then later decreases with depth.

(b) Two of the samples (154, 161) are practically identical in composition.

(c) The waters of group IA generally flow along the ground or down manways and orepasses, on the northern side of the orebody, in the relatively dry upper levels of the mine. There is little visible augumentation of the flow on the floor by water from the roof or walls of the development. There are in fact very few places between surface and 22 level where substantial amounts of water can be seen flowing from the rock into the mine. These are at samplings points 163 (fissure, 1 l/min.), 162 (long borehole, 1 l/min.) and 143 (short borehole, 6 l/min.) and near One Shaft on eight level, where a showery flow issues from a fracture in the roof. Nevertheless it was in no case possible to trace the flow from an orebox etc. back to its original source in the wall rocks because of the extremely dangerous condition of the abandoned workings in this old part of the mine.

(d) All the samples in this group come from slow, low-pressure, non-artesian flows.

(2) *Group IB (Sample 162)*

(a) This single sample from 16 level is the only water with a low TDS value that could be found above the cone of dewatering. Its composition is radically different from the compositions of the waters of group IA. The differences in the concentrations of the three mobile ions, expressed as the ratio (Group IA mean value/Group IB value) are considerable:

Sulphate: 16,1
Chloride: 43,7
Sodium : 38,3 .

The Na/Cl^- ratio for sample 162 is unity and the sulphate/chloride ratio is extremely high, but it must be remembered that the relative precision of analysis is poor at these low concentrations.

(b) An important characteristic of sample 162 is that it emerges from the only aquiferous long borehole in the upper levels. The hole has a *southerly* azimuth and is directed well away from the workings and the orebody, in the vicinity of which all the other Upper Level waters were encountered. The flow from borehole 162 was very slow and under negligible pressure.

(B) *GROUP II. LOWER LEVEL WATERS*

The dividing line between the waters of Groups I and II is the poorly defined upper surface of the cone of dewatering at about 22 level. Although only about one half of the mine levels are below this surface, twenty nine of the thirty six samples collected from the mine belong to Group II. This simply reflects the difficulty of finding sampling points above the water table.

(1) *Group IIA. Shallow sodium waters (Samples 145,147,139,140)*

(a) These waters are chemically similar to those of Group IA but there are nevertheless some important differences:

Group IIA	$SO_4^=$	Cl^-	Na	Na/Cl^-	$SO_4^=/Cl^-$
$\bar{x}$	354	75	83	1,11	4,48
σ	243	40	35	0,04	3,18
$\%\sigma$	68,3	41,3	42,3	3,7	80,0
n = 4					

The chief characteristic of Group IIA is the remarkably constant Na/Cl^- ratio somewhat greater than unity. The constancy of this ratio is emphasized by the large range in $[SO_4^=]$, [Na] and $[Cl^-]$; for each of these ions the COV is more than double that of the corresponding value in Group IA. The values of the sulphate/chloride ratio are also more variable in Group IIA than in Group IA. In common with Group IA, the COV's for chloride and sodium are similar to each other and only about two thirds of the COV for sulphate.

The salt content of Group IIA is, in general, considerably lower than that of Group IA. The ratios $\bar{x}_{IA}/\bar{x}_{IIA}$ are as follows:

Sulphate: 1,91

Chloride: 1,75

Sodium : 1,39 .

This disparity also serves to emphasize that the Group IIA waters are relatively sodium-rich. Nevertheless, several values for sulphate, chloride and sodium for samples in Group IIA are of the same sort of magnitude as corresponding values in Group IA. The best example of this is the similarity between sample 140 (IIA) and samples 154 & 161 (IA).

(b) The location of the Group IIA samples is different in many respects from that of the Group IA samples. The relationship with respect to the water table is the most important disparity. The set of Group IIA samples is identical to the set of samples occurring on the southern side of the orebody between the contact between the dolomites of Zones 6 and 7, and the North Break Zone (NBZ).

(c) The pressures and rates of flow in the boreholes that provided the samples of Group IIA are quite low.

(2) *Group IIB. North Break chloride waters (Samples 137,148,166,146,158, 157,132,138,142,141 and 164)*

(a) This is a well-defined group of high-TDS waters that are distinctly different from any of the other samples collected in the mine. The group contains one *mauvais sujet*, number 164, which is rather different from the rest, but which is classified IIB because of its Na/Cl$^-$ratio. Sample 164 has vague affinities to number 147 (IIA) and certain samples in Group IID, but its Na/Cl$^-$ratio is atypical of either of these groups. Some statistical properties of Group IIB are as follows:

Group IIB	$SO_4^=$	Cl^-	Na	Na/Cl$^-$	$SO_4^=/Cl^-$
$\bar{x}$	586	245	158	0,65	2,39
σ	120	28	12	0,05	0,42
%σ	20,5	11,3	7,8	7,7	17,4

n = 10 (sample 164 excluded)

The sulphate content of these waters is high and is exceeded, on average, only by the waters of group IA. The concentration of chloride in the waters of Group IIB is not paralleled by any other TMW. Sodium is also abundant, and only a few samples in Groups IA and IIC have concentrations of this metal approaching those that are typical of the IIB waters. The mean Na/Cl$^-$value for Group IIB is distinctly lower than that of any other group, but the sulphate/chloride ratios are similar to those of many other samples in several different groups.

Another important feature of this group is the relatively low values of the COV for all parameters except Na/Cl$^-$(which is low but of the same magnitude as those of the other groups). That is to say, the similarity between the individual members of Group IIB is greater than the similarity between the members of any other group. The COV for sodium (written $Na_{\%\sigma}$) is slightly lower than $Cl^-_{\%\sigma}$, while $SO^=_{4\%\sigma}$ is much greater than either.

(b) Three major subgroups can be recognized within Group IIB. Samples 132 and 164 are the only "odd men out" that cannot be accomodated in any of the subdivisions:

		$SO_4^=$	Cl^-	Na	Na/Cl^-	$SO_4^=/Cl^-$
Subgroup IIB(i)	$\bar{x}$	713	266	171	0,65	2,73
	σ	4	42	6	0,09	0,45
	%σ	0,6	15,6	3,3	14,2	16,5
	n = 3 (137,148,166)					
Subgroup IIB(ii)	$\bar{x}$	635	249	163	0,66	2,55
	σ	23	13	3	0,04	0,17
	%σ	3,6	5,3	1,5	5,7	6,7
	n = 3(146,158,157)					
Subgroup IIB(iii)	$\bar{x}$	438	227	144	0,64	1,93
	σ	17	13	2	0,03	0,08
	% σ	3,8	5,8	1,4	4,5	4,1
	n = 3(138,142,141)					

To facilitate a comparison, the following table lists the mean of the COV's of the three subgroups, the COV value for Group IIB as a whole, and the ratio of these two values:

		$SO_4^=$	Cl^-	Na	Na/Cl^-	$SO_4^=/Cl^-$
Group IIB	%σ	20,5	11,3	7,8	7,7	17,4
Mean of subgroups	%σ	2,7	8,9	2,1	8,1	9,1
Ratio of the above		7,6	1,3	3,7	0,95	1,9

From this table it is clear that the internal similarity within the subgroups is generally better than that of Group IIB as a whole. The table emphasizes the relative constancy of the Na/Cl^- ratio, the low variability of [Na] and especially [Cl^-] and the fact that the principal feature distinguishing the three subgroups is the differing content of sulphate.

(c) The setting of the sampling points of this group is quite complex. These waters first appear about two levels above the NBZ and seven samples form a coherent group between 26 and 31 levels, to the north, northeast or northwest of the orebody, in the dolomites of Zones 5 and 6. Between 31 and 35 levels there are four samples, which appear to be associated with the central pipe structure or with the rocks somewhat to the south of it. Below

35 level the group becomes incoherent and interspersed with waters of Group IIC. It is not immediately obvious, for example, why sample 158 (IIB) and sample 156 (IIC) should be different, since they are both derived from boreholes that are similarly situated. The same applies to the pairs 157 (IIB) - 159 (IIC) and 164 (IIB) - 135 (IIC). Neither is there any apparent order in the distributions of the three subgroups, except perhaps for the waters of subgroup (iii), which are from three boreholes that lie within the uppermost portion of the region of distribution of the Group IIB samples. These three holes are on the northern side of the pipe, below the NBZ, and are drilled out into the country rock approximately in the plane of section of Fig. 1, or somewhat to the east of it. An important point to note, however, is that the two "chemical misfits" (132 & 164) have the deepest situations of all 11 samples in the group and are "sandwiched" between several samples belonging to Group IIC. It is not apparent why these samples should be different from their neighbours.

(d) Although water pressures and rates of flow for the waters of Group IIB are very variable, the mean values are high in comparison to those of any group previously described. The strongest flow noted hitherto from a borehole was in Group IA (number 143, 6 l/minute), but in Group IIB only three flows are equal to or weaker than this and most of the others are much stronger. Each subgroup has at least one strongly flowing borehole and several of the boreholes are artesian.

(3) *Group IIC. Intermediate waters (Samples 159,165,156,131,134,136,150, 135 and 133)*

(a) These waters are so named because they are intermediate, in both depth from surface and content of salt, between the waters of Group IIB on the one hand and those of Groups IID,E and F on the other. Group IIC waters are manifestly different from almost all other samples of mine water; Group IA only is somewhat similar.

Group IIC	$SO_4^=$	Cl^-	Na	Na/Cl^-	$SO_4^=/Cl^-$
$\bar{x}$	346	145	127	0,88	2,35
σ	84	23	16	0,04	0,25
$\%\sigma$	24,4	15,6	12,95	5,1	10,8
n = 9					

The familiar pattern of distribution of COV's appears again; sulphate$_{\%\sigma}$

is greater than $Cl^-_{\%\sigma}$, which is slightly greater than $Na^+_{\%\sigma}$. By comparing these values with the corresponding ones of Group IA, it can be seen that the chief difference between the two groups is that the former has less sulphate and consequently has a lower sulphate/chloride ratio, which happens also to be much less variable. The samples comprising Group IIC are not as closely related to one another as the samples of Group IIB are; the values of the COV for all three ions in IIB are somewhat lower than the corresponding values for IIC. It is therefore interesting that the %σ values for the two ratios are somewhat lower in IIC than in IIB.

The Intermediate waters have lower concentrations of the three mobile ions than Group IIB has. The ratios of the means ($\bar{x}_{IIB}/\bar{x}_{IIC}$) are as follows:

Sulphate: 1,694
Chloride: 1,690
Sodium : 1,244

These figures emphasize that the mean sulphate/chloride ratios for the two groups are practically the same but that the Na/Cl^- ratios differ because the IIC waters are relatively sodium-rich.

Subgroups can be distinguished within the waters of Group IIC. There are two of these and two additional samples (135 & 133) that fit into neither subgroup:

		$SO_4^=$	Cl^-	Na^+	Na/Cl^-	$SO_4^=/Cl^-$
Subgroup IIC(i)	$\bar{x}$	467	178	148	0,83	2,63
	σ	14	6	11	0,03	0,01
	%σ	3,0	3,6	7,2	3,4	0,5
	n = 2 (159, 165)					
Subgroup IIC(ii)	$\bar{x}$	339	142	128	0,90	2,38
	σ	14	5	7	0,03	0,11
	%σ	4,0	3,7	5,4	3,4	4,8
	n = 5 (156,131,134,136,150)					

The ratios ($\bar{x}_{IICi}/\bar{x}_{IICii}$) are as follows:

Sulphate: 1,38
Chloride: 1,25
Sodium : 1,16
Na $/Cl^-$: 0,92
$SO_4^=/Cl^-$; 1,11

The subgroups are characterized by differences in $[Cl^-]$ and especially $[SO_4^=]$. The COV's of either subgroup are much better than for Group IIC taken as a whole, except in the case of the Na/Cl^-ratio, where the improvement is slight.

(b) The location and geological setting of the samples of Group IIC are quite complex. The samples of the group occur in a coherent pattern, but this is "intruded" by a vertical finger of three samples of Group IIB. The majority of the IIC samples are from boreholes that are drilled either (i) to the west of the orebody, into the country rock or (ii) deep into or just through the orebody. However, sample 150 comes from a borehole that was drilled into dolomite to the northeast of the pipe structure. The relationship between the samples constituting the subgroups of Group IIC is less well-ordered. The two black sheep (135 & 133) were derived from boreholes that are congruently situated and penetrate through ore. However, the two members of subgroup IIC(i), although comparatively near to each other, are in very dissimilar geological settings and there is no obvious connection between them. Subgroup (ii) is also scattered; sample points 131, 134 and 136 are congruently situated to the west but sample 150 came from the northeast and sample 156 from the orebody. There is no apparent reason for the chemical similarity of these five waters.

(c) The waters of Group IIC (and indeed of all groups that will be described subsequently) were all derived from dolomites of Zone 5.

(d) As was the case with Group IIB, the waters of Group IIC are often under high pressure and come from sources that have large yields. At least one flow is strongly artesian.

(4). *Group IID. Deep sodium waters (Samples 144 and 151)*

(a) A gap of three levels separates the lowermost waters of Group IIC from the three small, deeply-located Groups IID, E and F. The paucity of samples below 38 level is due mainly to the very effective cementation of the wallrocks in the deepest levels of the mine, where the hydrostatic load is very great.

(b) The two Group IID waters are similar to each other and also to some

of the waters of Group IA, which occur many levels higher up in the mine. Compared to the IIC waters immediately above them, the IID samples have something like half as much sulphate, chloride and sodium and a higher Na/Cl ratio. They are, as a group, the most dilute waters thus far encountered below the single sample from Group IB, on 16 level. There are similarities between the waters of Group IID and the black sheep of both Groups IIB and IIC, but the resemblance is more apparent than real.
(c) The IID samples came from similar geological situations to the southwest of the orebody. The observed rates of flow are low, but this is probably because of cementation.

(5) *Group IIE. Deep dilute waters (Samples 149 and 153)*

(a) The lack of the three mobile ions in the waters of group IIE is very marked. The IID waters, themselves relatively dilute, have from 5 to 10 times more sulphate, chloride and sodium than the samples of Group IIE. The latter waters also have a very high Na/Cl ratio. Because of these properties, this group can be compared only to Groups IA and IIF. But although these three groups are superficially similar in that they all contain dilute waters, the concentration ratios of the mobile components in them are quite different.
(b) Although the two boreholes from which the samples of Group IIE were collected have adjacent collars, they are drilled in different directions - hole 149 into the ore and number 153 away from it.
(c) Sample 153 is from an artesian source with a fairly high rate of flow.

(6) *Group IIF. Deep chloride waters (Sample 152)*

This final sample came from a new, weakly-yielding artesian hole on 45 level. The borehole had apparently been cementated a short time before the sample was collected. The water is dilute and the only reasonably close relatives would be the samples of Group IIE. However, sample 152 has significantly higher concentrations of sulphate, chloride and sodium and is relatively rich in chloride and poorer in sulphate.

4.3 The origin of bodies of related mine waters

(A) *INTRODUCTION*

In this section an attempt will be made to trace the origin and history of the groups of waters identified in subsection 4.2. It is impossible, in an exercise of this type, to avoid some subjective speculation. It is also necessary to make comparisons between samples that were separated both by time and space. For example, in subsection 4.3B a comparison will be made between the main set of orientation data, obtained in 1973, and a set of analyses of surface- and underground waters collected in 1975. Comparisons of this nature are valid only if "steady state" conditions prevail in the hydrological regime and are vitiated if sharp, random fluctuations in composition occur frequently. There is, fortunately, a measure of *prima facie* evidence (/52/, Table 4.3a, Fig. H1 and the data of subsection 4.2 and Appendix J, subsection J4.1) that suggests that the major bodies of waters studied in this orientation project change in composition only very slowly. In the absence of comprehensive data collected over a period of many years there is obviously no alternative, if any comparisons are to be made at all, but to accept that such comparisons can in fact be validly made.

It is convenient to discuss the various groups of waters systematically, from the surface downwards, as was done in subsection 4.2. The single most important assumption that will be made in this discussion is that many of the orientation samples contain a large proportion of water that has recirculated into the mine workings from the land surface above the orebody. Some of the water may have completed many cycles. This hypothesis is supported by much evidence, which is detailed in Appendix H.

(B) *ORIGIN OF THE UPPER LEVEL WATERS - GROUPS IA AND IB*

The seven samples defined as Upper Level waters all occurred above the cone of dewatering, which is steep but of unknown but probably complex shape. In 1972 the apex of the cone stood at around 22-23 level, some 680 m below the surface and was apparently still dropping slowly. It is therefore improbable that large, untapped bodies of pristine groundwater remain in the dolomitic formations around the Upper Levels of the Tsumeb mine. Some fresh groundwater, of local origin and derived from rainfall recharge, undoubtedly does make its way down through and around the old, shallow workings. Sample 162 (IIB) is probably an example of such a water. It issues from a borehole drilled well to the southeast of the pipe and it would not have had much chance to collect dissolved salts either from the country rocks or from the vicinity of the orebody.

In contrast, it seems unlikely that the waters of Group IA are natural groundwaters. How could they have achieved such high concentrations of sodium and chloride in percolating through such a limited thickness of rock? (compare, for example, the typical values for $[Cl^-]$ and $[Na^+]$ in the waters from surface boreholes, described in Section 3). And even were it possible to leach these large quantities of salts from this rock or from the mine complex, why then do [Cl^-] and [Na^+] in the Group IA samples tend to decrease rather than increase with depth? The writer therefore proposes the following hypothesis:

The Group IA waters are derived from industrial and domestic water wasted on the surface within the Mine Area; i.e. the typical water discarded into the Jordan river (Map 2 and Fig. 1a). Part of this waste water percolates down through the permeable dolomites and in so doing may be diluted to a greater or lesser extent by fresh waters of type IB. The two kinds of water may mingle within the country rock or while running down through the old workings. This dilution would alter the concentrations of sodium and chloride, but would not influence the Na/Cl^- ratio, because in sample 162 this ratio is unity. Waters derived in this manner might enter the mine at several points and at various stages of dilution. Generally speaking, the deeper the location of the sampling point below the surface, the more diluted the water will have become.

This hypothesis can be made somewhat more rigorous by posing and quantitatively answering two questions:

(i) It has been demonstrated in Appendix H that the Jordan River waters could provide the observed amounts of sodium and chloride in the shallow mine waters. The Na/Cl^- ratios, too, are similar (Jordan waters 0,86 to 0,87; IA waters 0,84 to 0,94). But is there a rational relationship between the composition of the waste waters of the mine area and that of the Jordan flow?

The available evidence suggests that there is. Most of the water in circuit with the Mine Area is either domestic water or Raw Mine water and most of what is wasted locally ends up in the Jordan. (Any heavily polluted waters are piped directly to the slimes dams). Table 4.3A compares the compositions of these waters and that of Jordan River water. It appears that the water of the Jordan is a fair approximation of the type of water likely to be available within the Mine Area for recycling into the upper levels of the mine.

(ii) Is there enough downward seepage from the surface within the Mine Area to account for the observed volumes of water leaking into the upper levels?

This is more difficult to answer rigorously but the writer has attempted to do so by measuring the loss of water from the Jordan due to seepage. On most days a considerable volume of water is discarded into the Jordan and its minor tributary, the Little Jordan, within the Mine Area between De Wet shaft and the old glory hole (Map 2 and Fig. H3 in Appendix H).

TABLE 4.3A

A comparison of some properties of Jordan River water, Tsumeb domestic water and Raw Mine water

	Domestic[1]		Raw Mine[1]		Jordan[2]	
	$SO_4^{=}$	Cl^{-}	$SO_4^{=}$	Cl^{-}	$SO_4^{=}$	Cl^{-}
$\bar{x}$	409	167	434	169	494	188
σ	44	14	29	10	71	8

NOTES:

(1) Nineteen determinations at regular intervals between Dec. 1971 and June 1975. /52/

(2) Two analyses, October 1975.

All values are in milligrams per litre.
No data are available for sodium in these waters.

The beds of these streams are natural and unlined and there are long periods during the day when the flow is steady enough to be measured with reasonable accuracy. The flow was measured at two points below the confluence of the streams in October 1975, at the end of the dry season, when the runoff could not in any way have been influenced by rainfall. At these two points, which were 250 m apart, the flow was constrained to pass through concrete pipes and gauged with a large bucket and a stopwatch. No water was being added to or extracted from the stream between these two points.

The mean of nineteen estimates of the rate of flow at the confluence was 37,8 l/second. At the station downstream the mean of seventeen measurements was 30,2 l/second. It appeared that 7,6 litres of stream water was soaking into the ground in this section of the river bed in each second. The total length of the Jordan-Little Jordan system within the Mine Area is about 800m. If water is lost equally over this distance, then some 24,3l/sec. may be percolating down into the rocks around the Upper levels from this source. This is of course an extremely crude estimate.

The other side of the equation - the rate of inflow into the Upper levels - is even less well known. The writer's estimate, based on the collected inflow to the sumps on 16 level, is not greater than 50 l/sec. This suggests that perhaps a half or somewhat more of the inflow into the uppermost sections of the mine could be supplied by direct seepage from the Jordan River system. Although the data collected are primitive, they are good enough to show that no impossible imbalance exists between the volume of water entering the upper levels and the volume lost on the surface directly above.

The Group IA waters show some interesting trends that are related to depth below the surface (Table 4.3B). Note the following:

(a) As expected, the temperature of the water generally increases with depth but is never more than a few degrees warmer than the ambient temperature of the air, suggesting that the water is well exposed to aeration. This is supported by observation underground.

(b) Chloride and sodium are diluted as the depth increases. It is clear that sulphate is - at least initially - being added to the water at a rate exceeding the rate of dilution. The amount of sulphate added can be estimated by assuming that (i) all samples were derived from a common, homogeneous source and (ii) the diluent water was practically free of sulphate; and then multiplying the observed [$SO_4^=$] by the ratio of the observed [Cl^-] in any sample/observed [Cl^-] in sample 163. The latter sample is taken as the most likely approximation of the parent water, because of the high concentration in it of chloride and the shallow location of the site where it was collected.

TABLE 4.3B: Depth-dependent properties of the Group IA waters

Sample	Level	Description	Air, ^0C	Water, ^0C	Cl^-	Na	$SO_4^=$ observed	$SO_4^=$ predilution	$SO_4^=$ difference
163	6	fissure	19	19	153	138	433	433	0
154	10	orebox	23,9	21	130	109	631	743	112
161	12	orebox	23,5	24	134	115	638	728	90
155	16	orebox	23	30	100	94	1056	1616	560
160	20	orebox	24,5	30	103	95	748	1111	363
143	22	orebox	22,4	26,4	164	140	553	515	-38

NOTES: All analytical values are in mg/l
Calculation of predilution concentration of sulphate is based on the chloride content of sample number 163.

It appears that the addition of sulphate is very rapid. The value for "predilution $[SO_4^=]$" rises from 433 mg/l on 6 level to 1616 mg/l on 16 level, where a peak is reached. Below this the values appear to decrease with depth, although the data are limited and the estimation of predilution $[SO_4^=]$ for the deepest sample in the Group is meaningless because $[Cl^-]_{143}/[Cl^-]_{163}$ exceeds unity. This is probably because sample 143 issues from a borehole drilled away from the orebody and which may tap water coming fairly directly from the surface. This sample is very similar to the waters of the Jordan (Tables 4.2 and H2).

These observations are consistent with the hypothesis that sulphate is being produced rapidly and in quantity in the uppermost parts of the mine by the aerial, electrochemical or bacterial oxidation of sulphides.

$$2H_2O + 2S^= + 3O_2 = 2H_2SO_4 = 4H^+ + 2SO_4^=$$

More than anywhere else in the Tsumeb mine, conditions in the upper levels are conducive to the promotion of oxidation. The stopes are well ventilated, and damp but not flooded. Various kinds of moulds grow ubiquitously. Some of the material filling the old stopes has a base metal content of several percent and this waste is fragmented and porous. Many authors have noted that the oxidation of sulphides is strongly promoted under these circumstances /50,116,782,1151/. Woodmansee /730/ pointed out that the most important factor favouring an accelerated rate of oxidation is the permanent depression of the level of the water table. It should be noted that the mechanisms and kinetics of these oxidation processes can be very complex and may, through galvanic action, involve more than just local portions of the orebody (Thorber, 1975 /281/).

All else being equal, the increase in the concentration of sulphate in the upper levels of the Tsumeb mine is likely to be linearly related to the length of time the water is in contact with the waste material and vestigial sulphides, and the extent of the surface area of mineral matter over which it passes. It is therefore not surprising that we find here the highest concentrations of sulphate of any of the mine waters.

However, as the depth increases the effect of dilution accelerates owing to the greater influx of relatively fresh groundwater. It is also likely that the rate of production of sulphate decreases in the deeper, younger and more thoroughly exploited stopes. This may explain the reversal, below 16 level, of the earlier trend of net increase in sulphate despite the dilution. It is probably no coincidence that the first running borehole drilled out into the country rock is encountered on 16 level.

It is well known that the oxidation of sulphides tends to lower the pH of adjacent waters /23,43-4,49,53,116/. This is not observed in the Tsumeb mine; in the presence of massive excesses of dolomite and calcite any sulphur acids produced by oxidation will be very rapidly neutralized and the buffering effects of the carbonic system will effectively prevent the accumulation of H^+ ions.

$$2H^+ + SO_4^= + 2HCO_3^- = SO_4^= + 2CO_2 + 2H_2O \quad .$$

(C) *ORIGIN OF THE LOWER LEVEL WATERS*

(1) *General*

Below about 24 level the country rocks are saturated with water and the observed pressures and rates of flow generally increase with depth. These increases are not altogether regular because of variations in the permeability of the rock, the degree of cementation and similar factors. Although the choice of sampling points in the deeper levels is wider, it must be remembered that all boreholes and fissures that might allow large volumes of water into the workings are permanently sealed. The samples collected were therefore merely leakages from the main reservoirs of groundwater. Although the influx of water into the mine is about one million litres per hour - indicating a dynamic surrounding hydrological system - it is probable that the samples seen in some parts of the lower levels will not reflect all of the hydrochemical events occurring in those parts.

The detailed structure and locations of the various channels that conduct water about the Tsumeb pipe, and the amounts of water contained in them, are very little known.The relationships between moving bodies of pristine and (apparently) recirculated waters are also obscure and have to be inferred from the chemical data. This interpretation can be difficult and subjective when the available information is ambiguous.

(2) *Group IIA (Shallow sodium waters)*

This is a rather problematic group of samples. It is necessary to explain the similar and relatively high Na/Cl^- ratios of the four samples, which at the same time exhibit wide variations in $[SO_4^=]$, $[Na^+]$, $[Cl^-]$ and sulphate/chloride ratio. The waters of Group IIA appear suddenly as a coherent pattern of samples on the southern or southwestern sides of the orebody (the northern side being quite dry here). The uppermost sample in the Group (145) came from an orebox, and if the orebox waters are regarded as being representative of the type of water moving through the old stopes, then it is apparent that the composition of the stope waters changes significantly between about 20 and 24 level. The following table compares the compositions of sample 145 and the two stope waters of Group IA that occur at somewhat shallower levels:

Level	Group	Sample	$SO_4^=$	Cl^-	Na^+	Na/Cl^-	$SO_4^=/Cl^-$
16	IA	155	1056	100	94	0,94	10,56
20	IA	160	748	103	95	0,92	7,26
24	IIA	145	444	54	62	1,15	8,22

Some possible sources of the waters of Group IIA are listed below:

(a) They may have resulted from the evolution of waters of Group IA during downward migration. Note that the Group is characterized by high concentrations of sulphate and the continued trend of dilution of chloride and sodium with depth (sample 140 being the exception). It is necessary to postulate a relatively sodium-rich diluent to account for the increased Na/Cl^- ratio. Sample 139, from a borehole drilled from the south haulage into the country rock south of the orebody, provides some evidence that such waters may exist. It has a slight excess of sodium but is relatively dilute and is therefore unlikely to be very closely related to the postulated diluent.

(b) Although the waters of Group IIA now appear to be flowing mainly from the dolomites to the southwest of the pipe, they may have migrated down dip from the north and passed the orebody (Figs. 1, 1a and 1f). It is therefore reasonable to postulate that these waters have been influenced by fluids migrating down dip from the slimes dams, which are the most feasible source of the excess sodium (Appendix H). The value of the Na/Cl^- ratio in the waters of the slimes dams varies from 0,86 on the north side to 1,37 on the south side. The slimes dams complex is more than a kilometre wide (Map 2) and covers dipping strata and at least one important fault /52/. It is conceivable that water from this complex is not recirculated as a homogeneous mass but may be channeled into several chemically distinctive bodies via different major systems of fractures. Note that sample 140, which relative to the mean for the Group has high $[SO_4^=]$, [Na] and $[Cl^-]$, comes from the only borehole in the Group that is drilled across the section of the orebody towards the northeast, near the space occupied by the waters of Group IIB (*vide infra*), where the influence of recirculated fluids from the slimes dams is thought to be strongest.

Any fluids that the slimes dams are contributing to the Group IIA waters must be heavily diluted *en route* by both fresh country rock waters (cf. Group IB) and waters of type IA. Dilution by type IB water alone cannot account for the observed compositions of the samples in Group IIA. For example, the sulphate/chloride ratio in the slimes dam waters never reaches three, but for sample 140 this value is nearly six and for sample 145 it exceeds eight (Table 4.2). Nor can dilution by waters of Group IA alone account for the observed, low concentrations of sodium and chloride in Group IIA.

It is the writer's opinion that the members of this Group were derived from various blendings of waters of types IA and IB, and sodium-rich waters of the type found on the southern side of the slimes dam complex. In a situation such as this the number of theoretically possible dilutions and blendings becomes enormous and arithmetical "cake mixing" to obtain the observed concentrations of ions in the samples becomes pointless. Nevertheless the failure to unravel all the details of the evolution of the Group IIA samples is not a fatal shortcoming. It remains highly probable that they have been influenced by effluents from one source or another and for the purposes of this orientation study they can be loosely conjoined with the waters of Group IA and treated with suspicion.

(3) *Group IIB. North Break chloride waters*

The nature and origin of this group of samples have already been discussed in some detail in subsection 4.2 and Appendix H and there is convincing circumstantial evidence that recirculated water from the slimes dams is an important and perhaps even dominant component of the Group.

The chief (and in the writer's opinion insuperable) difficulty with any alternative hypothesis is to explain the reversal of the trend of dilution with increasing depth by the sudden appearance of large volumes of high-pressure water with elevated concentrations of chloride, sulphate and sodium. The writer cannot accept that any significant portion of the sulphate in the waters of Group IIB could be derived from sulphidic ore during a single passage of these waters from the surface down to the haulages. There is relatively little sulphide in the North Break, or anywhere else outside the pipe (/52/, Fig. 1A, Appendix A) and it is clear that the waters of Group IIB do not come from *within* the orebody. All the available evidence suggests that the processes of oxidation are at maximum intensity in the uppermost levels of the mine and decrease steadily with depth. Yet on 26 and 27 levels are strong flows of water, which apparently have not been in contact with any substantial amounts of ore, but with concentrations of sulphate exceeding anything short of the peaks reached in but a couple of the stope waters of Group IA. And even were the sulphate attributable to oxidation processes at depth, the unprecedented concentrations of chloride and sodium would remain unexplained, because waters of this type are otherwise unknown in the Otavi dolomites (Section 3; except, as noted in Chapter 6 and on page 22, where the influence of water from the Karoo or post-Karoo formations prevails. There are no such formations close to the Tsumeb mine).

The division between the waters of Group IIA, on the one hand, and of IIB on the other is quite sharp, except perhaps in the case of sample 140 (IIA), which may have been influenced by waters akin to those of Group IIB. The division coincides more or less with the North Break Zone, which, together with the surrounding dolomites some tens of meters below or above, is a powerful but structurally and hydrogeologically complex aquifer /52/. It appears likely that the Break and the contiguous dolomites constitute a major pathway for recirculation and are the source of the IIB waters. The orebody is apparently not an impenetrable barrier to these high-pressure fluids, which migrate around and to some extent into the pipe.

Group IIB can be divided into subgroups containing samples that are very closely related. As was the case with Group IIA, it is almost impossible to elucidate the details of the origin, pathways of migration and chemical inter-relationships of the various subgroups on the basis of the limited data available. Nor again is it important to do so, because the strong possibility that the whole Group has been contaminated by effluents raises grave doubts about using the chemical data from these samples for purposes of orientation. Some further discussion of the properties of the Group is nevertheless necessary and is given below in point form:

(a) A comparison of data from Tables 4.2 and H2 indicates that the downward--moving slimes dam waters are diluted to varying degrees before emerging in the mine workings. Sample 164, for instance, is about 3,1 to 3,3 times more dilute than sample 137, depending on which ion is selected as the index. The diluent is probably rainfall recharge.

The degree of dilution that is necessary to produce the observed IIB samples from slimes dam water is a little uncertain because the waters of the dams are inhomogeneous (in space and perhaps in time) and because the composition of the diluting water is unknown. However, by assuming that the diluent had negligible amounts of chloride, sodium and sulphate, an order-of-magnitude estimation can be made by comparing values in the abovementioned two tables. By comparing the various data for the North Break waters analyzed in 1973 with the mean values for the slimes dam waters analyzed in 1975, one finds that the ranges of dilutions required to produce the observed concentrations of the three ions are:

Sodium: 2,7 to 8,9
Chloride: 1,5 to 5,0
Sulphate: 1,3 to 4,1

These values are in fact the ranges of the ratios (mean slimes dam conc. / conc. in samples of Group IIB).

Using the data for the samples of slimes dam and North Break waters collected in 1975 a similar calculation yields the following corresponding values:

Sodium: 1,4 to 3,4
Chloride: 1,6 to 3,1
Sulphate: 0,86 to 2,8

(The minimum value for the range of sulphate values is in this case less than one. The concentration of sulphate in some samples in Group IIB exceeds the mean value for slimes dam waters, but not the maximum for those waters). From this it appears that during migration to the boreholes delivering waters of type IIB the slimes dam waters are diluted by masses of fresher water varying from somewhat less than an equal volume to as much as about eight times the volume of migrating effluent. The most probable mean dilution is about one part slimes dam water to two parts of rainwater, to give a final concentration ratio of about one third.

Because all of the Group IIB samples have similar Na/Cl^- ratios and fairly similar sulphate/chloride ratios, they can be regarded as members of a continuous, consanguineous series derived by diluting a bulk, ion-rich source fluid with increasing volumes of water that is practically free of ions. It does not follow that they did originate in this manner, but it is nevertheless possible to produce good approximations of most of the IIB samples by mixing various proportions of various other waters in the Group. For example, a good approximation of sample 158 can be obtained by mixing samples 137 and 164 in the ratio 6,98 : 1, or alternatively, by mixing samples 137 and 132 in the ratio 2,48 : 1 (Table 4.3C). In this situation it is idle to speculate about which sample is the parent and which the offspring.

(b) Unlike Group IA, and perhaps IIA, the samples of Group IIB exhibit no marked systematic variations in chemical properties with depth (Table 4.3D). Moreover, the distribution of values within the three IIB subgroups (subsection 4.2) is not significantly more ordered than for the group as a whole. This is probably because the North Break water is under considerable hydrostatic pressure and that the point of emergence of a sample is controlled more by geological structure than by simple gravitational movement of the flow. For example, samples 141 and 146 are from boreholes drilled into the North Break Zone relatively close together, but they yield waters of different subtypes. It is probably for the same reason that one cannot convincingly relate the chemical compositions of the samples to the spatial orientations of the boreholes from which they issued (Table 4.3E).

(c) In view of the apparently random distribution of the subtypes of Group IIB waters and the strong indication that the mobile ions in them were - in the main - carried down from the surface rather than picked up along the way, it is scarcely surprising to find that the presence or absence of records of intersected ore in the various borehole logs cannot be related to water type (Table 4.3E).

(4) *Intermediate waters. Group IIC.*

The relationship between Groups IIB and IIC is complex. The two groups are interfingered within the same general block of dolomite; there is no obvious reason, for example, why samples 157 and 159 should belong to different groups. Furthermore, the two lowermost samples of Group IIB are "chemical misfits", although not obviously intermediates between Groups IIB and IIC. The high rates of flow recorded for several of the boreholes yielding waters of type IIC (Table 4.2) indicate that this group is not the result of small-scale mixing but is a major hydrogeochemical feature.

For these reasons it seems likely that the waters of Group IIC are also a variation on the theme of recirculated slimes dam water. They may represent either:

(a) A discrete body of relatively sodium-enriched water moving down through the dolomites of Zone 5 well below the NBZ. This water would be progressively diluted by rainfall recharge.

(b) A continuation of or a parallel to the sequence of dilution observed in Group IIB, but one in which the diluent is relatively more enriched in sodium than the hypothetical diluent for the IIB series. A hypothetical diluent that could produce sample 165 (highest TDS in Group IIC) by 1:1 dilution of sample 137 (highest TDS in Group IIB) would have the following properties:

$SO_4^=$	Cl^-	$Na^·$	Na/Cl^-	$SO_4^=/Cl^-$
237	70	134	1,91	3,39

There is no water amongst the thirty six orientation samples with a sodium/chloride ratio this high. This does not mean that such a water does not exist; the mixing and dilution that produced the fluids collected in the

TABLE 4.3C

Hypothetical approximations of some Group IIB samples produced by mixing two other IIB waters

Example 1, based on equalized concentrations of sulphate

Sample	$SO_4^=$	Cl^-	Na^+
137	717	294	176
132	505	224	150
164	230	89	53
158	656	258	166
(137:164::6,98:1)	656	268	161
(137:132::2,475:1)	656	273	168

Example 2, based on equalized sodium

148	712	285	172
(137:164::29,75:1)	701	287	172
158	656	258	166
(137:164::11,3:1)	677	277	166

Explanation of arithmetic: The mixing proportion needed to produce the observed concentration of the selected ion (sulphate in this example) is calculated. The same factor is then applied to the remaining ionic concentrations. Water Z is to be derived by mixing waters X and Y. Water N has nSO4 mg/l $SO_4^=$. xSO4>zSO4>ySO4. Let mSO4 be $[SO_4^=]$ resulting from any mixture of X and Y. Let p be parts of X to be added to one part of Y to make mSO4 = zSO4. Then (pxSO4 + ySO4)/(p + 1) = zSO4 .....(i)

pxSO4 + ySO4 = pzSO4 + zSO4. pxSO4 - pzSO4 = zSO4 - ySO4. Therefore

p = (zSO4 - ySO4)/(xSO4 - zSO4)

One may then substitute p and xCl, yCl in (i) to get zCl, and so on.

TABLE 4.3D. Systematic examination of the properties of the subgroups of Group IIB as a function of decreasing $[SO_4^=]$, $[Cl^-]$, [Na], Na/Cl^- and $SO_4^=/Cl^-$

Sub-group	Sample	$SO_4^=$	Level	Sub-group	Sample	Cl^-	Level	Sub-group	Sample	Na	Level	Sub-group	Sample	Na/Cl^-	Level	Sub-group	Sample	$SO_4^=/Cl^-$	Level
i	137	717	27	i	137	294	27	i	137	176	27	i	166	0,76	33	i	166	3,25	33
i	148	712	26	i	148	285	26	i	148	172	26	ii	157	0,70	31	ii	157	2,73	31
i	166	709	33	ii	158	258	31	ii	158	166	31	ms*	132	0,67	34	ms	164	2,58	35
ii	158	656	31	ii	146	256	26	i	166	165	33	iii	141	0,67	27	ii	158	2,54	31
ii	157	638	31	iii	142	237	30	ii	157	163	31	ii	158	0,64	31	i	148	2,50	26
ii	146	611	26	ii	157	234	31	ii	146	161	26	ii	146	0,63	26	i	137	2,44	27
ms	132	505	34	iii	138	232	28	ms	132	150	34	iii	138	0,62	28	ii	146	2,39	26
iii	138	455	28	ms	132	224	34	iii	142	146	30	iii	142	0,62	30	ms	132	2,25	34
iii	142	436	30	i	166	218	33	iii	138	143	28	i	137	0,60	27	iii	141	1,99	27
ii	141	422	27	iii	141	212	27	iii	141	142	27	i	148	0,60	26	iii	138	1,96	28
ms	164	230	35	ms	164	89	35	ms	164	53	35	ms	164	o,60	35	iii	142	1,84	30

* ms = "black sheep"

TABLE 4.3E

Correlation between subgroups of waters of type IIB that came from boreholes and the azimuth of the borehole and the grade of mineralization intersected

Sample	Subgroup	Azimuth	Mineralization intersected
137	i	SW	moderate
148	i	NE	slight
166	i	NE	strong
158	ii	SW	moderate
157	ii	W	percussion hole, not directed at ore
146	ii	NE	strong
138	iii	NE	very slight
142	iii	ENE	good
141	iii	NNE	percussion hole, not directed at ore

mine workings may have occurred hundreds of metres up dip. The observed values for the Na/Cl^- ratios in the slimes dam waters ranged up to 1,37 (Table H2) and could conceivably be higher at times. The highest Na/Cl^- ratio observed in the mine waters was 1,78 (sample 149, Group IIE, Table 4.2). Mixing this water in the ratio 1:1,9 with sample 137 (IIB) will produce the following approximation of sample 165 (IIC):

	$SO_4^=$	Cl^-	Na^+	Na/Cl^-	$SO_4^=/Cl^-$
165 observed	477	182	155	0,85	2,62
165 calculated	477	196	121	0,62	2,43

This hypothetical mixture inevitably lacks sodium. Nevertheless the difference between the properties of the two end members (137 & 149) is great and therefore the agreement is good enough to permit the suggestion that the waters of Group IIC may have been derived in part from the waters of type IIB or their precursors, by admixture with waters quite closely related to those in Group IIE.

Be that as it may, in practical terms these alternatives (a and b above) amount to six of one and half a dozen of the other, because in both cases the effluents from the slimes dams are once again implicated. If this is correct then the orientation data for the waters of type IIC, like the data for Groups IIA and IIB, must be treated with circumspection.

As was the case with Group IIB, it is difficult to visualize any alternative explanation of the origin of the relatively salty IIC waters. Why should they be so different from the purer, very deeply located waters of Groups IIE and IIF (Table 4.2)? One can postulate only the influx of waters enriched in sodium, chloride and sulphate from some remote source such as the Kalahari formations many kilometres to the north of Tsumeb. Not only is there no supporting evidence at all for this theory, but it leaves one with the ticklish problem of explaining how water migrating from a distant source to a relatively localized geological feature - the Tsumeb pipe - arrives there in at least two very chemically distinctive masses of water.

The following are additional notable observations concerning the origin of the waters of Group IIC:

(a) As was the case with Group IIB, the IIC waters are not restricted to one side of the orebody but are encountered to the north (sample 150), within or very close to the orebody (135,132,156,165) and south or southwest of it (136,134,131,159). The Tsumeb pipe appears to be no obstacle to these high pressure waters.

(b) The saltier subgroup IIC(i) tends to occur at shallow depths, the IIC(ii) waters of lower TDS constitute the bottom of the Group and the most dilute, "non-conformist" samples occur at intermediate levels (data on page 54; cf. Table 4.3D, page 70, for Group IIB). This invites speculation about whether subgroup IICii can be derived by admixture of the other two kinds. Table 4.3F compares the observed sulphate, chloride and sodium values of subgroup IICii with those of various theoretical mixtures of samples 165 and 135. The agreement is good enough to warrant the view that the samples of Group IIC form a series inter-related by dilution. As was the case with the dilution series of Group IIB, the end members are unknown, but in this case the diluent is enriched in sodium relative to Group IIB.

(5) *The waters of the Seven Shaft area: Groups IID (Deep sodium waters), IIE (Deep dilute waters) and IIF (Deep chloride waters)*

It is convenient to collocate these three last groups (five samples) for purposes of discussion.

Figures 1a and 1f show that there is a clear physical separation between Groups IIC and IID, which corresponds approximately to the bottom of De Wet shaft on 38 level. This is probably not entirely a coincidence. De Wet shaft is a relatively old feature, whereas Seven shaft, which provides access to all sampling points below 38 level, is new (1970-2). This deep subvertical shaft and all the drives from it have been extensively protected by cementation against the possibility of high-pressure water bursts. Thus very little water finds its way into the workings below 38 level and there has been relatively little turnover in the groundwater reservoir in this region, compared to, say, the North Break area between 26 and 28 levels.

It therefore seems logical to expect the Seven shaft waters to be relatively unaffected by recirculation and to approach the composition of the original, pristine groundwaters of these deep dolomitic formations. It is probable that the two samples of Group IID represent the tail end of the process of downward migration and continuous dilution of the waters from the slimes dam complex. Compared with sample 137 (IIB), the salt content of sample 151 (IID) has been diluted 2,0-3,5 times (assuming ion-free water) and, compared with the waters of the slimes dams (Table H2; data from 1975), some 3,8 to 6,5 times.

It has been implied in preceding paragraphs that Group IIE was probably the best available approximation of the deep pristine waters. It is therefore no surprise to find that the samples of Group IID can be very well imitated by theoretical mixtures of selected waters of Groups IIE and IIC. For example:

TABLE 4.3F

Hypothetical derivation of subgroup IIC(ii) by mixing of samples 165 (IICi) and 135 (IIC ms)

Sample	Proportion*	$SO_4^=$		Cl^-		Na^+	
		calc.	obs.	calc.	obs.	calc.	obs.
156	0,4179	343	343	152	147	127	126
131	0,5200	352	352	154	148	129	138
134	0,2102	320	320	146	143	123	129
136	0,4961	350	350	153	137	129	126
150	0,2925	330	330	149	137	125	119

* parts of sample 165 to one part of sample 135.
Calculation based on equalized sulphate. For arithmetic see Table 4.3C, page 69.
All analytical values are in milligrams per litre.

	$SO_4^=$	Cl^-	Na
149	216	77	83
136:149::1:1,46	216	85	81

Because there are only two IID samples, isolated from the Groups above and below, there is little more that can be deduced from their locations. There is a similarity between some samples of Groups IID and IIA, but the significance of this is unknown.

With Group IIE we finally reach deep, unadulterated waters. They appear to be unaffected by the waning influences of recirculated effluents, but the location of these two isolated samples tells us little more about their origin. The relatively high yield of sample 153 suggests that fairly extensive reserves of this type of water exist.

The final sample, number 152, which is the sole member of the Group IIF, is something of an enigma, in that it reverses the trend of decreasing TDS and rising Na/Cl^- ratio with depth. It is possible that the differences between the chemistry of Group IIF and that of IIE merely reflect natural variations in ionic concentrations that are to be found in groundwaters distributed through a complex series of aquifers in a thick dolomitic succession. It seems rather less probable that sample 152 could be a chemical intermediate between Groups IIE and IID that had somehow physically bypassed the Group IIE samples and is now found below them. Furthermore, both the Na/Cl^- and sulphate/chloride ratios of sample 152 are too low to support this suggestion. The writer's view is that sample 152 is in fact a non-equilibrated, residual, post-cementation leakage and not a true sample of groundwater in the sense that the term has been used in the discussion thus far. Appendix A shows that this sample emerged as a very slow trickle (2 litres/minute) from amongst a forest of cementation borehole casings in the Six shaft/Seven shaft drive. This area had been cementated about six months prior to sampling. Between February 1973 and March 1974 the mass of $CaCl_2$ added to the cement used in cementation operations below 37 level averaged 600 kg/month /52/. Assuming that the rate of flow of sample 152 had remained constant over this period, it follows that a total of

$2 \times 60 \times 24 \times 365 \times 0,5 = 525\ 600$ litres of water had emerged from this leakage point prior to sampling. If it is assumed further that the observed composition of the sample is due to ideal mixing of Tsumeb Raw Mine water (which would approximate to the water used to make the cement slurry) and type IIE water, then the proportion of the former component can be calculated. The following estimate is based on sulphate, because there is probably less soluble sulphate than sodium or chloride in the cement mix:

Mean conc. of sulphate in Bulk Mine water (Table 4.3A) = 434 mg/l;
Mean conc. of sulphate in waters of Group IIE = 23,5 mg/l;

Therefore the ideal mixing ratio required to produce the observed concentration of sulphate in sample 152 is

1 part Bulk water : 14,29 parts of IIE water.

i.e., an original volume of only 34 375 litres of Bulk water would, in theory, have observed the observed flow of sample 152 for six months. This amount of water could very easily have been injected during a major cementation operation around a deep level such as this one. It follows that it is not justifiable to assert that sample 152 is definitely representative of the groundwater that may eventually emerge from this particular borehole casing. The data for this sample should therefore be interpreted with caution.

4.4 Summarized "three ion" hydrological model of the Tsumeb mine as a basis for the construction of a more complete hydrogeochemical model

(A) *Synopsis*

With this summary we reach the first goal of Chapter 4 - the presentation of a hydrological model for the Tsumeb mine waters. It is a simple and limited model, but it will suffice. We have by now some understanding of the distributions and significance of certain ions (Na^+, Cl^- and sulphate) within the framework of the model. In the following subsections (4.5 and 4.6) the remaining data for the mine waters will be examined in terms of this model and assimilated into it to evolve a more detailed hydrogeochemical model;thereby achieving the second goal of Chapter 4 and completing the orientation survey of the Tsumeb mine waters. The main features of the hydrological model and the probable impact of these upon the hydrogeochemical model are summarized below:

(1) The model is fairly general and, provided that it is correct in its essential features (cf. Appendix D), any errors of detail are likely to be of little consequence.

(2) The thirty six samples can be divided into rationally-constituted and inter-related groups and subgroups principally on the basis of the Na/Cl^- ratio, the depth below surface and the concentration of sulphate. The groups appear to be related more by dilution than by dissolution-precipitation reactions on a large scale. The composition of the diluent appears to be variable. The remaining data for the mine waters should be examined for and parallel intragroup or intergroup trends.

(3) Variations in the the concentrations of sodium and chloride between the samples of any group or subgroup appear to bear little relation to the

presence of mineralization or to the orientation in space of the boreholes that produced the waters of that type. The same is generally true for sulphate in the deeper waters, but there is strong evidence that this ion is being released in appreciable amounts into some of the shallowest samples as a consequence of the oxidation of sulphide minerals.

(4) There is relatively little influx of water into the Upper levels of the mine. Variations in the concentrations of trace elements within Groups IA and IB may therefore be especially interesting.

(5) There is only a handful of samples that have not been heavily influenced by recirculated water. One must be extremely wary of the possibility of drawing incorrect conclusions about orientation criteria (pathfinder elements, expected mobility, concentration levels, inter-element ratios etc.) as a result of this unnatural influence.

(B) *Recommendations. I: Relevant to the Hydrogeochemical Exploration Project*

Irrespective of the results of any subsequent interpretation of the remaining data for the mine water, a second orientation study should be performed around the Tsumeb mine (and elsewhere), utilizing only water drawn from boreholes drilled from the surface, and from springs. This is the only practical way of obtaining data that might serve as a baseline from which to judge the real significance and usefulness of the analyses of the Tsumeb mine waters.

(C) *Recommendations. II: Not directly relevant to the Exploration Project*

It is self-evident that the question of recycling of groundwater should be investigated in detail in order to anticipate and minimize any serious threat of pollution of the regional reservoirs of groundwater. The writer would stress that he has not *proved* that any serios pollution has occurred. It is merely suggested that there is sufficient circumstantial evidence pointing to the possibility of the existence of some such problem to justify a separate investigation into the relationship between the waters of the slimes dam complex and those of the mine.

4.5 The Hydrogeochemical Model (I): Inclusion of the less-mobile major components of Tsumeb Mine water - calcium, magnesium and bicarbonate (the carbonic system)

(A) *Introduction: some general features of the carbonic system*

The relatively less-mobile major components of TMW (calcium, magnesium and bicarbonate) are also the most important soluble members of the carbonic system (at least in the pH range typically found in TMW). Thus some understanding of the nature of the carbonic system is mandatory if one is to make sense of the data for these three components. We will first briefly examine some general features of the system and then, more specifically, the significance of the carbonic system in TMW's.

Those aspects of the carbonic system that will be of interest here have been described by McCoy /17/, Owen and Brinkley /334/ and especially in the extensive treatise of Loewenthal /23/.

The relationship between the aqueous members of the system, atmospheric carbon dioxide and various solid-phase compounds such as calcium carbonate, $Mg(OH)_2$ etc. is governed by a set of simultaneous equilibria, which can be expressed in the general form

$$[C]\ [D]/[A]\ [B] = k_f/k_r = K$$

for the reaction

$$A + B \leftrightarrow C + D \qquad ,$$

where k_f and k_r are respectively the constants of proportionality for the forward and reverse reactions and K is the equilibrium constant for the overall reaction. K is temperature-dependent and may also be influenced by factors such as ionic strength of the solution, ion paring phenomena, hydrostatic pressure and the presence of the members of other weak acid-base systems.

Thus in the equilibrated state of the carbonic system under given physicochemical conditions the parameters $[Ca^{++}]$, $[Mg^{++}]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^=]$, $[OH^-]$ and $[H^+]$ are uniquely inter-related and any one of these values can be quantitatively calculated if certain of the others are known. The following useful operations are possible:

If the calculated equilibrium and experimentally observed states of the carbonic system in a given water are compared, then the degree to which the system departs from the equilibrium state can be accurately estimated. Furthermore, the changes that the system must undergo in order to achieve the equilibrium state can be predicted precisely.

One can calculate what the new equilibrium conditions will be if one of the variables or components in the system is changed e.g. if the pressure is raised or a known mass of acid is added, and predict the changes that the system will tend to undergo in order to move once again towards a state of equilibrium; e.g., by a shift in pH or by precipitation of calcite.

The following important features of the carbonic system must also be noted:

(1) The carbonic system is not directly affected by non-carbonic ions of strong acids and bases, such as sulphate, chloride and sodium. The only effects are indirect, through ion pairing and changes in ionic strength of the solution.

(2) The carbonic system is often slow to equilibrate and the observed state is frequently quite different from the predicted state. The kinetics of the carbonic reactions is a much more complex matter than the study of the equilibrium states /332-3/. Equilibration times vary from a few milliseconds for aqueous ionic reactions to days or weeks for changes such as the exchange of carbon dioxide between the waters of reservoirs and the atmosphere, or the deposition of excess calcite from supersaturated solutions of the salt.

(3) Where magnesium is not precipitated or dissolved, the Mg^{++} system in natural water can be regarded as independent of the Ca^{++} system.

(4) Carbonic equilibria are affected by other weak acid/base systems. Fortunately, the concentrations of nitrogen acids, phosphate and cyanide in TMW are negligible (Chapter 3 and /52/), while the concentration of silicon seldom exceeds 2 mg/l. The concentrations of boron and organic acid/base compounds are unknown but are believd to be very low /9/. All interferences of this sort can therefore be ignored in the study of the waters of the mine.

(B) *The carbonic system in Tsumeb Mine waters: Rationale*

There are two important reasons for undertaking an examination of the carbonic system in TMW:

(1) In subsection 4.1 the members of the system were dismissed as potential natural hydrological tracers on theoretical grounds. It was considered that the effects on the concentrations of calcium, magnesium and bicarbonate of mixing and dilution of bodies of groundwater could be greatly complicated or masked by solid-liquid reactions involving the wallrocks /331,306/. As a simple example /23/, a body of groundwater in limestone, which was previously saturated with respect to Ca^{++}, and which is diluted by an influx of calcium-poor recharge water, will tend to dissolve the wallrocks to regain an equilibrated value for $[Ca^{++}]$. After a sufficiently long period this influx of rainwater will not be detectable by analysis for dissolved calcium.

Nevertheless, there may well be those who will want a stronger case than this for rejecting the use of calcium, magnesium and bicarbonate ions in the process of identifying anomalous Tsumeb Mine waters; we have seen that a dissenting opinion on this subject was voiced early on in this project (Appendix D). It was therefore incumbent upon the writer to examine the behaviour of these three ions somewhat more closely. It was necessary, in particular, to see how well different bodies of TMW could be characterized by the carbonic species in them and, *ipso facto*, to establish the degree to which the empirical chemical data justified the abovementioned dismissal of the role of these ions in prospecting under local conditions. Some understanding was needed of the extent to which the TMW samples were equilibrated with respect to the carbonic system, the factors that were most likely to disturb this balance, the probable resultant changes and the rates at which these changes were likely to occur.

(2) Both theory and observation indicate clearly that precipitation and dissolution reactions involving the carbonic system /23,331/ occur in the waters of the Tsumeb mine on a large scale (Plate 6). It is possible that concomitant co-precipitation reactions could have a strong influence on the concentrations of certain trace elements /44/. It seemed necessary to establish whether waters that were actively precipitating calcite were at the same time being stripped of some microcomponents.

(C) *Results of the observation and calculation of carbonic system parameters (excluding magnesium) in Tsumeb Mine waters, and the interpretation thereof.*

A computer program was written that could produce a listing of the important observed (i.e. analyzed) and saturated (i.e. equilibrated) carbonic parameters for each of the mine water samples. The program allows for all important deviations caused by factors such as hydrostatic pressure and differences in ionic strength. The description of the program and its mathematical basis is lengthy and has therefore been placed in Appendix I. The output of the program is given as Table 4.5, from which the following conclusions are obvious:

(1) The effect of hydrostatic pressure on pH is not negligible in the deeper parts of the mine. At high pressures the shift in pH may exceed the precision of the pH measurement. The effect is more serious at lower pH values.

(2) The data in the column (SAT-OBS(Ca)) show clearly that the mine waters are, in general, well equilibrated with respect to $[Ca^{++}]$. This confirms that the carbonic system parameters tend to be independent of non-carbonic influences and that there is therefore very little scope for using the carbonic ions as indicators of mineralization. There is nothing in Table 4.5 or Fig. 1h to suggest that changes in the concentration of calcium may be in any way related to the distribution of ore. The same conclusion applies,

TABLE 4.5

VALUES OF IMPORTANT OBSERVED AND SATURATED CARBONIC SYSTEM PARAMETERS IN TSUMEB MINE WATERS

				ALL IN P.P.M. CALCIUM CARBONATE						
SPL NO.	OBS LP PH	OBS HP PH	LP -HP PH	*OBS *ALK	OBS CA	SAT CA	SAT -OBS CA	EST ERR CA	SAT* ALK*	SAT PH
131	6.88	6.83	.05	440	344	348	3	10	443	6.84
132	6.92	6.87	.05	308	404	415	10	8	318	6.92
133	6.75	6.70	.05	435	309	319	9	11	444	6.73
134	6.92	6.87	.05	435	347	344	-2	8	432	6.86
135	6.84	6.79	.05	445	342	331	-11	10	433	6.76
136	6.90	6.85	.05	448	354	324	-30	9	417	6.75
137	6.80	6.76	.04	355	471	470	-1	9	353	6.76
138	6.80	6.76	.04	388	384	386	1	10	389	6.77
139	6.60	6.56	.04	434	289	343	53	14	487	6.67
140	6.40	6.36	.04	318	382	523	141	18	459	6.67
141	6.90	6.86	.04	391	394	377	-17	9	373	6.80
142	6.40	6.36	.04	395	394	499	105	18	500	6.55
143	6.65	6.62	.03	399	447	497	50	14	449	6.74
144	6.60	6.54	.06	456	307	362	55	14	511	6.65
145	6.65	6.65	.00	295	354	403	49	11	344	6.81
146	6.70	6.66	.04	382	442	460	18	11	400	6.71
147	7.00	6.97	.03	440	342	317	-24	8	415	6.88
148	7.10	7.06	.04	351	464	430	-34	6	316	6.89
149	6.45	6.38	.07	470	254	340	85	17	555	6.52
150	7.50	7.44	.06	439	352	274	-77	3	361	6.96
151	6.65	6.59	.06	460	314	354	39	13	499	6.67
152	6.70	6.63	.07	457	259	280	20	12	477	6.68
153	6.65	6.58	.07	463	254	275	20	12	483	6.63
154	7.20	7.20	-.00	157	387	397	10	3	167	7.35
155	7.40	7.40	-.00	170	656	634	-21	1	148	7.07
156	6.75	6.70	.05	441	372	396	24	13	465	6.76
157	6.90	6.85	.05	395	484	473	-10	9	384	6.82
158	7.15	7.11	.04	298	461	436	-25	5	272	6.94
159	6.90	6.85	.05	445	409	388	-21	10	423	6.79
160	8.20	8.21	-.01	250	359	312	-47	1	202	7.20
161	7.22	7.22	-.00	156	339	347	7	4	163	7.34
162	8.30	8.28	.02	494	267	164	-102	1	391	7.18
163	8.30	8.31	-.01	139	229	219	-10	1	128	7.72
164	6.80	6.75	.05	455	304	303	-1	9	453	6.74
165	6.93	6.88	.05	425	364	364	0	9	425	6.88
166	7.08	7.03	.05	158	417	433	16	5	174	7.25

NOTE: ABBREVIATIONS USED ARE (FROM LEFT TO RIGHT), SAMPLE NUMBER, OBSERVED, LOW OR HIGH PRESSURE, ALKALINITY, CALCIUM CONCENTRATION, SATURATED, AND ESTIMATED ERROR (IN THE VALUE OF (SAT - OBS)CA++).

mutatis mutandis, to the data for pH and bicarbonate. The pH does decrease somewhat with depth - and the concentration of bicarbonate does increase - (Figs. 11 and 1d) but it is clearly demonstrated in Appendix I that this is due in great measure to the effects of hydrostatic pressure and the concomitant rise in the partial pressure of carbon dioxide. This phenomenon can hardly be regarded as a prospecting criterion under the circumstances prevailing in the mine.

(3) The principle observations of paragraph (2) notwithstanding, it is obvious from Table 4.5 that the concentration of calcium is seldom perfectly equilibrated; nor should we expect it to be, since it is obvious from the carbonate growths that occur throughout the mine that slight dissolution and reprecipitation of carbonate takes place continuously in response to small physical and chemical changes that occur in the migrating waters. The precipitation of calcium carbonate can be responsible for stripping trace elements from water either by co-precipitation or through ion exchange reactions. That carbonates are highly effective scavengers of trace metals has been clearly demonstrated by Popova /793/ and by Kitano *et al*. /1154/. Scavenging by carbonates is also well known to chemists concerned with the treatment of metalliferous effluents (Marais, pers. comm.). Many stalagtitic growths in the Tsumeb mine are highly coloured; blacks, browns, greys, yellows, blues and greens are common and reds are occasionally seen. These colourations are almost certainly due to the incorporation of trace metals from the mine waters into the calcitic growths. Note also that high concentrations of calcium in TSS samples (Chapter 3) are generally accompanied by high concentrations of copper, lead, zinc and occasionally other metals.

The writer found it impossible to make any quantitative estimate of the balance between the total mass of metal in solution in the various types of TMW's and the amount that is immobilized in this manner. However, it is clear that calcium-oversaturation is a powerful, potential force for effecting radical changes in the trace element composition of mobile Tsumeb Mine waters.

(D) *Magnesium in Tsumeb Mine waters*

Figure 1g shows that the concentration of magnesium, like that of calcium, shows a general but not strong tendency to decrease with depth.

The theoretical basis for the calculation of solution equilibrium data for magnesium has been adequately described by Loewenthal /23/ and Stumm and Morgan /43/. These calculations are much less complicated than the corresponding ones for calcium (Appendix I); this owing principally to the fact that the equilibrium relationship between calcite, dolomite and dissolved magnesium is essentially independent of pCO_2, pH and (moderate) pressure. We have seen that most TMW's are nearly in equilibrium with calcite. Stumm and Morgan have shown that natural waters in equilibrium with both calcite and dolomite will have molar [Mg]/[Ca] ratios of 0,8 ± 0,1 (the uncertainty representing experimental error). The range of this ratio for TMW's is 0,81 to 1,65 and the mean is 1,05. Thus the Tsumeb waters are consistently, and in most cases slightly, oversaturated with magnesium. This, rather than being anomalous, is to be expected /1204-5/. Wigley (1973 /1205/) stated that "groundwaters from dolomite rocks in cool climates frequently contain an excess of magnesium over calcium...This can only come about if the solution of dolomite is accompanied by the concurrent precipitation of calcite: this would necessarily lead to the incongruent solution of dolomite" (p. 1397).

The dissolution of dolomite is an irreversible reaction and the state of equilibration between this mineral and calcite and aqueous Mg^{++} can be approached from undersaturation only. Because all common salts of magnesium are more soluble than dolomite (see nomogram in Fig. 11, Appendix I), excess magnesium can be removed from solution only through the reaction

(s = solid) $$2CaCO_3(s) + Mg^{++} \rightarrow CaMg(CO_3)_2 + Ca^{++} ,$$

which is extremely slow. Thus it may be noted that magnesium occurs less frequently that caclium in TSS samples from TMW's, and in much lower concentrations (Table 3.41). That it occurs at all is probably because of the effects of co-precipitation or the presence of mechanically comminuted dolomite. It appears that Mg/Ca ratios will tend to climb above the equilibrium value in those dolomitic formational waters that are hydrologically active; i.e., whenever there is a continuous process of simultaneous corrosion of dolomite and precipitation of calcite, with a resultant accumulation of dissolved magnesium. This process is probably a natural state of affairs in any karstic, dolomitic terrane that is undergoing chemical weathering and erosion /1205/. Thus it may be noted that the mean molar Mg/Ca ratio for the waters from shallow boreholes in the Otavi Mountainland (Chapter 5) is 1,08 - almost exactly the same as the mean value in the TMW samples - although the range of observed values in the borehole waters is larger (probably because much greater variations in lithological environments and hydrogeochemical conditions are encountered in the host rocks). Furthermore, the ratio for the only Upper dilute Group Ib water, which is apparently an example of natural, unrecirculated recharge water, is also 1,08. According to Loewenthal (pers. comm.) the Mg/Ca disequilibrium can be expected to affect the dolomitic formational waters to a very great depth, provided that some slow exchange of water continues to take place there. This is because all waters entering the deep strata must, at some stage, have passed through shallower, weathered strata and will have carried along an excess of magnesium. This excess can be lost - if at all - only by the very slow ion-exchange processes that convert calcite into dolomite. Thus it may be noted that the deepset, least disturbed TMW's - the two samples of Group IIE - have molar Mg/Ca ratios of 1,05 and 0,99.

In most parts of the mine the corrosion of dolomite is likely to be accelerated by two factors, although it is impossible to say to what degree either of them boosts the natural rate of dissolution. The first factor is recycling of groundwater. Preferential precipitation of calcite will be promoted by recycling, for example through the loss of carbon dioxide or in water softening. There is no corresponding compound of magnesium that will be precipitated in nearly neutral waters. Secondly, the oxidation of sulphidic ore, with the release of corrosive sulphuric acid, will contribute to high Mg/Ca ratios if calcium is subsequently removed from the spent acidic solution as calcite. A very high Mg/Ca ratio could therefore, in theory at least, be regarded as a potential indicator of sulphidic mineralization in dolomitic host rocks. An examination of the analytical data shows that there is a weak tendency for the waters of Group IA (Stope waters, in contact with the shallowest, most aerated ore) to have elevated Mg/Ca ratios. However, the correlation is tenuous and it may be objected that it is meaningless, because the stope waters are also prime candidates for examples of directly recycled waters. Under the circumstances it can scarcely be claimed that the Mg/Ca ratio can be used for the purpose of delineating ore zones within the Tsumeb mine. In Chapter 5 (second orientation study of waters from shallow boreholes) it will again be shown that there is a vague but not unique relationship between the locations of sulphidic ore and high Mg/Ca ratios in associated groundwaters. It will also be shown that several serious difficulties stand in the way of using this ratio as a pathfinder.

(E) *Interim summary; The major components as pathfinders in TMW*

It does not appear to be possible, from this study of TMW, to identify any of the major components other than sulphate as a potential pathfinder. Sodium, chloride and sulphate appear to be recycled on a large scale, although the last of these is being leached from the ore in the upper levels. Calcium, magnesium, pH and bicarbonate are controlled more by the carbonic system than by other factors. Although the release of magnesium into the water may be related to the action of sulphuric acid from the orebody, there are important complications that vitiate the usefulness of this ion or the Mg/Ca ratio as pathfinders.

If any pathfinder other than sulphate can be identified in this study, it will be amongst the trace elements (subsection 4.6 following). It is nonetheless worth noting that recycling in the TMW's effectively disguised the role of sulphate as a pathfinder in several of the most important bodies of groundwaters occurring at depth. It remains possible that subtle but important features of the natural distributions around the mine of sodium and chloride have been totally overprinted by this recycling; one must consider the possibility that some proportion of the sodium chloride that is being recirculated was originally derived from the ore, just as the recycled sulphate was. The possible role of these two ions as pathfinders for sulphidic ore in the Otavi Mountainland should therefore be carefully reconsidered in the planned second orientation survey (Chapter 5).

4.6 The Hydrogeochemical Model (II): Inclusion of the data for the trace elements

(A) *INTRODUCTION*

The objects of this subsection are (i) to examine the data for the trace elements and to see how well the distribution of these elements correlates with the distribution of the major groups of waters encountered in the Tsumeb mine. (ii) on the basis of (i) above, to identify potential pathfinder trace elements, while bearing in mind the strict limitations imposed upon this task by the fact that most of the TMWs are recycled and are very probably no longer truly representative of the natural waters that would normally be in contact with the orebody.

The principle approaches that were employed in testing for meaningful patterns within the trace element data are summarized below. Most of the bulky tables of detailed computed data and statistical calculations have been omitted, especially where no positive features are demonstrated by them. Many elements that were analyzed but which proved to be of very little interest in terms of prospecting are discussed only briefly or not at all and the diagrams showing the distributions of these metals have been omitted in order to save space. These include silicon, which has a very uninteresting distribution and others such as Mn, Fe, Co, Mo, Ni and Sb, which were detected in so few samples that it was not worthwhile plotting the data. Yet others (Rb, Cs, V, Au, Ag, Al, Tl and Bi) had concentrations that were so consistently below the detection limit that it is impossible to comment upon their distributions. Chromium is an interesting special case. Most of the observed concentrations are near the detection limit and do not have an interesting distribution, but there are a small number of anomalous values that appear to be due mainly to the presence of kersantite dykes emplaced in and near the shallower portions of the orebody. It therefore seems likely that these chromium anomalies are specious and they have been ignored. The metal is in any case rather immobile /345,55,775/ and there is little chance that it could serve as a regional pathfinder for base metals /783/. This conclusion was supported by experiments described in Chapter 5.

(B) *EXAMINATION OF THE DISTRIBUTION DIAGRAMS FOR THE MORE IMPORTANT TRACE ELEMENTS, AND SOME RELATED STATISTICAL OBSERVATIONS*

(*Note*

Many of the variations of Fig. 1, and especially those showing the distributions of the trace elements, are reproduced in the text as paper prints rather than as sepia overlays in Vol. II. This was done with reluctance, but was necessitated by the escalating financial burden of reproducing the hundreds of diagrams required for the several copies of this thesis. During the interval between planning of the required diagrams and the final preparation of them the overall effective cost of sepia overlays rose about ten-fold. Nor do the computer-drawn diagrams used here compare in quality with those produced for the second orientation survey described in the following Chapters 5 and 6. This was because Chapters 1 to 4 were practically finalized before the new plotter, which has a very fine pen-increment and three pens, became available at UCT. The old plotter was so slow, and the demand on it so high, that it was not feasible to use it to make many copies of each diagram, as it is with the new instrument. Neither could the author justify the time and cost that would have been involved in re-creating all the diagrams for the mine water data with the new plotting programs so that they could be redrawn on the new plotter).

The abundance of a trace element in water will obviously be sensitive to factors that will hardly affect the concentration of a major component. It is therefore not surprising to find that the distributions of trace elements in TMW's, as depicted on the appropriate versions of Fig. 1, do not - *generally speaking* - appear to be closely correlated with the distributions of the major Groups of water. This observation was tested formally by a non-parametric statistical method /6/ and it was found that lithium alone showed a definite (95% confidence) tendency to vary systematically in concentration between all of the different groups; i.e., lithium is the only trace element that could be used with some confidence to characterize and identify each of the major types of TMW's. The rather random nature of the distribution of trace elements in these waters can be illustrated more directly by comparing smaller groups of samples with very similar major element compositions. Five such groups, comprising a total of fifteen samples, are shown in Table 4.6A. (The numbers used to identify these groups are arbitrary and have nothing to do with the numbering of the major types of mine waters described in subsection 4.2). Casual observation of these data suggests that the ranges of concentrations of most trace elements in any group are much wider than those of the major components of that group. This is confirmed by the data of Table 4.6, which shows, separately for each group, the ranges of observed concentrations of various chemical species as a percentage of the mean concentration of each. An example of how these numbers were derived is given at the foot of the table. It can be seen that bicarbonate, sulphate, calcium, magnesium, chloride, sodium and TDS have values less than 20%, i.e., these species have a relatively constant abundance. Lithium, potassium, strontium and silicon vary by about 20-30%, and tellurium, selenium and cadmium by about 40-70%. The values for all the other trace elements indicate much more variation. Closely related waters thus have different abundances of trace elements, and especially of heavy metals. Note in addition that the value for TSS is very variable. It seems likely that the concentrations of elements that are in colloidal suspension rather than in true solution, or which are readily hydrolyzed, will be profoundly influenced by the effects of simple filtration as the water percolated through the host dolomites.

Despite the general disorder in the data for the trace elements, many of the diagrams reveal some less universal trends and partial correlations that may be of significance in the process of identification of potential pathfinder species. Only a few trace elements have distributions that do not appear to be related in any manner whatsoever to lithological factors or other external controls. The diagrams for the individual trace elements are discussed below:

(1) *Trace elements that appear to be randomly distributed*

These are germanium (Fig. 1r), phosphate (Fig. 1v) and strontium (1x). High or low concentrations of each of these elements appear at random in the different groups of TMW's and there is no evidence, from the respective diagrams, that their presence is in any way related to the orebody or to specific geological features. Strontium is a common minor component of dolomites and other naturally-formed carbonate minerals (500-3000 µg/g; /35, 1203,1206/) and the strontium content of carbonate groundwaters is often as

TABLE 4.6A. EXAMINATION OF TRACE ELEMENT DATA FOR SEVERAL GROUPS OF MINE WATERS THAT HAVE SIMILAR MAJOR ELEMENT COMPOSITIONS

Group	*Group 1*					*Group 2*		*Group 3*		*Group 4*			*Group 5*		
Sample	156	131	134	136	150	148	137	154	161	141	138	142	164	151	144
TSS*	0,0000	0,0004	0,0536	0,0034	0,0008	0,0008	0,0008	0,0014	0,0000	0,0000	0,0002	0,0004	0,0002	0,0006	0,0000
TDS*	1,26	1,30	1,40	1,45	1,22	2,04	2,02	0,94	1,10	1,56	1,44	1,64	1,18	0,96	0,90
Mg**	90	99	91	96	92	115	115	102	115	89	95	91	74	84	80
Ca**	149	138	139	142	141	186	189	155	136	158	154	158	122	126	123
HCO_3^-**	538	537	531	546	536	428	433	192	190	477	473	482	555	561	556
Cl^-**	147	148	143	137	137	285	294	130	134	212	232	237	89	86	77
$SO_4^=$ **	343	352	320	350	330	712	717	631	638	422	455	436	230	204	216
F^-**	0,13	0,13	0,19	0,21	0,12	0,27	0,26	0,77	0,79	0,33	0,26	0,41	0,64	0,13	0,10
PO_4^{3-} **	0,167	0,023	0,054	0,077	0,198	0,171	0,045	0,230	0,063	0,059	0,054	0,122	0,189	0,203	0,117
Na **	126	138	129	126	119	172	176	109	115	142	143	146	53	88	83
K **	10	11	10	9	10	12	11	15	15	9	8	8	3	8	7
Li ***	13	11	8	10	10	13	12	29	27	10	9	9	6	8	7
Sr ***	350	213	188	225	263	263	263	263	225	150	188	175	213	300	338
Cr **	0,003	0,003	0,006	0,006	0,007	0,004	0,003	0,008	0,011	0,003	0,006	<0,001	0,014	0,006	0,006
Mn **	<0,028	<0,028	0,141	0,338	<0,028	<0,028	<0,028	<0,028	<0,028	<0,028	<0,028	<0,028	<0,028	<0,028	0,028
Fe ***	<30	<30	50	67	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Mo ***	<10	<10	<10	<10	<10	<10	<10	<10	10	<10	<10	<10	<10	<10	<10
Co ***	<1,5	2,6	5,6	13,2	8,2	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	1,9
Ni ***	<2,2	<2,2	3,3	<2,2	5,0	<2,2	<2,2	<2,2	<2,2	<2,2	<2,2	<2,2	<2,2	<2,2	<2,2
Cu ***	<10	<10	<10	<10	<10	10	40	10	91	20	<10	<10	<10	<10	<10
Zn ***	43	50	36	86	<20	29	50	1800	292	57	20	43	29	<20	43
Cd ***	0,9	1,1	1,4	0,7	0,7	1,5	1,5	320	100	1,7	4,6	1,2	0,6	0,4	0,8
Hg ****	167	111	1278	777	389	2111	3777	56	56	2666	2722	2722	<56	389	667
Si **	2,0	1,5	1,7	2,0	2,0	1,3	1,7	1,7	1,0	1,3	1,3	1,3	1,3	2,3	1,7
Ge ***	<3	57	7	90	64	33	80	30	30	<3	13	13	<3	55	13
As ***	<4	1	12	4	10	17	12	17	26	18	10	9	<4	<2	<1
Se ***	185	218	80	112	158	168	239	115	240	104	240	241	105	125	85
Te ***	35	48	62	49	37	48	143	40	21	87	67	70	19	21	15
Pb ***	4,6	6,4	94	4,5	4,8	10,4	20,0	15,9	13,3	10,8	12,1	9,7	42	1,9	18,3

* = g/l. ** = mg/l. *** = µg/l. ****= ng/l.

TABLE 4.6B

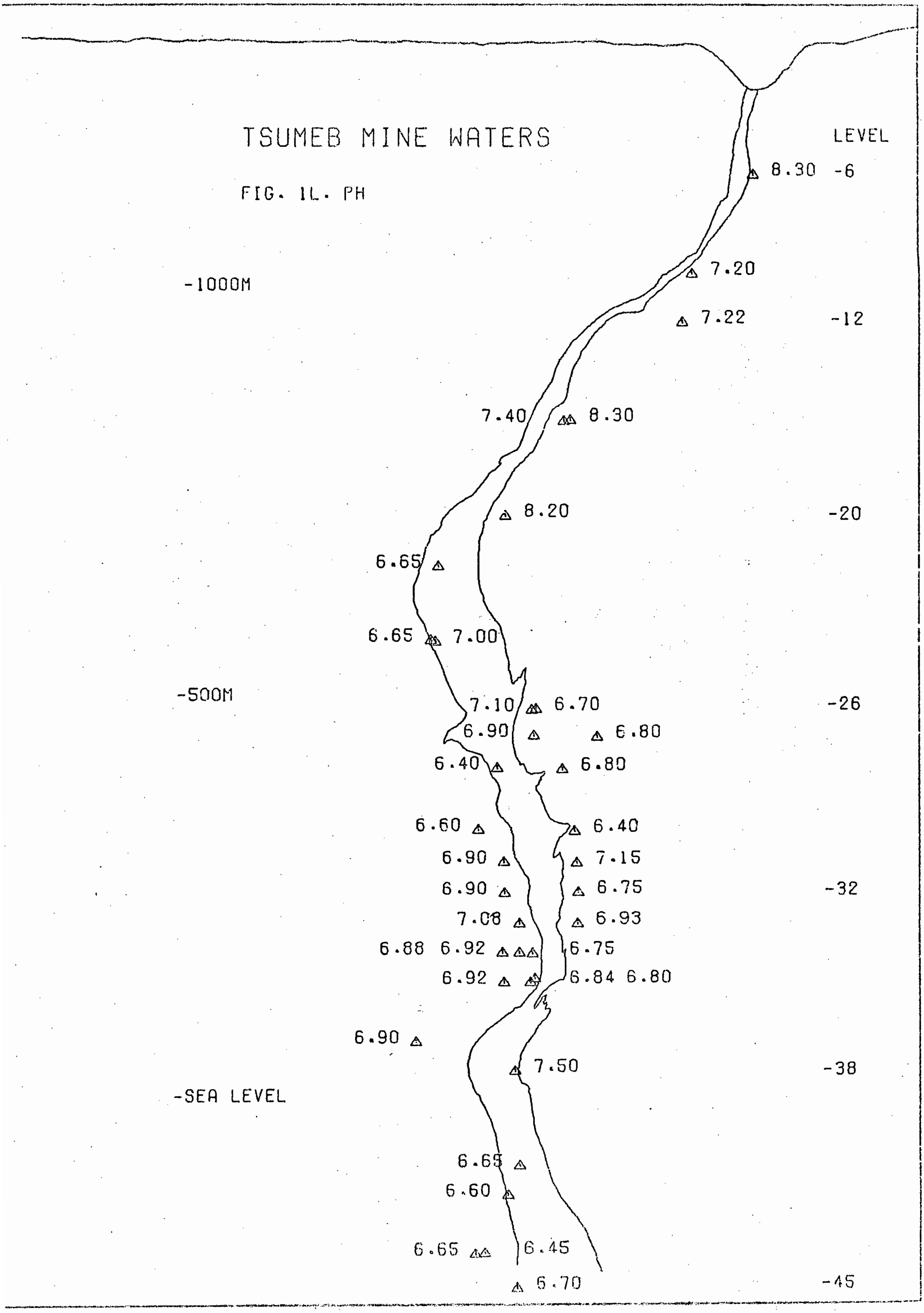
The range of observed concentrations of various chemical species as percentage of the mean of the concentrations for the five groups of related waters defined in Table 4.6A

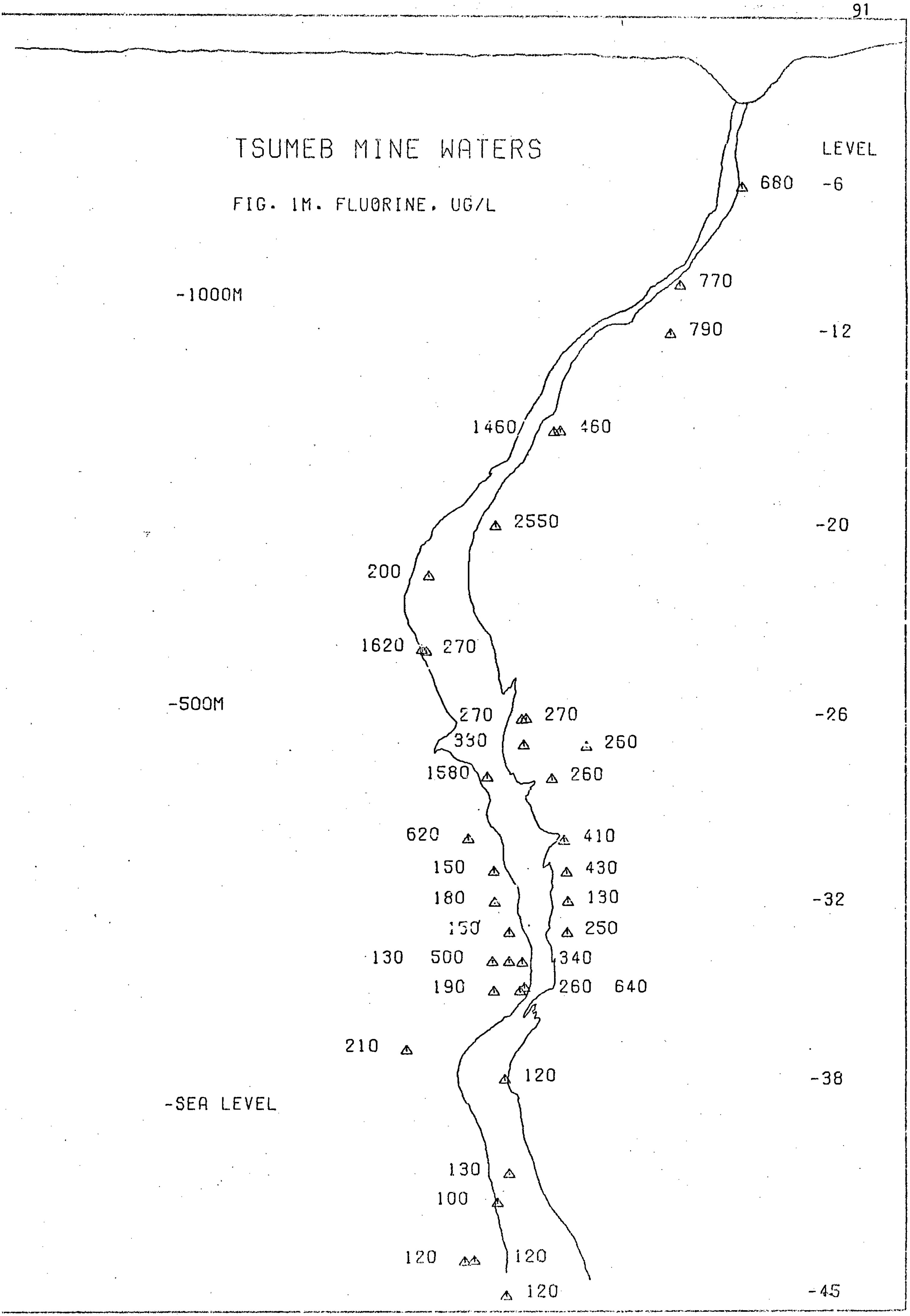
	(A) Range of values as a % of mean					(B) Mean of 5 values in (A)
			Group			
	1	2	3	4	5	
TSS	460	0	200	200	150	203
TDS	17	1	16	13	28	15
Mg	10	0	12	7	13	8
Ca	8	2	13	3	3	7
HCO_3^-	3	1	1	2	1	2
Cl^-	8	3	3	11	14	11
F^-	58	4	3	45	160	67
$SO_4^=$	9	1	1	8	12	10
$PO_4^{\equiv}$	169	116	114	89	51	108
Na	15	2	5	3	47	31
K	20	9	0	12	95	27
Li	48	8	7	11	29	21
Sr	65	0	16	22	44	26
Cr	80	29	32	>150	92	>90
Mo	-	-	>0	-	-	-
Mn	>275	-	-	-	-	>275
Fe	>89	-	-	-	-	>89
Co	>188	-	-	-	>34	>188
Ni	>94	-	-	-	-	>94
Cu	>0	120	160	>75	-	140
Zn	>140	53	144	93	>75	97
Cd	73	0	105	85	67	66
Hg	233	57	0	2	>165	117
Si	16	27	52	0	57	31
Ge	>197	83	0	>103	>220	>100
As	>177	34	42	73	-	>95
Se	92	35	70	173	38	65
Te	63	99	69	27	33	38
Pb	391	63	18	22	193	156

Example: From Table 4.6A, the values for TDS in Group i are 126, 130, 140, 145 and 122 mg/l. The mean is 132,6. The range is 145-122 = 23, which is 23 x 100/132,6 = 17,3% of the mean. This is rounded to 17 and entered above in the columns marked (A), under Group 1. Values are similarly calculated for Groups 2 to 5. The mean of the row of five values in (A) (17, 1, 16, 13, 28) is 15,0 and is recorded as 15 in the column marked (B). Some semi-quantitative approximation is unavoidable when several inequalities are involved because many of the concentrations were below the detection limit. The units used for concentrations are the same as those of Table 4.6A.

TSUMEB MINE WATERS

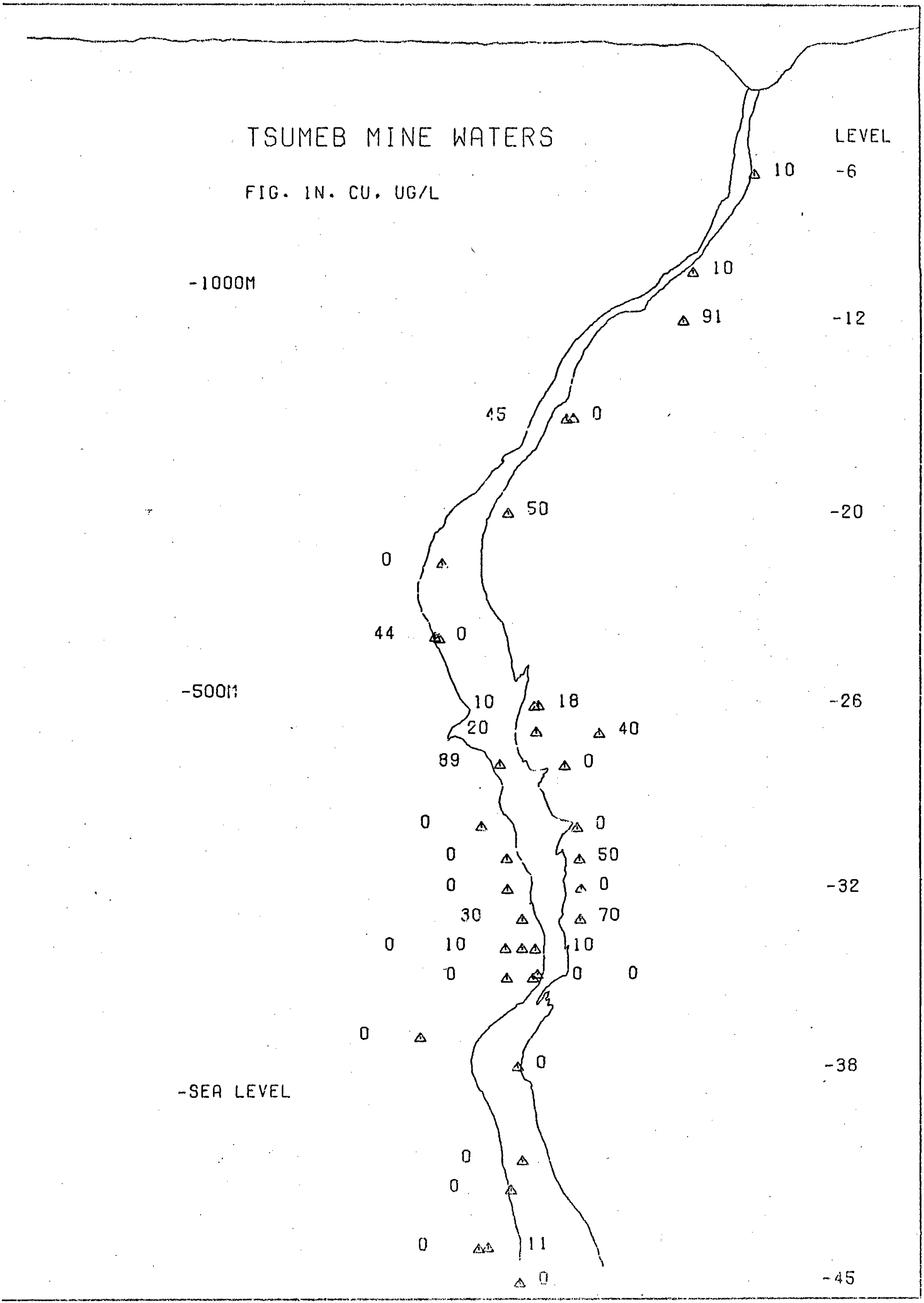
FIG. 1L. PH





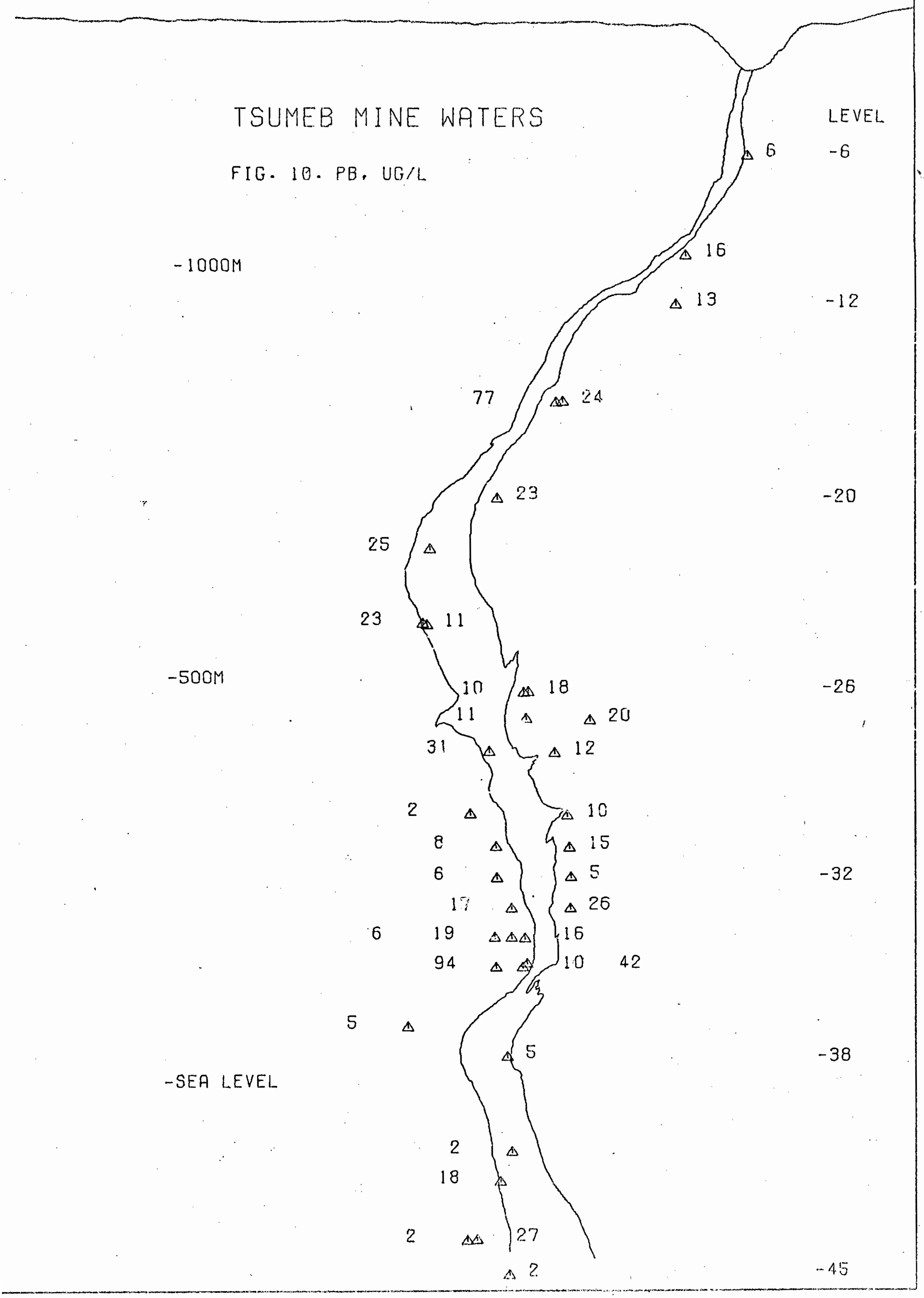
TSUMEB MINE WATERS

FIG. 1M. FLUORINE, UG/L



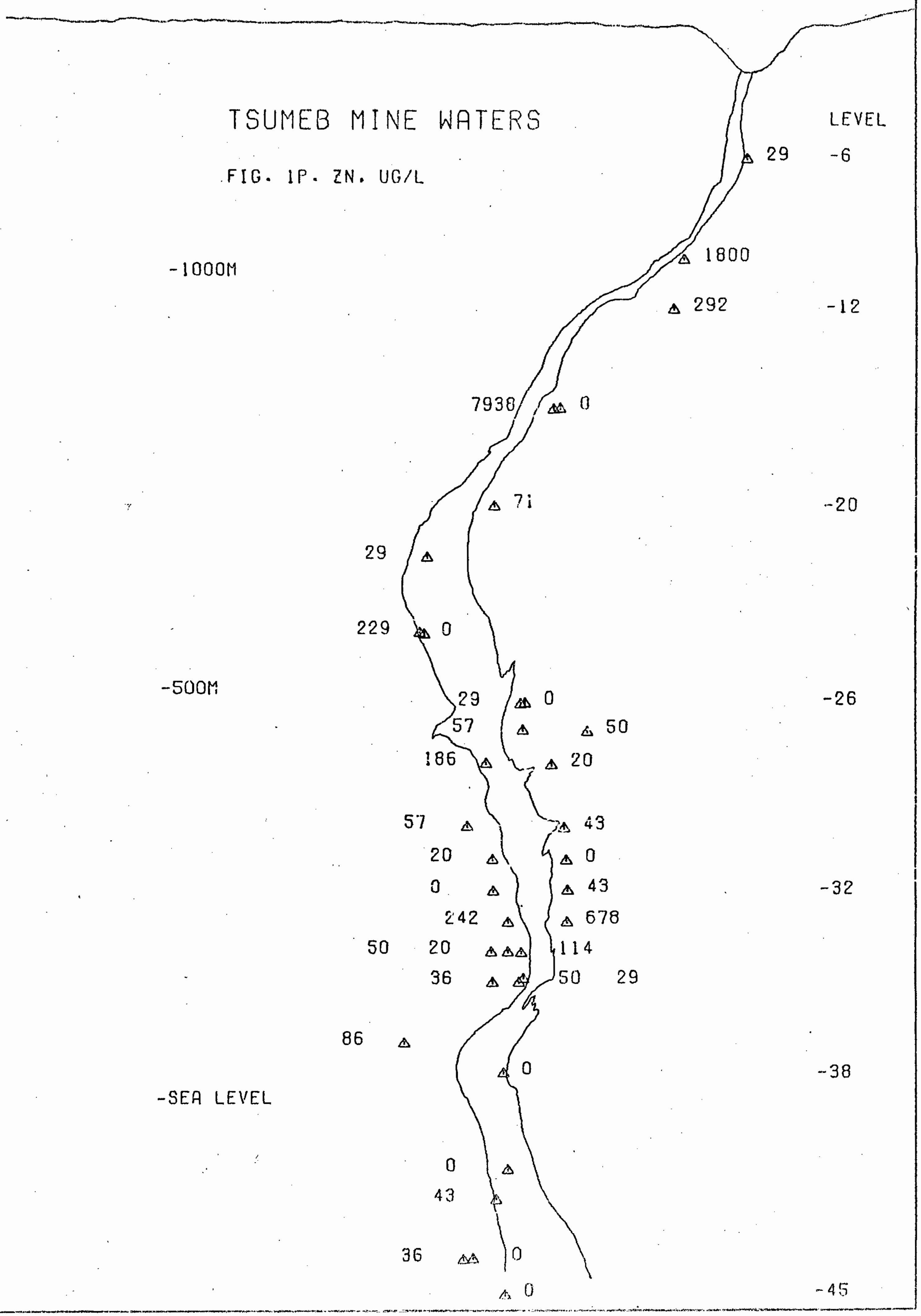
TSUMEB MINE WATERS

FIG. IN. CU, UG/L



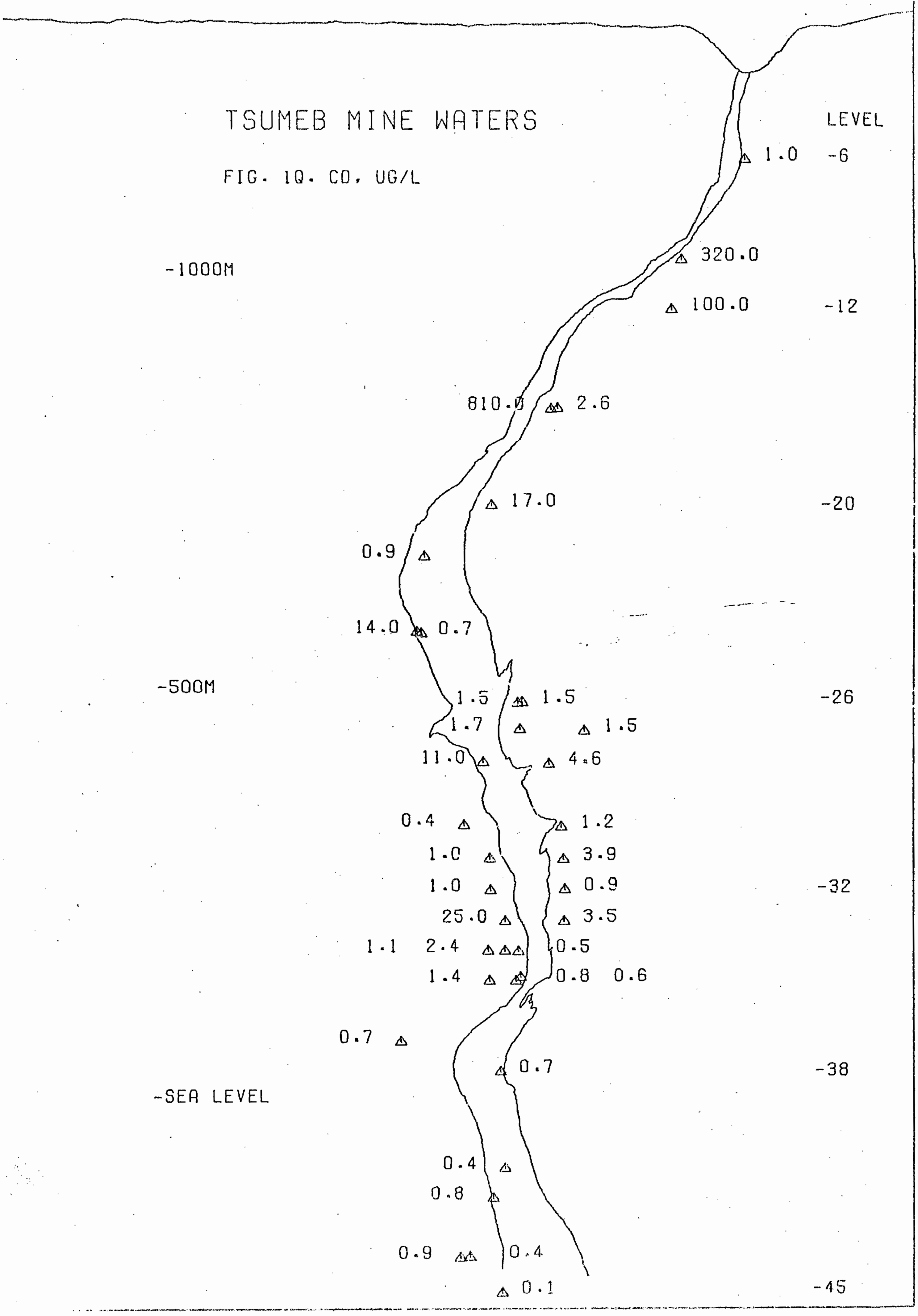
TSUMEB MINE WATERS

FIG. 10. PB, UG/L



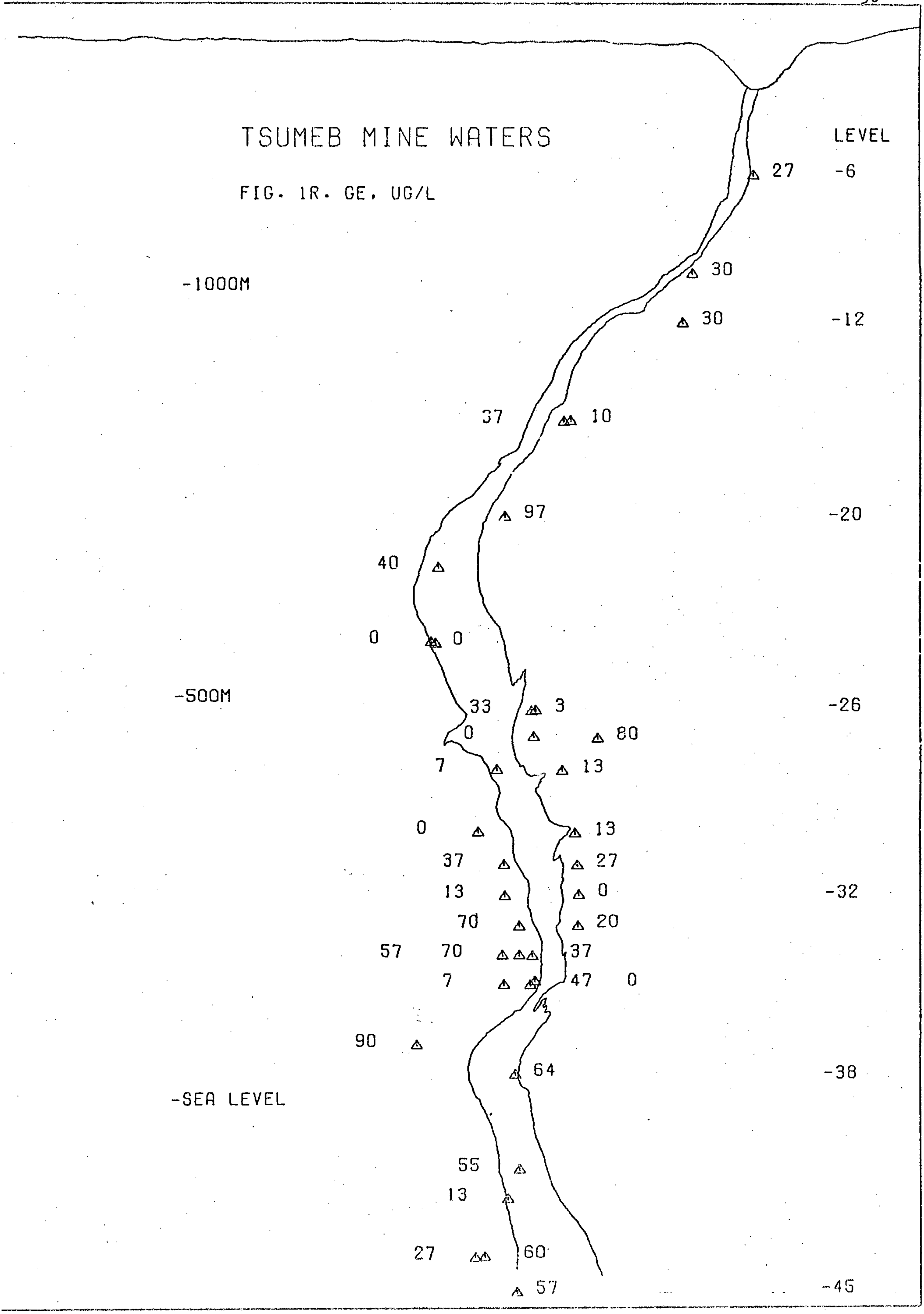
TSUMEB MINE WATERS

FIG. 1P. ZN. UG/L



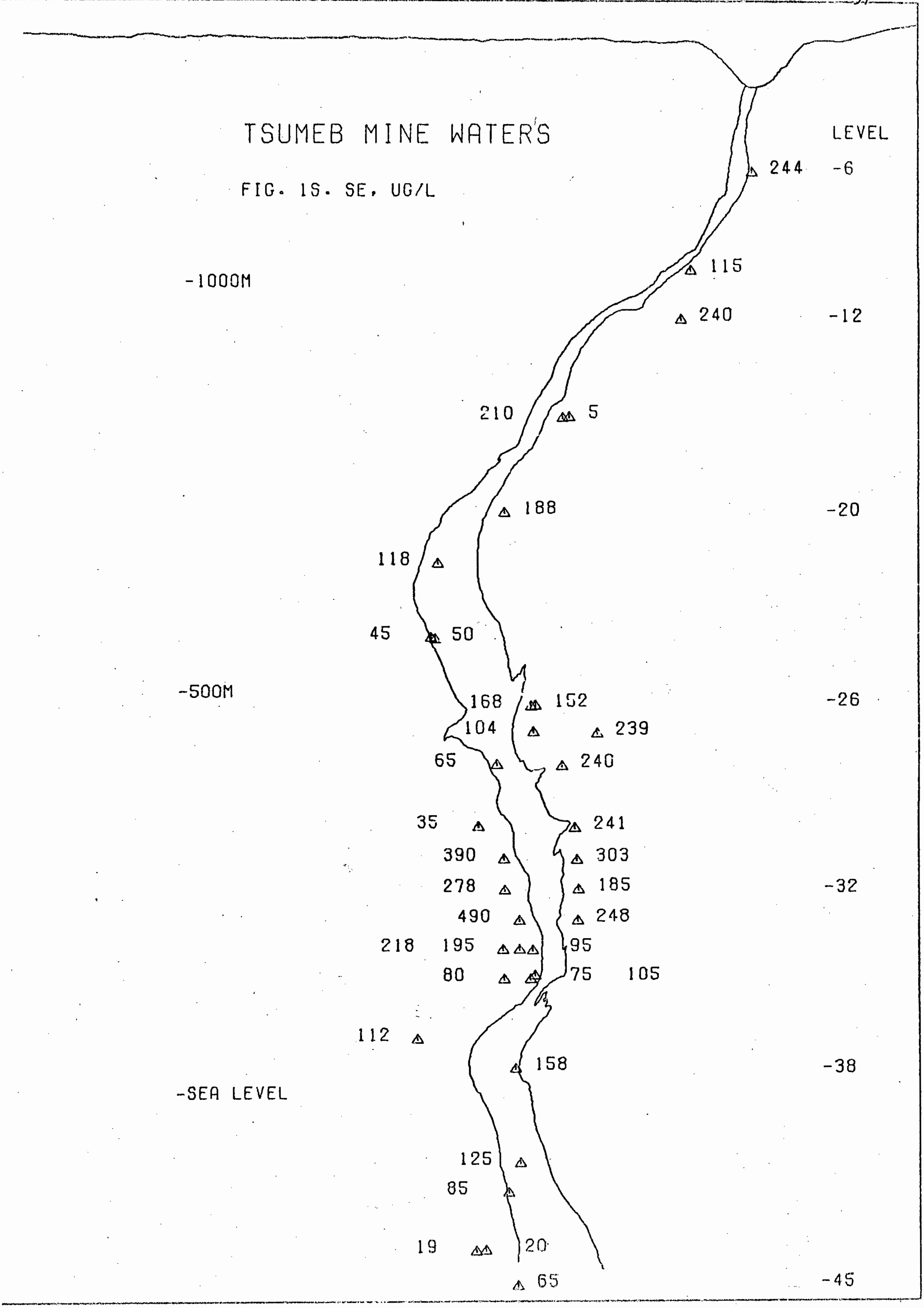
TSUMEB MINE WATERS

FIG. 1Q. CD, UG/L



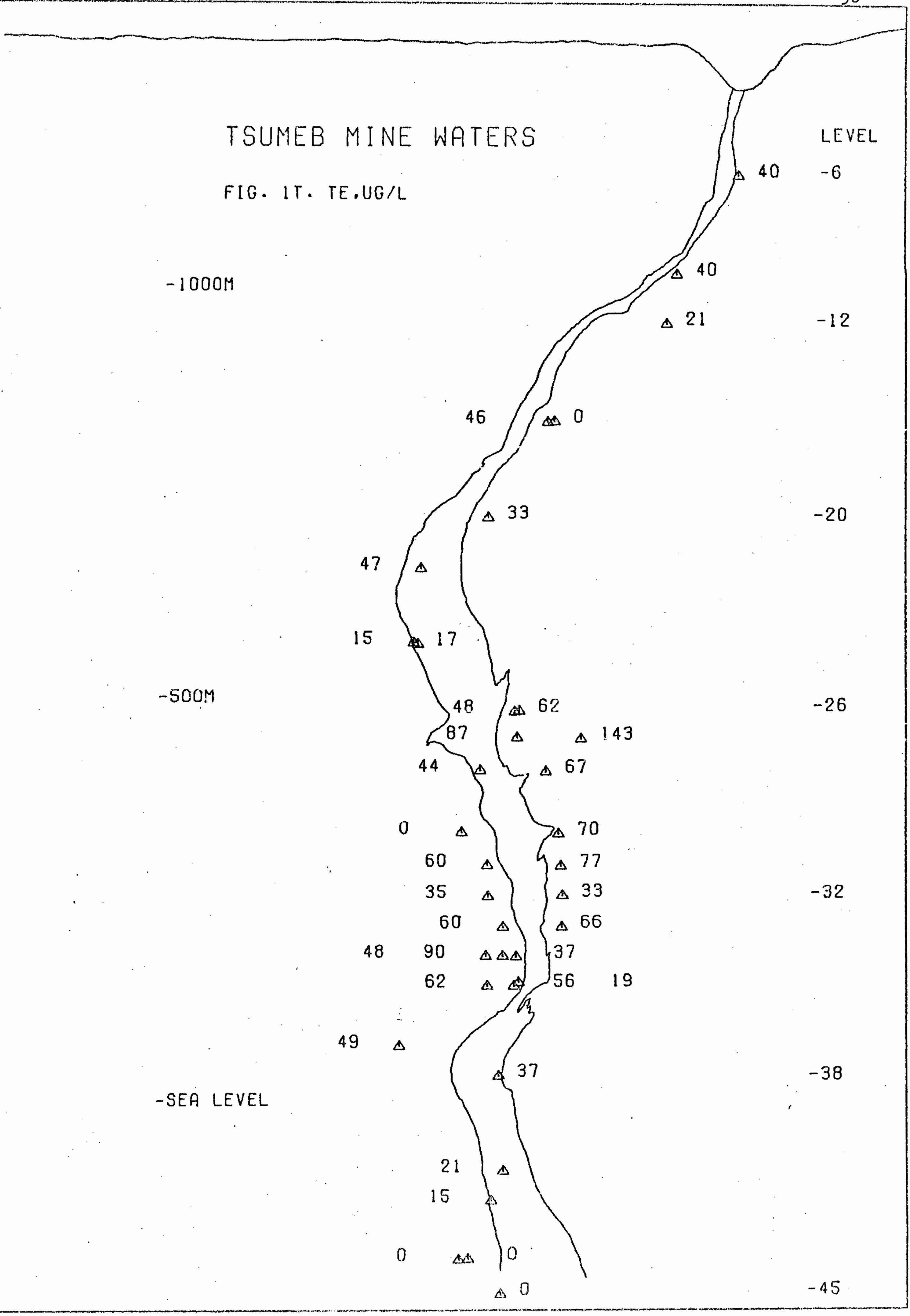
TSUMEB MINE WATERS

FIG. 1R. GE, UG/L



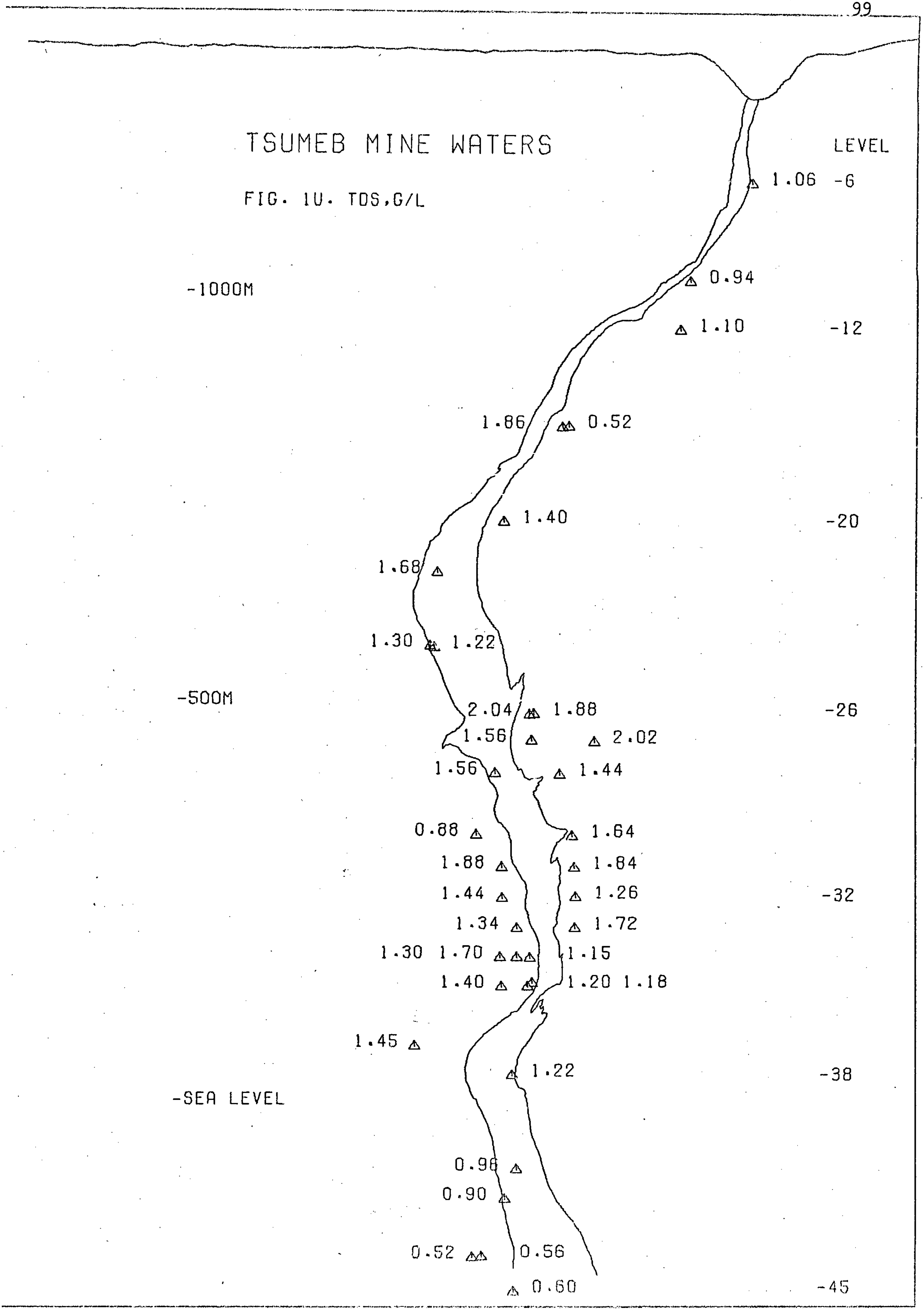
TSUMEB MINE WATERS

FIG. 15. SE, UG/L



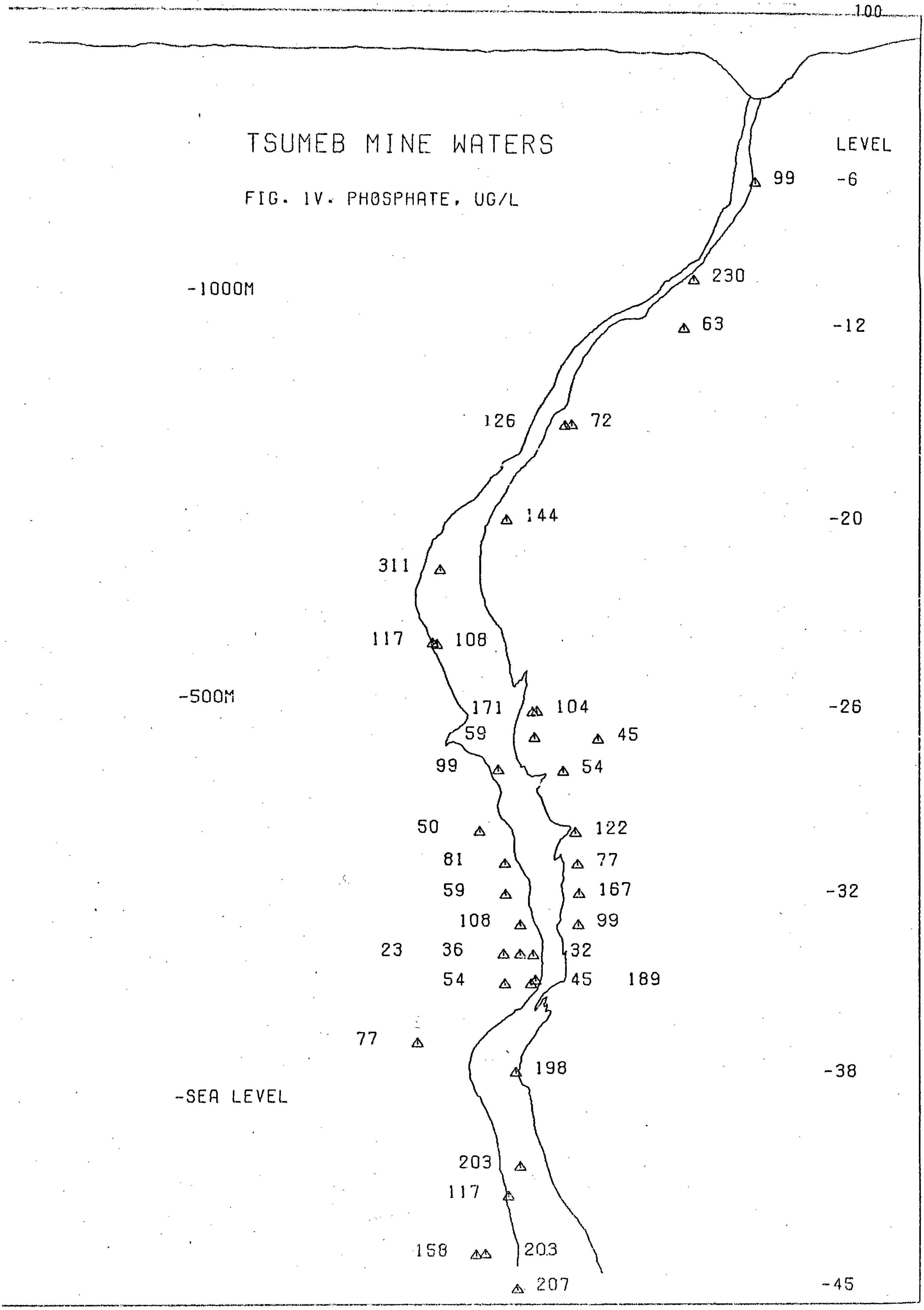
TSUMEB MINE WATERS

FIG. 1T. TE,UG/L



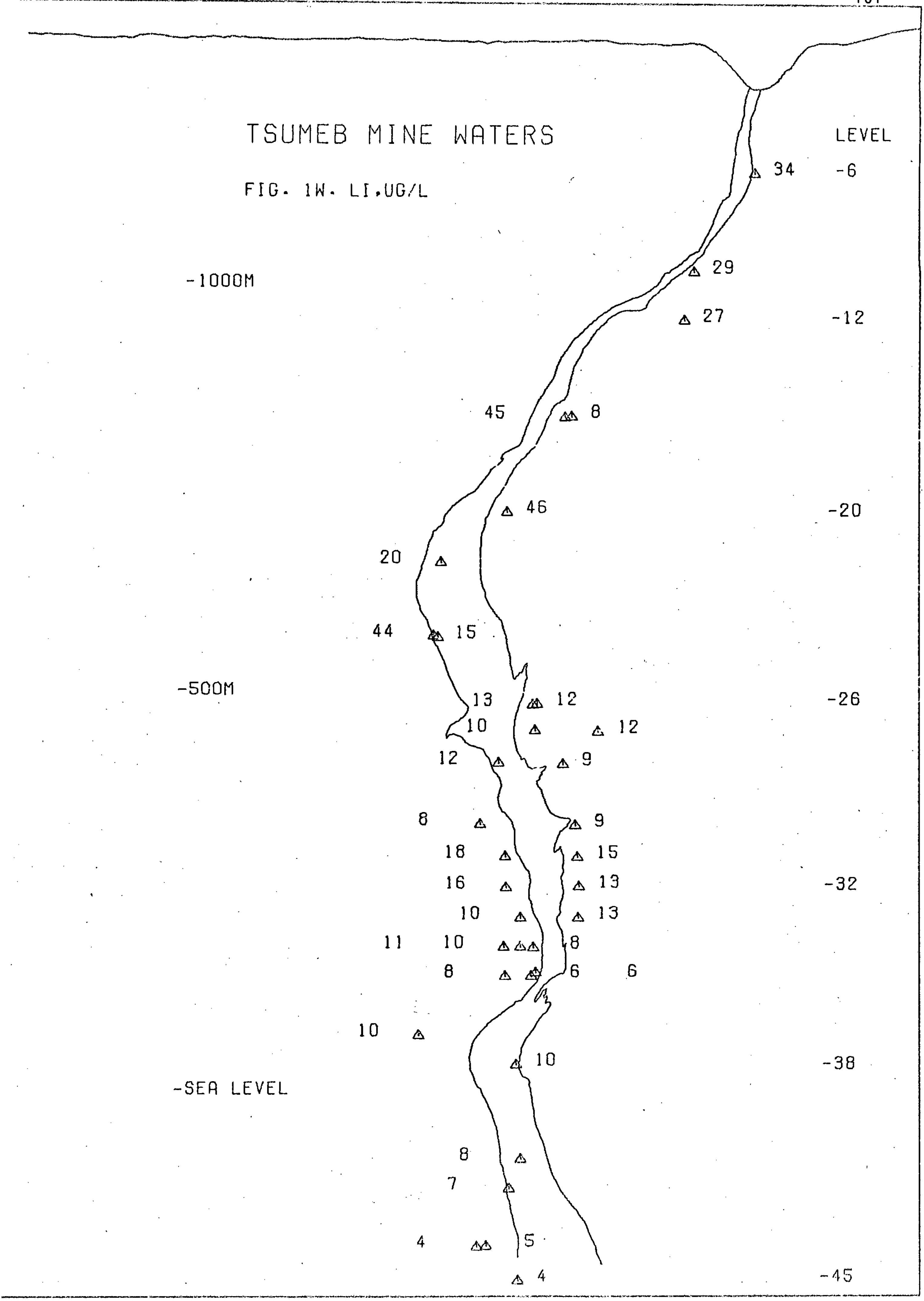
TSUMEB MINE WATERS

FIG. 1U. TDS,G/L



TSUMEB MINE WATERS

FIG. IV. PHOSPHATE, UG/L

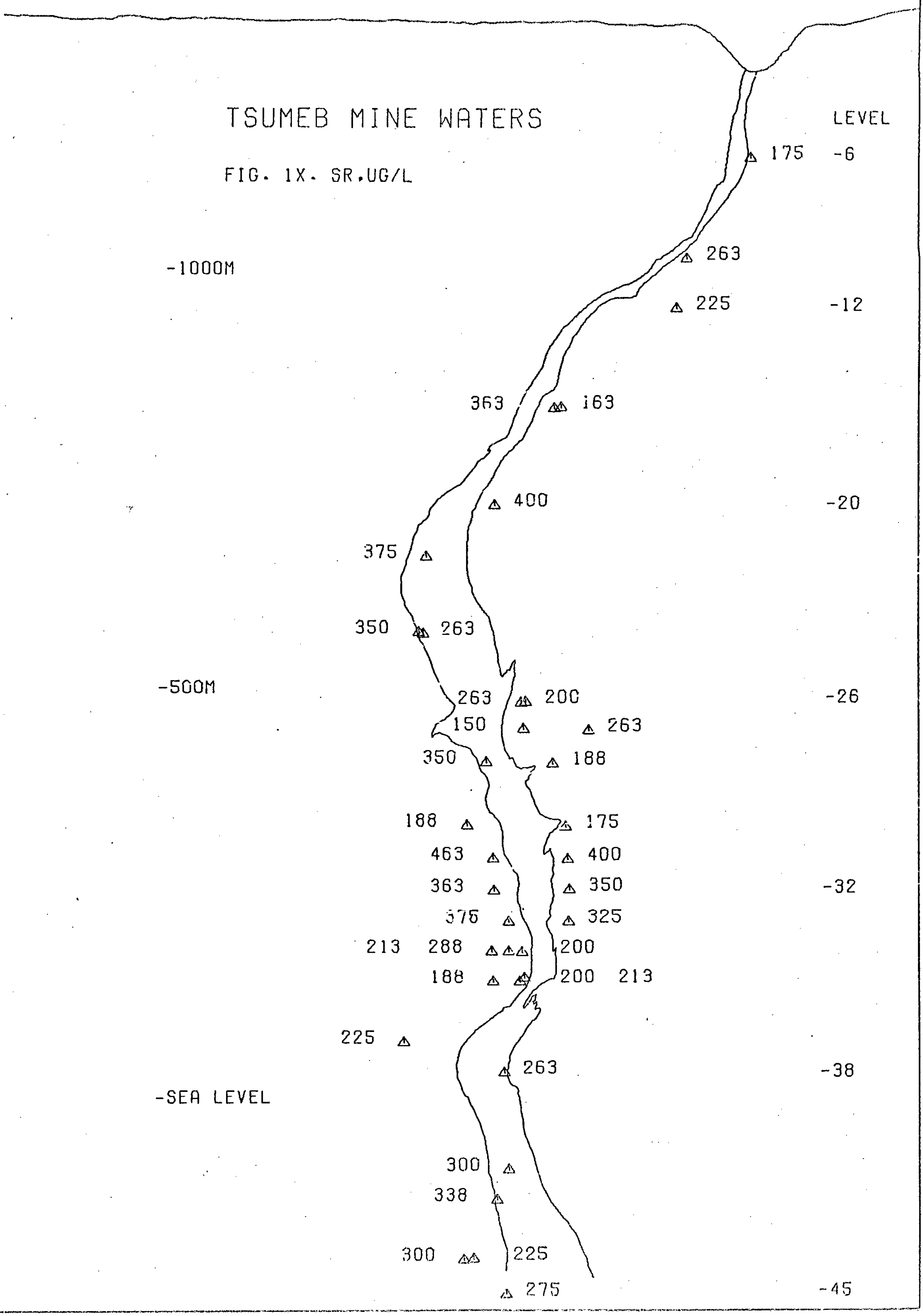


TSUMEB MINE WATERS

FIG. 1W. LI,UG/L

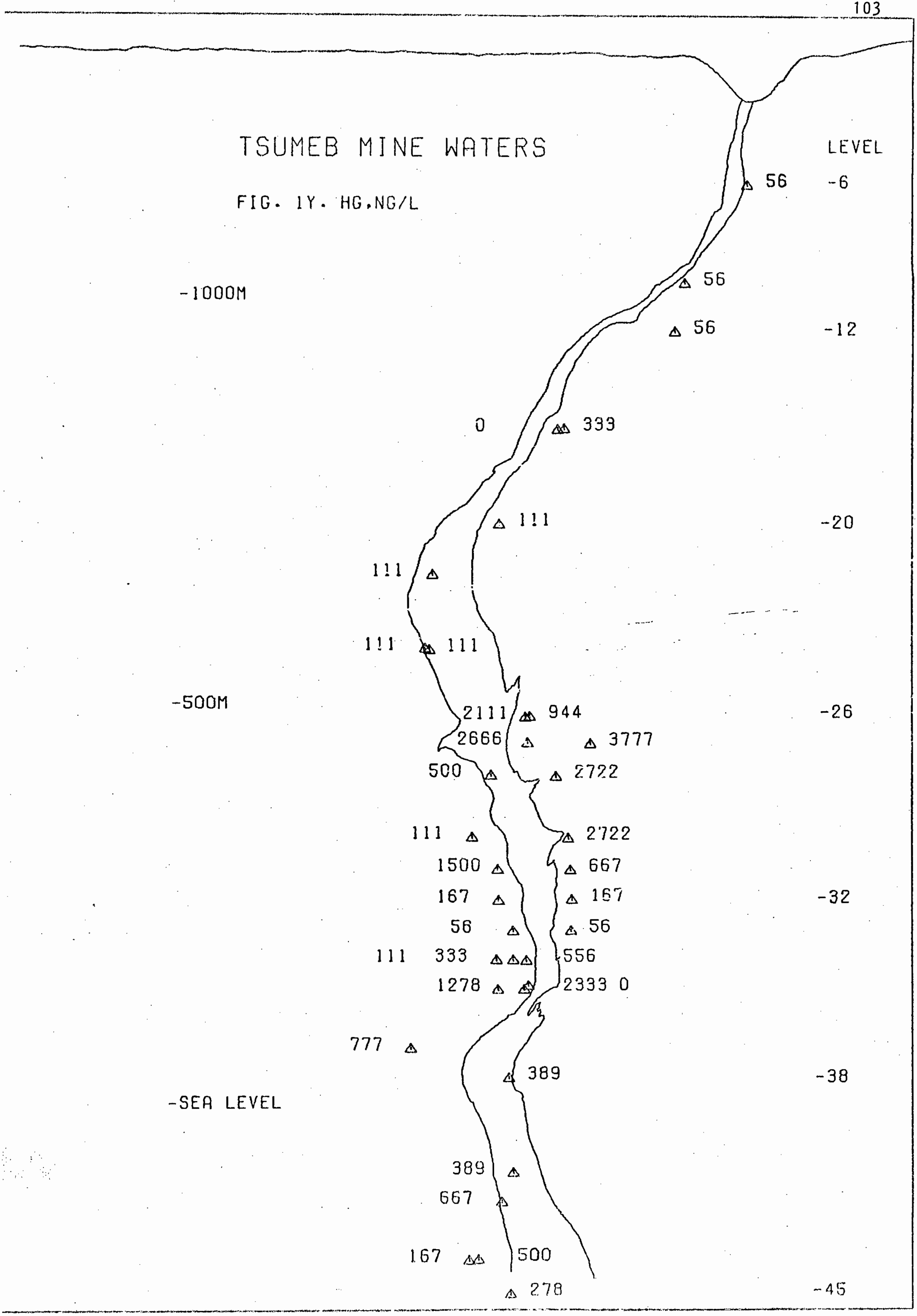
TSUMEB MINE WATERS

FIG. 1X. SR.UG/L



TSUMEB MINE WATERS

FIG. 1Y. HG,NG/L



high as one milligram per litre /35/. The concentration of the metal in the Tsumeb ore is unknown.

Phosphate, too, can be a common minor component of many carbonate rocks /35/, but is a trace element (about 10 µg/g /52/) in the Tsumeb ore. Little is known about the abundance of phosphate in unpolluted groundwaters /35/ but 60 µg/l is regarded as a typical figure. It is known that the phosphate content of formational waters does not correlate well with the lithology of the host rocks.

The behaviour of germanium is a little more difficult to understand. Its concentration in carbonate groundwaters is typically 0-60 µg/l /35/. The element is not generally concentrated in limestones, but may be encountered at levels from less than 0,1 to 1 µg/g in these rocks. The amount of the element in the Otavi dolomites near the Tsumeb mine is not known but may well be higher than average, since the element is somewhat concentrated in the Tsumeb ore and for a time it was extracted as a by-product and sold. The metal is present in significant amounts throughout the orebody (/1174/ and Appendix E). The mean value is apparently about 50 µg/g but there were zones, especially on the shallower levels, where concentrations of 1000 to 1700 µg/g were encountered (Appendix E). It is unclear why there are no germanium anomalies in waters such as those of Groups IA or IIB and it will certainly be worth taking a second look at the distribution of this element in the planned second orientation study of the shallow borehole waters of the Mountainland (Chapter 5).

(2) *Trace elements that are more concentrated in some groups of mine waters than in others*

These are potassium (Fig. 1i), fluorine (1m), copper (1n), lead (1o), zinc (1p), cadmium (1q), selenium (1s), tellurium (1t), lithium (1w) and mercury (1y). These all show a tendency to be relatively less abundant in the dilute waters of Groups 1B, IID, IIE and IIF and correspondingly more abundant in Groups IA, IIA, IIB and IIC. It has been shown that these latter, more saline, waters have probably been recycled and that the reliability of any pathfinders provisionally identified in them must remain uncertain until checked by a second orientation effort using undisturbed groundwaters.

The significance of either potassium or lithium as pathfinders is dubious. The range of potassium is small (1-35 mg/l) and although the metal tends to be more abundant in the more saline waters this is probably because potassium to some extent follows sodium through the cycle of recirculation.

The range of observed concentrations of lithium is from 4 to 46 µg/l and the distribution of the metal is strongly and inversely related to depth below the surface. The deepest waters have 4 to 8 µg of lithium per litre. The shallow waters of Groups 1A and 1B have the highest values (8-46 µg/l, of which the second lowest value is 20 µg/l). The waters at intermediate depths have from 6 to 44 µg of lithium per litre, with the second highest value being 18 µg/l. The cause and significance of this trend are unknown. The lithium content of the Tsumeb pipe is unknown. The dispersion of lithium around the outcrop of the orebody should be checked in the second orientation survey.

Fluorine is a trace element in the Tsumeb ore (about 50 µg/g /52/) but is known to serve as a useful pathfinder for some types of base metal deposits /830,969/. On the other hand, fluorine is often present in appreciable amounts in carbonate rocks /35/ and may simply have accumulated in the TMW from that source during recycling or because of acidic attack on the host rocks. The distribution of this anion must be re-examined in the second orientation exercise.

Selenium and tellurium are homologues of sulphur and occur in the Tsumeb ore in concentrations of less than 100 µg/g /52/. Nonetheless they are, in a relative sense, strongly concentrated in the Tsumeb pipe along with germanium and arsenic /52,1171/. There is some doubt about the magnitude of the Clarke values for selenium and tellurium /1200,1202/ but the ratio (ppm/ppm) for S:Se is estimated at between 9400:1 and 15 000:1 and for S:Te at about 470 000:1. But in the Tsumeb ore these proportions are around 800:1 and 2000:1 respectively. There is very little published information about the use of selenium or tellurium in hydrogeochemical exploration. Neither element is normally as mobile as S(VI) in the supergene environment /35,61/. Nevertheless, it has been shown that these elements can become highly concentrated in mine waters. Faramazyan and Zar'yan /808/ reported mean values of 640 µg Se and 45 µg Te per litre in waters from a base metal mine. The proportion S:Se:Te was 60 000:14:1. The corresponding values for TMW are about 158 µg Se/l, 45 µg Te/l and 3285:3,7:1. Both of these elements tend to show a maximum abundance in the recycled waters between 26 and 35 levels. High concentrations of selenium are also found in the shallow IA waters, but tellurium is less well-represented there. The significance of these features of the distribution of the two elements is uncertain. The second orientation study should show whether complexes of these metalloids are capable of migrating beyond the immediate vicinity of the ore.

The remaining base metals (Cu, Pb, Zn, Cd and Hg) are all present in the orebody in amounts in excess of 100 µg/g and the first three are major components of the ore. All five metals - and especially zinc and copper - have been used as pathfinders for deposits of base metals /48,345,802,822, 1033,1035,1039,1096/.

Mercury is present in the mine waters in very small absolute amounts (56 to 3800 ng/l) and most of the peak values occur near the North Break Zone in waters of Group IIB. This is very significant because it is known that mercury mineralization is practically confined to the North Break region of the pipe (Appendix E).

Copper and lead anomalies occur in all parts of the mine above 33 level. This is generally true for zinc also, but the extreme values for this metal occur in waters of Group IA, which are particularly well exposed to oxidized ore.

Cadmium tends to follow zinc geochemically and it is therefore reasonable to find that the peak values for cadmium are also in samples from Group IA. The metal is a valuable minor component of the ore (mean value 400 µg/g; range up to 0,5% in some parts of the mine /52/, Appendix E) and is recovered for sale.

The abovementioned five base metals all appear to be potential pathfinders for mineralization in the Otavi dolomites and must be studied closely in the planned additional orientation work.

(C) *ADDITIONAL GRAPHICAL METHODS*

Various calculated parameters such as (trace element/TDS) ratios and sums of components (e.g. [Cu] + [Pb] + [Zn]) were plotted and examined. In addition, a great deal of effort was expended in trying to get useful information out of the raw data by casting the samples into groups on the basis of similarity of Durov diagrams /486/ and related graphical representations of composition (/247/: Appendix D). This effort was, in the opinion of the writer, totally fruitless and the many diagrams and graphs that were developed are therefore not included here.

(D) *NONPARAMETRIC REGRESSION CORRELATION ANALYSIS OF ALL TMW DATA*

The examinations of the TMW data described in foregoing subsections have revealed several significant relationships between variables (e.g. pH with depth and Na with Cl^-). In order to search sytematically for any additional, potentially useful inter-relationships in the TMW data, the BMDP program for nonparametric correlation /281/ was used. Values of zero or less than the detection limit were deleted.

Any correlation analysis that is performed on data that sum to 100% is bound to produce some essentially meaningless correlations because of the effects of closure /1192/. Furthermore, many of the variables encountered in this case are not really independent of all other variables. Sodium and chloride, for example, must obviously be related; these two ions and the other major components must necessarily correlate with TDS. Moreover, it is well known that some trace elements tend to concentrate in waters with high TDS values / 1143/; these therefore also correlate well with TDS and a host of cross-correlations is spawned. Examples: (i) Zn with TDS; Na with TDS; therefore Zn with Na. (ii) pH varies with depth as pCO_2 rises (subsection 4.5); temperature of the groundwater rises with depth (geothermal gradient); therefore pH is correlated with temperature.

It is thus not surprising and certainly not very useful to find that 99 out of 496 possible correlations are significant at the 99% level of confidence. Many of these correlations are ridiculous; for instance the concentration of chromium is inversely proportional to air temperature. One way around this problem is to select only the very highly significant correlations by setting the confidence levels extremely high. The writer has arbitrarily forced the number of "significant" correlations down to about 5% of the maximum number of combinations by setting the threshold coefficient at about 0,70, which corresponds to a level of confidence well in excess of 99,99%. These highly significant correlations are compiled in Table 4.6C. Most of these correlations are predictable or were already obvious from the examination of the variants of Figure 1. Thus (i) the temperature of the water and the concentration of lithium are related to depth below surface. (ii) TDS correlates with many major components, which therefore show correlations amongst themselves. (iii) Lead, being relatively immobile /55/ and probably present in many of the mine water samples largely as a suspension /52/, correlates strongly with TSS. (iv) It was shown that most of the peak values for selenium and tellurium were associated with saline waters near the NBZ; hence the correlations between these two elements and NaCl. (v) Cadmium follows zinc closely.

The only remaining (i.e., previously unnoticed) correlations are those between lithium and bicarbonate and fluoride. These probably result from the fact that the concentrations of all three ions are related to depth below surface. In any case the relationships are not obviously useful from the point of view of exploration.

It appears that correlation analysis of the TMW data has provided scant additional information that might be of use in identifying pathfinders in this project.

(E) *ESTIMATION OF THE OCCURRENCE OF ANOMALIES IN WATERS RECENTLY IN CONTACT WITH ORE*

TABLE 4.6C

Highly significant correlation values for TMW data

Correlated parameters	Value	Sample size
Water temperature-Level	0,79	36
TDS-Ca	0,82	36
TDS-Cl^-	0,85	36
TDS-sulphate	0,78	36
TDS-Na	0,84	36
Mg-Ca	0,71	36
Mg-sulphate	0,86	36
Ca-sulphate	0,84	36
Bicarbonate-sulphate	-0,72	36
TSS-Pb	0,70	24
Na-Cl^-	0,94	36
Te-Cl^-	0,79	31
Na-Se	0,71	36
Na-Te	0,74	31
Zn-Cd	0,98	27
Li-Level	-0,71	36
Li-bicarbonate	-0,74	36
Li-F^-	0,77	36

It was shown in subsection (B) above that the distributions of trace elements were not generally related to the principal types of mine waters. An alternative possibility is that the trace element anomalies occur in only those samples, of whatever type, that had been in contact with large masses of weathered ore shortly before being collected. This hypothesis was tested by constructing a table (Table 4.6D) showing how the five highest values for each important trace element (plus sulphate) are distributed amongst the thirty six orientation samples. The six samples that were collected from oreboxes (Appendix A) are specially marked in the table. IF the hypothesis is correct then the samples from the oreboxes - i.e. those waters that had definitely been exposed to some significant degree to broken ore - ought to be well represented amongst the anomalous samples identified in this table. The correlations in the table can be regarded from the point of view of either "rows" or "columns":

(i) Column correlations show the tendency of individual elements to concentrate in orebox waters rather than in waters from other sources. At the bottom of Table 4.6D is a row of totals that show how many of the peak values for each element were recorded from orebox waters. Thus two of the five samples most anomalous in molybdenum came from this type of source. On the basis of pure chance these totals should each have a value of one. It appears therefore that Mn, Co, Ni, Hg, Se , Te and Pb are not being freely liberated from the broken ore. (The values for iron and antimony are indeterminate since neither of these metals was present in amounts that could be termed anomalous in more than one or two samples; see Chapter 3). A value of 2 for the total can be regarded as possibly significant but could also be due to coincidence in a high proportion of cases. Molybdenum, copper, germanium and arsenic fall into this group. Zinc and cadmium, with values of 4 or 5, are almost certainly being released in relatively large amounts from the ore. This observation is generally in keeping with the findings of the foregoing subsections and with the known hydrogeochemical properties of these metals /55,802/.

Sulphate has a value of three and it, too, is certainly being released by the ore (cf. subsection 4.3, where it was shown that recirculation cannot account for all of the sulphate present in the majority of orebox or stope waters).

(ii) Row correlations show the tendency of individual orebox samples to be rich in several trace elements. On the right hand side of Table 4.6D is given the total number of anomalous values associated with each sample of mine water. Also given is the corresponding subtotal for those species - Ge, As, Se, Te and S - that tend to form anionic complexes. The data for Fe and Sb are included in these totals. It can be seen from a comparison of this

TABLE 4.6D

The distribution of the five most anomalous values for each of several elements determined in the orientation samples of Tsumeb Mine waters

Sample number																	TOTALS	
↓ ↓ ↓	Mo	Mn	Fe	Co	Ni	Cu	Zn	Cd	Hg	Ge	As	Sb	Se	Te	Pb	S	all	anion
131																	0	0
132	x	x		x	x					x	x	x		x			8	4
133																	0	0
134		x	x	x	x										x		5	0
135					x				x								2	0
136		x	x	x						x							4	1
137									x	x				x		x	4	3
138									x								1	0
139																	0	0
140	x					x					x				x		4	1
141									x					x			2	1
142									x					x			2	1
143																	0	0
144																	0	0
145*	x		x								x						3	1
146																	0	0
147																	0	0
148																x	1	1
149															x		1	0
150				x	x												2	0
151																	0	0
152	x										x						2	1
153																	0	0
154*							x	x									2	0
155*							x	x							x	x	4	1
156																	0	0
157		x		x									x				3	1
158						x							x	x			3	2
159													x				1	1
160*					x	x		x		x	x					x	6	3
161*	x					x	x	x									4	0
162																	0	0
163																	0	0
164															x		1	0
165						x	x						x				3	1
166*		x					x	x		x			x			x	6	3
→ → →	*2*	*1*	*(1)*	*0*	*1*	*2*	*4*	*5*	*0*	*2*	*2*	*(0)*	*1*	*0*	*1*	*3*		

↑
↑ ← ← Totals for oreboxes. * indicates samples from oreboxes.

TABLE 4.6E

A comparison of the concentrations of various elements in the Tsumeb orebody and in the waters of the mine ([E]$_r$/[E]$_w$)

	[E]$_r$ (%)^1	[E]$_w$ (µg/l)^2	[E]$_r$/[E]$_w^3$	NOTES
Cu	4	<10	>-1	
Pb	12	10	0	
Zn	3	10	-1	
Ag	0,000001	<10	>-7	OM
Au	0,000001	<100	>-8	OM
Cd	0,04	1	-2	
Ge	0,005	10	-4	
As	1	10	-1	
Sb	0,015	<10	>-3	
Hg	0,01	0,1	-1	
Se	0,005	100	-5	
Te	0,002	10	-4	
Tl	0,0005	<1	>-4	TY*
V	0,001	<10	>-4	OM SE
Cr	0,001	1	-3	OM SE
Mo	0,05	<10	>-3	
Mn	0,01	<10	>-3	OM SE
Re	<0,0001	ND		OM TY
Co	0,0005	<1	>-4	SE
Ni	0,002	<1	>-3	
Ga	<0,0001	ND		OM TY
In	<0,0001	ND		OM TY
Sn	0,001	ND		OM SE
P	0,001	10	-4	OM SE
Bi	0,0001	<10	>-5	OM
F	0,005	100	-5	
Cl	0,05	100000	-7	
Br	<0,0001	ND		OM TY
Fe	1,5	<10	>-4	
Si	9	1000	-2	
Ca	14	100000	-4	
Mg	5	10000	-4	
Al	0,5	<10	>-2	
S	4	100000	-5	
$CO_3^{=}$	20	100000	-4	
K	U	10000		
Na	U	100000		
Li	U	10		
Rb	U	<10		
Cs	U	<10		
Sr	U	100		

(1) Most [E]r values are from run-of-the-mill ore between 1964 and 1974 /52, 30/. (2) All [E]w values are order of magnitude. (3) The ratio is expressed as a power of ten. *Codes:* U = unknown; ND = not determined; the following apply to [E]r only: OM = order of magnitude; TY = concentration in baghouse dust over ten year period; Se = spectral estimate; * = may be higher than estimated.

table with Table 4.2, and also from the variants of Figure 1, that samples that are highly anomalous with respect to several individual elements occur widely in the groups of mine waters that were designated IA, IIA, IIB and IIC (subsection 4.2). However, the anomalies are not evenly distributed amongst these waters and a few samples are very "multi-anomalous" compared to the other samples of TMW. This is true for both the total trace element patterns and for the nonmetallic ("anionic") microcomponents. Some of the orebox waters are multi-anomalous, but many of the most multi-anomalous waters did not come from oreboxes. Only 28 out of a total of 74 (38%) individual anomalous entries (marked with an x) in the table are associated with the orebox waters. The success rate for the anionic species (9 out of 30 = 30%) is somewhat poorer.

One must conclude that there does not appear to be much chance of producing a useful multi-element index of anomalousness for Tsumeb Mine waters, such as those proposed for certain North American and Soviet base metal deposits /1097,1030/.

(F) *COMPARISON OF THE RELATIVE ABUNDANCES AND MOBILITIES OF THE DISSOLVED ELEMENTS IN TSUMEB MINE WATER*

Another feasible method of attempting to pinpoint potential pathfinder elements is to examine the relative mobilities of various microcomponents in waters closely associated with the orebody being studied /50/. A comparison was made of the average concentration of each element in the TMW's ([E]w) with the corresponding average concentration in the orebody ([E]r). Table 4.6E gives the approximate average concentrations of various elements in Tsumeb ore /30,52/ and in the mine water. In most cases this is given on an "order of magnitude" basis. The ratio ore/water is given as %/µg/l, the units being relative and unimportant. A high value for this ratio characterizes those elements that are poorly represented in the water compared to their concentrations in the ore; the smaller the value of the ratio, the greater the relative hydrogeochemical mobility of the element concerned. The ratios recorded in the table vary from 10^0 to 10^{-7}, which is an extremely wide range. Some values for the ratio can be given only as inequalities because either the numerator or the denominator has a concentration less than the detection limit. The data in the table can be summarized as follows in terms of the ratio [E]r/[E]w (power of ten):

-7 Cl (Au)
-6 (Ag)
-5 S F Se (Bi)
-4 Ge Te P Ca Mg C as HCO_3^-
-3 Cr (Tl) (V) (Co) (Fe)
-2 Cd Si (Sb) (Mo) (Mn) (Ni)
-1 Cu Zn As Hg (Al)
0 Pb

The elements given in parentheses are those for which the values of the ratio are inequalities. They are placed in the lowest possible category in which they may occur. For example, the real position for bismuth may be in the 10^{-4} class or in a higher class, but it is definitely not in the 10^{-6} class.

The distribution of the elements analyzed amongst these groups is a fair reflection of their general periodic properties. The non-metallic elements show lower ratios and the metallic elements higher ones. The heavy metals are, without exception, concentrated towards the upper end of the range and not one of them is singled out as particularly and relatively abundant. On the contrary, the list may perhaps be regarded as an indication that anionic species such as S, Se, Te and F are potentially the most useful pathfinders in TMW.

These results are only partly consistent with the conclusions reached in the foregoing subsections. However, it is probably not reasonable to make a direct comparison between the pathfinders "identified" by these radically different approaches; the one using the plotted data tests for individual anomalies well above the threshold value, while the one using rock/water concentration ratios is concerned with average mobilities in all samples. Nevertheless, the latter approach supports the writer's belief that no unexpectedly mobile element has been accidentally overlooked or underemphasized during the search for pathfinders.

4.7 Conclusion of Section II. Evaluation of the Tsumeb Mine as a site for hydrogeochemical orientation surveys

(A) *Summary discussion*

The reader will recall that in Section 1 of this work we examined the possibility of and procedures for locating buried orebodies similar to the Tsumeb deposit. It was decided that it would be desirable to do some initial orientation work on waters closely associated with this type of ore and the obvious place for this was at the Tsumeb mine. This approach is theoretically sound /53/ and has been used successfully by several workers /113,115-6,511, 121/.

The study of the Tsumeb Mine waters has nevertheless shown that one cannot confidently establish well-defined hydrogeochemical exploration criteria for an ore deposit like the Tsumeb body from a study of the waters that presently circulate through that body. The reasons for this are readily apparent. In hydrogeochemical exploration one rarely finds a situation where the relationship between ore and the distribution of dissolved trace elements is not affected by independent factors such as hydrology, geology and major element hydrogeochemistry. If these variable extraneous factors become powerful, then the interpretation of the relationship between the distribution of dissolved trace elements and the location of ore becomes correspondingly more difficult. In the preceding subsections it has been demonstrated that the hydrogeochemical situation in the Tsumeb mine is a particularly complex one, strongly influenced by the existence of dynamic, separate bodies of water, recycling, accumulation of ions and variations in geological setting. The hydrological regime can be outlined only in a rather general manner and the effects of these individual influences cannot be properly resolved in most cases.

It is therefore not surprising to find that important difficulties are encountered in trying to construct a rational picture of the behaviour of trace elements in TMW's, or in attempting to identify any indicator elements dissolved in them. Several workers have run into similar problems while attempting to use mine waters for orientation purposes /800,512,541/. Suetin /1150/, in particular, warned that orientation studies of the waters of orebodies should preferably be completed before mining commences, since the mining operations may cause serious changes in the composition of the groundwater associated with the ore.

Nonetheless, the study of the waters of the Tsumeb mine has provided a short list of elements and ions that should be carefully re-examined in a second orientation exercise and has given some indication of what analytical methods to use and what levels of concentration may be expected for the various dissolved components. The list of "most probable" candidate pathfinders comprises the base metals copper, lead, mercury, zinc and cadmium, of which the last two are particularly favoured, and sulphate, lithium, selenium and tellurium. The "less probable" candidates are molybdenum, germanium, arsenic, sodium and chloride ion.

(B) *Summary conclusions and recommendations*

The study of the Tsumeb orebody and its waters has not provided a shortcut to the development of a hydrogeochemical prospecting method for locating sulphide ore in the Otavi dolomites. The alternative available at the termination of the study of the mine waters was to attempt a new orientation project using waters from surface boreholes situated in the vicinity of known ore deposits. The nature of such an orientation survey makes it much less susceptible to the kinds of problems encountered in the study of the mine waters. (Some complications due to recycling were encountered in the second study, but proved to be of only minor significance). The second orientation survey is described in Section 3, following.

SECTION 3. ORIENTATION STUDIES USING NORMAL SHALLOW GROUNDWATERS AND THE APPLICATION OF THIS INFORMATION TO THE SEARCH FOR ORE IN THE KALAHARI AREAS

Chapter 5. Orientation studies of the hydrogeochemistry of groundwaters from boreholes and other subsurface sources in the vicinity of the Tsumeb and Kombat mines

5.1 Introduction

This portion of the thesis is constructed similarly to the preceding one (mine water orientation) but is considerably shorter, because many points and principles covered in the foregoing chapters, and in the Appendices, are also relevant to this chapter and need not be repeated.

The reader should note especially that a great deal of ancillary experimental data, which are germane to this section, have been removed from the text and placed in Appendix J. This appendix includes the results of pumping tests on and contamination studies of boreholes, contamination tests on the sample containers, tests to monitor the stability of water samples and studies of seasonal changes in the compositions of borehole waters. The principle results of these experiments are included in the summary given at the end of this chapter.

There are cogent *prima facie* reasons /49/ for expecting to find significant changes in the compositions of ordinary groundwaters that have been influenced by either weathered sulphidic ore or the lithogeochemical anomalies associated with deposits of these ores. This is especially true of the Tsumeb and Kombat orebodies, which are well-oxidized and have been -at least until recently - abundantly supplied with groundwaters from the host dolomites during the process of weathering. Sohnge /67/ noted that the weathering and oxidation of the upper part of the Tsumeb orebody caused metal-rich waters to be fed both down into the hypogene portions of the lode and away from the pipe into the country rock.

To test the relationship between known, shallow orebodies of the Damara dolomites and the chemistry of adjacent groundwaters (as sampled from the surface), some 80 sources of groundwaters in the Otavi Mountainland were selected for study. Most of these were boreholes marked on TCL maps, or perennial springs. Boreholes and springs are fairly common in this region and there was little limitation on the geographical distribution of selected sources. Many of the water sources originally selected could not be used, however, usually because of collapses in the boreholes or inoperative pumping equipment. In all 54 sources were eventually sampled. This gave good coverage of two large orebodies (Tsumeb and Kombat), as well as coverage of several independent areas with no known major mineralization, which were taken to be background zones. Three points should be made clear at the outset:

(1) It was a foregone conclusion that the orientation work was going to be somewhat inadequate (cf. discussion in Section I). The two orientation targets - the orebodies at Tsumeb and Kombat - are emplaced in dolomite, exposed at the surface, and heavily dewatered. Our would-be target orebody will be thickly covered by overburden permeated by formational waters that possess hydrogeochemical characteristics unlike dolomitic waters, and will not have been strongly dewatered or affected by recirculation. There is nothing that can be done about this, for we do not have a known orebody conveniently buried under 20 metres of calcrete and sand. We can but study the hydrogeochemical halo of the ore in the dolomite, and observe the chemical patterns in the waters of the Kalahari areas, and then make hopefully intelligent guesses about how the former should look were it superimposed upon the latter. This is dangerous, but everyone involved in an exploration project of this type has to come to terms with the fact that we are geochemists and not magicians.

(2) The type of pumping equipment installed on the various water points that were sampled varies greatly. They are powered by hand, wind, electricity or internal combustion engines running on a variety of fuels. Only a few sources, e.g. springs, did not have any kind of pumping hardware nearby. A danger of contamination therefore exists in most cases (Appendix J). Any attempt to minimize metallic contamination by dismantling the pumping equipment and using a down-hole sampler was out of the question for several reasons:

(i) It is often highly impractical and in some cases almost impossible to dismantle these installations. Plate 2 gives some idea of what is involved.

(ii) Many boreholes are cased to unknown depths or have submersible pump casings which cannot be removed.

(iii) Most farmers will in any case not permit the dismantling of pumping equipment, because to do so would endanger their water supply and hence their livelihood. Nor will they permit one to lower a sampler for fear of it jamming and blocking the borehole.

(iv) Boreholes that had not been pumped for some time prior to sampling (described as "standing holes") needed to be pumped for a while before sampling, in order to clear stagnant water, rust, organic matter etc. from the hole.

Thus it was necessary to use the borehole installations as one found them, and to make the most of the data obtained from them in this manner.

(3) The hydrology of this part of Namibia is not well known /270/ and a bare

minimum of hydrogeochemical and hydrological data and information from borehole logs was available to the writer. Much of this limited collection of data was provided by the Administration of the Territory on the clear understanding that it was not to be reproduced in detail here or elsewhere; it is permissible only to make very general comments about the implications of these records. Nevertheless, this information proved to be very useful and has had an important influence on many of the general deductions that the writer has based on the chemical data compiled in this thesis.

There was no question of being able to supplement the small store of unpublished hydrological records with additional studies of this kind. Neither the time not the equipment was available for an undertaking of this nature. This is a fairly average state of affairs in practical hydrogeochemical exploration projects. Although the importance of hydrology in these undertakings is widely recognized /55,1080,1007,992/, most workers have found that it is seldom feasible to combine large-scale hydrological and chemical studies of groundwaters during prospecting ventures.

5.2 Sampling

The general procedures followed during sampling were similar to those described in Chapter 3. It was decided to modify the method by acidifying one aliquot of each sample with nitric acid at the collection point. (Note, however, that it is undesirable to add an *oxidizing* acid to water samples that are to be analyzed for metalloids such as Se and Te by the hydride reduction procedure /171-3/; see Appendix B4 for details. Hydrochloric acid may be used for these samples). The samples were acidified for the following reasons:

(1) Many of the samples had to be transported for long distances over poor roads and up to 14 hours elapsed between sampling and freezing. The samples from the mine were always frozen within six hours. (Appendix J3 shows that the major components in the samples collected during the second orientation study were not affected by the extra delay before analysis).

(2) Many of the borehole waters are rich in micro-organisms. When exposed to sunlight, these can effect radical changes in the concentrations of some elements within minutes /1187/. These organisms are indisposed at low pH values.

(3) Many of the waters are very hard and saturated with respect to compounds such as calcite, iron hydroxides, phosphates etc. Undesirable precipitation and co-precipitation effects are prevented by acidification.

(4) Acidification, in addition to freezing, reinforces the immobilization of trace elements that are stored for some time prior to analysis /55,49,1002, 1004,158/

(5) The orientation study of the mine waters had shown that many of the elements of interest in dolomitic waters may be partly in suspension and partly in solution. Most of this suspended matter is soluble in dilute acid and addition of the acid is therefore desirable in order to achieve a determination of the total concentration (suspended conc. plus dissolved conc.) of the analyte in the sample.

The effect of the addition of nitric acid on the pH of local waters is shown in Table 5.2. The addition of even 10 ml of acid lowers the pH to less than 2.

At each sampling point six one-litre HDPE bottles with press-fit, plastic closures were filled as follows:

(a) two, unacidified, for wet chemical analyses immediately upon return to the laboratory.

(b) four, filled to a previously-marked 800 ml reference line, with 20 ml of Analar grade nitric acid (Merck) added immediately from an auto-dispenser. These samples were placed in a freezer immediately after returing to Tsumeb, and kept at -20^{0}C until required.

Samples were collected as near to the source as possible and in some cases this entailed the dismantling of piping. Pumps that had been idle for more than a couple of days were allowed to run for at least ten minutes before a sample was collected (see Appendix J for details). A record was made of the type of source and pumping equipment and of the pH and temperature of the water. Any available hydrological data was noted. Sampling was completed during March 1974.

5.3 Summarized analytical data and results

Details of the analytical methods used will be found in Appendix B. Most of the methods used have already been encountered in the examination of the analytical data collected during the study of the mine waters (Chapter 3 and the corresponding subsection B3 of Appendix B). New or modified methods used for the first time in the second orientation study are compiled in subsection B4 of that appendix, which also contains details of checks on precision etc.

Because of doubts about the the ultimate reliablity and usefulness of the hydrogeochemical exploration criteria established in the first orientation study of the disturbed and recycled Tsumeb Mine waters, it was decided to re--examine in the second study all of the species that had been determined in the first one. Particular attention was, of course, paid to the determination of the "candidate" pathfinders identified in the mine waters. The only observations made during the first orientation and not repeated during the

TABLE 5.2

Effect of nitric acid, added as a preservative, on the pH of local waters

Sample	Original pH	+10 ml HNO_3	+20 ml HNO_3
Tsumeb tap water[1]	7,0	1,x	0,x
Otjikoto Lake[2]	7,0	1,2	0,8
Otjikoto Lake[2]	8,7	1,2	0,7
Borehole 1	6,8	-	0,5
Borehole 2	6,8	-	0,2
Borehole 3	6,1	0,6	-

(1) Mean values for several samples.

(2) The pH varies in different parts of the lake.

The original volume of all aliquots tested was 400 ml.

second were air temperature and rate of flow of the source of the water. The following observations and determinations remained essentially unchanged, except for some minor variations in the volumes of reagents used, or in the blank procedure, which may have resulted in slightly different detection limits or precision figures; in all appropriate instances blank corrections were made for the acid added to the samples in the field:

description of the type of source, water temperature, pH, TSS colour, TSS mass, TDS, Mg, Ca, hydroxide ion, carbonate, bicarbonate, chloride, fluoride, sulphate, phosphate, Na, K, Li, Rb, Cs, Sr, V, Mo, Tl, Si, Sb and Bi.

New or highly modified AAS techniques were used for the following groups of elements; in all cases these new techniques were adopted to reduce interferences and improve limits of detection:

(i) Hg
(ii) Cr Mn Fe Co Ni Cu Au Zn Cd Pb
(iii) Ag Al
(iv) As Se Te Ge

The precision data for these sets of data are generally not very different from those compiled in Chapter 3 but any changes were always improvements. For certain elements such as Au, Se and Te the improvements were marked. Many of the results obtained during multiple analysis of real check samples are compiled in Appendix B4. The quality of the analysis was consistently good. All total analyses were checked by the method of ionic balances (B3 in Appendix B). Any assay in which the percentage difference (100(C-A)/(C + A), where C = total cations (meq) and A = total anions (meq), exceeded 4% was rejected and the sample was re-analyzed.

The principal data collected during the analysis of the samples of the second orientation survey are compiled in Tables 5.3(1) to 5.3(9).

5.4 Interpretation of the orientation results

(A) *INTRODUCTION*

An examination of Table 5.3(n) shows that many of the species listed are clearly useless as pathfinders in this study because they show too small a range in concentration or because they could not be detected in a large proportion of the samples analysed. Hydroxide, carbonate, Li, Rb, Cs, V, Cr, Mo, Ag, Au, Cd, Hg, Tl, Ge, As, Sb, Bi, Se and Te must all be immediately dismissed on these grounds.

Note that this eliminates many of the "candidate" pathfinders that were identified in the study of the mine waters in section II. It is apparent that

TABLE 5.3(1) MEASUREMENTS MADE *IN SITU*

Sample number	Name	Source code	Water temp.	pH
271	Kommando Skietbaan	BD	25,5	7,35
272	New Lucerne	BE	22,9	7,6
273	Kiln Tsumeb	BE	27,0	7,7
274	Kiln Otjikoto	BE	27,5	6,7
275	Paviaansdam Tsumeb	BD	26,0	5,9
276	Dairy Post	BD	25,0	6,7
277	Dampos	BD	27,0	7,4
278	Alte Bobos	BD	28,0	7,6
279	Stephanus Post	BD	26,8	6,2
280	Welcome Post	BD	26,2	7,2
281	Stasiepos	BD	25,8	6,6
282	Petruspos	BD	27,2	6,85
283	Tsumeb West	BD	26,0	7,2
284	Abo	BD	27,2	7,0
285	Cook's House	BD	24,8	6,8
286	Smiths 480/18	BG	25,8	6,8
287	Vegetable Garden West	BE	26,0	6,8
288	Vegetable Garden East-Central	BE	26,0	6,7
289	Westerwald HQ	S	23,4	7,15
290	Westerwald Hill	S	24,0	7,7
291	Pfafferot HQ	S	22,8	7,7
292	Pfafferot MQ	S	23,2	7,3
293	Pfafferot Cattle Post	WH	19,0	7,05
294	Olifantsfontein	S	24,8	6,2
295	Acra	BD	25,0	7,15
296	Cooktown	BD	25,8	7,40
297	Cork	BD	25,8	8,3-8,4*
298	New Colombo	BD	26,0	7,10
299	Old Colombo	BD	27,0	6,90
300	Alborg	BD	25,0	6,90
301	Van Biljon Skietbaan	BD	22,2	7,65
302	Van Biljon Huis	BD	22,3	7,58
303	Kombat Store	BA	19,5	7,08
304	Avondrust	BG	22,2	7,4
305	Rogerberg	BD	23,2	6,9
306	Rietfontein	S	28,5	7,6
307	Asis West	BD	19,0	7,2
308	Station Arkose	BP	18,0	7,20
309	Kranzberg East	BD	18,8	7,2
310	Kranzberg West	BD	22,5	6,7
311	Gross Otavi	BA	20,8	6,2
312	Karlsruh	BA	21,2	6,3
313	Sinkhole Harasib	BD	23,8	6,40
314	Uitsab	BD	22,8	6,70
315	Lucas Post	BD	21,8	7,48
316	Otjikoto	L	27,0	8,40
317	Bergpomp	BE	22,0	6,9
318	Vegetable Garden Far East	BE	26,5	6,55-6,65*
319	Otavifontein	S	24,5	7,60
320	Kupferberg	BA	18,6	8,4
321	KW622	U	24,0	7,40
322	KC473	U	23,8	6,90
323	KW739	U	22,0	7,08
324	Felsenquell	S	18,3	7,05

Source codes and other abbreviations used: A = wind pump. B = borehole D = Diesel pump. E = electrical pump. G = petrol pump. P = paraffin pump. H = hand pump. S = perennial spring. L = sinkhole lake. W = open well. U = shallow underground borehole. HQ = Hausquelle. MQ = mineralquelle. * = varies.

TABLE 5.3(2) HARDNESS; SUSPENDED AND DISSOLVED SOLIDS

Sample	Colour of TSS	(Munsell /1191/)	TSS g/l	TDS g/l	Hardness mg/l Mg	Ca
271	pale yellow	2.5Y8/6	0,0006	0,598	64	108
272	reddish yellow	7.5Y6/6	0,0320	0,979	96	58
273	brown	*	0,0022	0,469	56	92
274	-----	**	0,0000	0,466	55	90
275	yellow & black	α2.5Y8/6***	0,0016	0,450	57	96
276	reddish yellow	7.5YR7/8	0,0050	0,802	49	140
277	pale yellow	*	0,0012	0,481	53	108
278	pale yellow	*	0,0006	0,488	32	152
279	-----	**	0,0000	0,489	27	172
280	pink	5YR7/3	0,0612	0,461	50	108
281	mottled yellow	α2.5Y8/4***	0,0010	0,475	29	148
282	-----	**	0,0000	0,498	24	168
283	reddish yellow	7.5YR6/8	0,0042	0,461	27	152
284	pale yellow & grey	*	0,0000	0,511	27	164
285	reddish yellow	7.5YR7/8	0,0078	0,695	80	104
286	pale yellow & grey	*	0,0012	0,530	46	136
287	grey	*	0,0006	0,466	51	116
288	grey	*	0,0006	0,971	91	129
289	grey	*	0,0004	0,449	34	148
290	grey	*	0,0000	0,475	56	116
291	grey & green	*	0,0006	0,479	49	112
292	grey	*	0,0004	0,511	56	128
293	pale yellow	*	0,0002	0,525	51	148
294	grey	*	0,0010	0,412	10	164
295	reddish yellow	7.5YR7/8	0,0058	0,470	24	176
296	pale yellow	*	0,0000	0,615	53	176
297	very pale brown	10YR7/4	0,0860	0,678	93	114
298	reddish yellow	7.5YR7/8	0,0070	0,508	39	172
299	pale yellow	*	0,0082	1,491	147	198
300	grey	*	0,0010	0,520	51	152
301	yellow	2.5Y8/6	0,0028	0,386	35	51
302	reddish yellow	7.5YR6/8	0,0072	0,280	23	64
303	yellow	5Y8/6	0,0000	0,722	90	72
304	pale yellow	2.5Y8/4	0,0108	0,524	105	32
305	brown & yellow	α2.5Y8/6***	0,0028	0,463	50	84
306	grey	*	0,0004	0,407	48	82
307	black & brown	α10YR6/6***	0,0116	3,658	53	373
308	l. yellowish brown	10YR6/4	0,1152	0,400	51	76
309	dark grey	10YR4/1	0,1344	0,400	83	52
310	strong brown	7.5YR5/6	0,0276	0,498	49	160
311	yellow	10YR8/8	0,0016	0,720	80	76
312	yellow	2.5Y8/6	0,0018	0,310	29	52
313	pale yellow	*	0,0002	0,410	66	88
314	pale yellow	2.5Y8/4	0,0008	0,290	61	60
315	pale yellow	5Y8/4	0,0014	0,389	78	40
316	yellow	5Y8/6	0,0086	0,259	51	32
317	very pale brown	10YR8/4	0,0408	0,489	85	56
318	pale yellow	α2.5Y8/4*	0,0162	0,914	114	84
319	-----	**	0,0002	0,300	50	90
320	yellow	2.5Y8/6	0,0046	0,430	46	116
321	-----	**	0,0000	0,360	50	90
322	white	2.5Y8/2	0,0738	0,350	39	116
323	light grey	2.5Y7/2	0,1274	0,360	53	104
324	-----	**	0,0024	0,370	56	88

l = light. α = approximate. * = insufficient material to make a good judgement of the colour. ** = no discernable colour. *** = mixture of particles of two colours. Subjective attempt made to grade the overall colour.

TABLE 5.3(3) ANIONS (All in mg/l)

Sample	OH^-	$CO_3^=$	HCO_3^-	Cl^-	F^-	$SO_4^=$	PO_4^{3-}
271	0	0	609	58	0,16	42	0,07
272	0	0	581	127	0,25	315	0,17
273	0	0	584	15	0,15	13	0,07
274	0	0	598	15	0,28	11	0,06
275	0	0	598	10	0,11	6	0,26
276	0	0	558	17	0,20	208	0,38
277	0	0	732	12	0,22	14	0,33
278	0	0	611	3	0,32	27	0,14
279	0	0	599	3	0,21	47	0,22
280	0	0	904	11	0,18	14	0,17
281	0	0	571	3	0,23	21	0,23
282	0	0	621	3	0,32	30	0,11
283	0	0	592	24	0,14	3	0,22
284	0	0	611	36	0,47	7	0,06
285	0	0	683	30	0,12	52	0,17
286	0	0	586	18	0,24	11	0,12
287	0	0	592	18	0,18	15	0,21
288	0	0	567	127	0,17	166	0,05
289	0	0	622	12	<0,04	3	0,05
290	0	0	577	24	0,04	1	0,08
291	0	0	577	12	0,05	1	0,30
292	0	0	620	18	0,05	3	0,29
293	0	0	645	18	0,05	4	0,11
294	0	0	531	18	0,04	<0,4	0,14
295	0	0	636	24	0,11	18	0,21
296	0	0	706	73	0,18	0,4	0,12
297	0	0	738	30	0,21	7	0,07
298	0	0	695	36	0,21	2	0,04
299	0	0	742	370	0,29	60	0,30
300	0	0	688	24	0,31	13	<0,01
301	0	0	440	11	0,18	20	0,24
302	0	0	316	15	0,20	6	0,04
303	0	0	683	85	0,06	27	0,11
304	0	0	608	24	0,06	<0,4	0,05
305	0	0	516	21	0,10	6	0,25
306	0	0	514	24	0,07	6	0,37
307	0	0	780	1814	0,04	77	0,12
308	0	0	484	24	0,06	<0,4	0,20
309	0	0	556	18	0,05	<0,4	0,38
310	0	0	689	48	<0,04	<0,4	0,19
311	0	0	539	36	0,13	180	0,14
312	0	0	386	24	0,12	<0,4	0,06
313	0	0	595	18	<0,04	6	<0,01
314	0	0	489	12	<0,04	2	<0,01
315	0	0	478	36	0,04	0,8	<0,01
316	0	15,6	321	24	0,10	9	<0,01
317	0	0	582	30	0,08	<0,4	<0,01
318	0	0	577	146	0,08	193	<0,01
319	0	0	528	15	0,22	7	<0,01
320	0	0	494	60	0,04	1	0,05
321	0	0	542	24	0,17	4	<0,01
322	0	0	529	24	0,04	<0,4	<0,01
323	0	0	543	30	0,09	<0,4	0,13
324	0	0	542	30	0,07	2	<0,01

TABLE 5.3(4) ELEMENTS OF GROUPS IA AND IIA

Sample	Na mg/l	K mg/l	Li µg/l	Rb µg/l	Cs µg/l	Sr µg/l
271	11,3	0,9	<7	<15	<15	282
272	179	0,9	<7	<15	<15	336
273	5,1	0,8	<7	<15	<15	318
274	5,0	0,8	<7	<15	<15	345
275	4,1	0,9	<7	<15	<15	300
276	33,0	0,8	<7	<15	<15	418
277	6,2	0,9	<7	<15	<15	782
278	5,4	1,1	<7	<15	<15	745
279	6,0	1,3	<7	<15	<15	773
280	3,3	0,9	<7	<15	<15	564
281	4,0	1,1	<7	<15	<15	627
282	7,7	0,8	<7	<15	<15	664
283	8,4	1,5	7	<15	<15	464
284	6,3	0,5	21	<15	<15	218
285	20,8	1,2	<7	<15	<15	427
286	5,1	0,8	<7	<15	<15	273
287	6,8	0,7	<7	<15	<15	327
288	63,0	1,0	<7	<15	<15	555
289	2,5	1,8	<7	<15	<15	418
290	5,7	2,0	<7	<15	<15	327
291	2,8	0,5	<7	<15	<15	355
292	3,3	0,1	<7	<15	<15	409
293	3,2	1,9	<7	<15	<15	545
294	2,0	0,5	<7	<15	<15	100
295	10,7	0,9	7	<15	<15	400
296	13,0	0,9	11	<15	<15	427
297	16,2	0,9	<7	<15	<15	536
298	9,5	0,2	<7	<15	<15	445
299	85	0,5	32	<15	<15	1073
300	1,8	0,6	25	<15	<15	255
301	45,1	0,5	14	<15	<15	255
302	4,5	0,2	<7	<15	<15	73
303	61,0	<0,1	<7	<15	<15	118
304	5,6	0,9	<7	<15	<15	127
305	0,9	0,3	<7	<15	<15	45
306	1,0	0,5	<7	<15	<15	45
307	977	0,6	<7	<15	<15	191
308	2,1	0,5	<7	<15	<15	64
309	1,0	0,5	<7	<15	<15	64
310	1,5	0,4	<7	<15	<15	64
311	78,9	0,8	64	<15	<15	282
312	40,5	0,7	<7	<15	<15	100
313	1,8	0,6	<7	<15	<15	209
314	0,7	0,3	<7	<15	<15	45
315	6,8	1,4	<7	<15	<15	91
316	8,0	2,1	<7	<15	<15	700
317	4,8	0,7	<7	<15	<15	318
318	75,8	1,1	<7	<15	<15	455
319	2,2	0,7	<7	<15	<15	91
320	9,7	0,6	<7	<15	<15	55
321	2,3	0,3	<7	<15	<15	55
322	2,8	0,4	<7	<15	<15	109
323	2,5	0,8	<7	<15	<15	91
324	1,8	0,1	<7	<15	<15	73

TABLE 5.3(5) ELEMENTS OF GROUPS IIIB TO VIII (All in µg/l)

Sample	V	Cr	Mo	Mn	Fe	Co	Ni
271	<10	<0,1	<10	6,0	220	0,1	0,5
272	<10	0,1	<10	8,0	123	0,6	1,3
273	<10	<0,1	<10	0,5	10,3	<0,1	0,8
274	<10	<0,1	<10	0,2	6,5	<0,1	1,1
275	<10	<0,1	<10	9,7	528	<0,1	1,2
276	<10	<0,1	<10	44	3000	0,3	1,8
277	<10	0,2	<10	1,7	110	<0,1	0,7
278	<10	0,3	<10	2,1	28	<0,1	0,5
279	<10	0,2	<10	0,6	18	<0,1	0,8
280	<10	<0,1	<10	7,0	268	0,2	1,5
281	<10	<0,1	<10	9,6	250	0,1	1,2
282	<10	<0,1	<10	0,2	4,6	<0,1	0,5
283	<10	0,1	<10	22	3400	0,3	2,4
284	<10	<0,1	<10	0,8	30	0,1	0,9
285	<10	0,2	<10	8,0	612	0,3	2,3
286	<10	<0,1	<10	0,7	44	0,1	0,9
287	<10	0,1	<10	1,2	106	0,2	0,8
288	<10	<0,1	<10	<0,1	7,3	0,1	1,0
289	<10	0,1	<10	0,5	8,3	<0,1	0,8
290	<10	<0,1	<10	0,6	7,8	0,1	0,9
291	<10	<0,1	<10	0,8	10,0	0,1	0,8
292	<10	<0,1	<10	1,2	8,2	0,1	0,7
293	<10	<0,1	<10	1,0	66	0,1	0,7
294	<10	<0,1	<10	0,3	5,0	0,1	1,0
295	<10	<0,1	<10	60	1300	1,1	2,0
296	<10	<0,1	<10	9,0	68	0,3	1,1
297	<10	<0,1	<10	32	1720	0,5	0,9
298	<10	<0,1	<10	10	900	0,2	1,6
299	25	<0,1	<10	51	246	1,2	2,3
300	<10	<0,1	<10	2,1	86	0,3	1,2
301	<10	<0,1	<10	200	750	0,3	1,4
302	<10	<0,1	<10	15	2700	0,3	1,3
303	<10	<0,1	<10	4,6	350	0,1	0,3
304	<10	<0,1	<10	4,6	420	0,4	0,8
305	<10	<0,1	<10	1,9	240	0,2	0,7
306	<10	<0,1	<10	0,7	9,5	<0,1	0,3
307	<10	0,4	<10	434	7400	3,7	18,9
308	<10	<0,1	<10	46	1950	1,2	2,1
309	<10	<0,1	<10	5,1	5800	0,2	0,4
310	<10	0,1	<10	64	4400	0,3	1,0
311	<10	<0,1	<10	9,0	850	<0,1	0,4
312	<10	<0,1	<10	10	588	<0,1	0,2
313	<10	<0,1	<10	0,2	9,1	<0,1	0,7
314	<10	<0,1	<10	4,4	100	<0,1	0,5
315	<10	0,4	<10	16	480	0,2	0,9
316	<10	<0,1	<10	3,1	10,0	<0,1	0,2
317	<10	<0,1	<10	4,3	350	0,4	1,0
318	<10	<0,1	<10	3,9	86	<0,1	0,5
319	<10	<0,1	<10	0,8	200	<0,1	0,4
320	<10	<0,1	<10	9,8	320	0,2	0,4
321	<10	<0,1	<10	0,9	14	<0,1	0,2
322	<10	<0,1	<10	36	132	<0,1	0,1
323	<10	<0,1	<10	108	288	0,5	0,3
324	<10	<0,1	<10	0,5	6,8	<0,1	0,1

TABLE 5.3(6) ELEMENTS OF GROUPS IB AND IIB (All in µg/l)

Sample	Cu	Ag	Au	Zn	Cd	Hg
271	0,6	<0,1	0,7	8,2	<0,1	<0,01
272	24	0,9	0,5	3,8	0,3	<0,01
273	9,9	<0,1	0,3	2,2	<0,1	<0,01
274	7,6	0,1	0,4	3,2	<0,1	<0,01
275	4,6	0,1	0,2	230	<0,1	<0,01
276	2,5	<0,1	0,3	1900	0,1	<0,01
277	5,4	<0,1	<0,1	695	<0,1	<0,01
278	1,3	<0,1	<0,1	1400	<0,1	<0,01
279	4,0	<0,1	<0,1	915	<0,1	<0,01
280	1,6	<0,1	0,1	4550	0,2	<0,01
281	0,9	0,1	<0,1	95	<0,1	<0,01
282	6,5	0,1	<0,1	20	<0,1	<0,01
283	4,0	<0,1	0,2	10	<0,1	<0,01
284	0,6	<0,1	0,2	38	<0,1	<0,01
285	12	<0,1	<0,1	765	0,2	<0,01
286	1,5	<0,1	<0,1	28	<0,1	<0,01
287	9,0	<0,1	<0,1	42	<0,1	<0,01
288	4,1	0,1	<0,1	28	<0,1	0,01
289	1,3	0,1	0,2	42	<0,1	<0,01
290	1,5	<0,1	<0,1	10	<0,1	<0,01
291	1,5	<0,1	0,1	15	0,1	<0,01
292	3,3	0,1	<0,1	60	<0,1	<0,01
293	3,8	0,1	0,1	100	<0,1	<0,01
294	2,0	<0,1	0,1	15	<0,1	<0,01
295	2,0	0,1	<0,1	710	<0,1	<0,01
296	1,0	0,1	<0,1	32	<0,1	<0,01
297	2,4	<0,1	0,1	10 200	<0,1	<0,01
298	0,9	<0,1	0,1	15	<0,1	<0,01
299	4,8	0,2	0,1	300	<0,1	<0,01
300	1,1	<0,1	<0,1	42	<0,1	<0,01
301	3,8	0,1	<0,1	162	<0,1	<0,01
302	14	<0,1	<0,1	360	<0,1	<0,01
303	4,9	0,1	<0,1	45	<0,1	<0,01
304	54	0,1	<0,1	102	<0,1	<0,01
305	13	0,1	<0,1	1680	0,4	<0,01
306	5,6	<0,1	<0,1	45	<0,1	<0,01
307	116	0,5	<0,1	6100	0,7	<0,01
308	10,1	<0,1	<0,1	1450	<0,1	<0,01
309	636	<0,1	<0,1	61 000	2,3	<0,01
310	25	0,1	<0,1	9480	2,0	0,01
311	1,7	0,1	<0,1	295	<0,1	<0,01
312	3,6	<0,1	<0,1	150	<0,1	<0,01
313	1,8	<0,1	<0,1	38	<0,1	<0,01
314	0,9	<0,1	<0,1	48	<0,1	<0,01
315	2,1	<0,1	<0,1	190	<0,1	0,01
316	3,0	0,1	<0,1	10	<0,1	<0,01
317	10,0	0,1	<0,1	70	<0,1	0,01
318	22	0,2	0,1	11	<0,1	0,025
319	7,8	0,1	<0,1	28	<0,1	<0,01
320	13	<0,1	<0,1	350	<0,1	<0,01
321	6,4	<0,1	<0,1	10	<0,1	<0,01
322	8,8	0,1	<0,1	7,4	0,1	0,01
323	58	<0,1	<0,1	24	<0,1	0,10
324	0,7	<0,1	<0,1	1,1	<0,1	<0,01

TABLE 5.3(7) ELEMENTS OF GROUPS IIIA TO VIA (Si in mg/l, others in µg/l)

Sample	Al	Tl	Si	Ge	As	Sb	Bi	Se	Te	Pb
271	40	<10	5,0	<6	<0,6	<250	<25	<0,8	<0,9	3,0
272	873	<10	9,6	<6	1,2	<250	<25	<0,8	<0,9	10,0
273	2	<10	2,9	<6	<0,6	<250	<25	<0,8	<0,9	3,0
274	18	<10	3,2	<6	<0,6	<250	<25	<0,8	<0,9	0,5
275	7	<10	8,6	<6	<0,6	<250	<25	<0,8	<0,9	2,0
276	11	<10	14,6	<6	<0,6	<250	<25	<0,8	<0,9	0,9
277	22	<10	9,6	<6	<0,6	<250	<25	<0,8	<0,9	1,8
278	31	<10	6,1	<6	<0,6	<250	<25	<0,8	<0,9	1,5
279	<2	<10	7,9	<6	<0,6	<250	<25	<0,8	<0,9	1,1
280	2851	<10	7,1	<6	<0,6	<250	<25	<0,8	<0,9	9,5
281	59	<10	7,9	<6	<0,6	<250	<25	<0,8	<0,9	0,5
282	7	<10	8,6	<6	<0,6	<250	<25	<0,8	<0,9	0,2
283	26	<10	7,5	<6	<0,6	<250	<25	<0,8	<0,9	2,5
284	37	<10	14,3	<6	<0,6	<250	<25	<0,8	<0,9	0,4
285	42	<10	8,9	<6	<0,6	<250	<25	<0,8	<0,9	7,6
286	57	<5	9,3	<6	<0,6	<100	<25	<0,8	<0,9	0,9
287	57	<5	8,9	<6	<0,6	<100	<25	<0,8	<0,9	4,8
288	11	<5	6,4	<6	<0,6	<100	<25	<0,8	<0,9	0,5
289	9	<5	7,5	<6	<0,6	<100	<25	<0,8	<0,9	0,8
290	2	<5	6,1	<6	<0,6	<100	<25	<0,8	<0,9	1,0
291	9	<5	6,8	<6	<0,6	<100	<25	<0,8	<0,9	4,8
292	15	<5	7,5	<6	<0,6	<100	<25	<0,8	<0,9	10,0
293	7	<5	2,1	<6	<0,6	<100	<25	<0,8	<0,9	1,5
294	4	<5	1,8	<6	<0,6	<100	<25	<0,8	<0,9	2,9
295	13	<5	9,6	<6	<0,6	<100	<25	<0,8	<0,9	10,2
296	9	<5	11,1	<6	<0,6	<100	<25	<0,8	<0,9	2,7
297	3296	<5	16,8	<6	<0,6	<100	<25	<0,8	<0,9	11,7
298	117	<5	19,6	<6	<0,6	<100	<25	<0,8	<0,9	1,2
299	253	<5	20,7	<6	<0,6	<100	<25	<0,8	<0,9	2,4
300	4	<5	11,1	<6	<0,6	<100	<25	<0,8	<0,9	2,5
301	106	<2	6,1	<6	<0,6	<25	<20	<0,8	<0,9	3,4
302	196	<2	3,6	<6	<0,6	<25	<20	<0,8	<0,9	20
303	64	<2	8,9	<6	<0,6	<25	<20	<0,8	<0,9	0,9
304	1732	<2	11,1	<6	<0,6	<25	<20	<0,8	<0,9	11,9
305	79	<2	3,9	<6	<0,6	<25	<20	<0,8	<0,9	6,0
306	24	<2	4,3	<6	<0,6	<25	<20	<0,8	<0,9	3,9
307	2706	<2	3,6	<6	<0,6	<25	<20	<0,8	<0,9	11,0
308	4279	<2	6,1	<6	<0,6	<25	<20	<0,8	<0,9	6,0
309	818	<2	5,4	<6	<0,6	<25	<20	<0,8	<0,9	788
310	35	<2	3,2	<6	<0,6	<25	<20	<0,8	<0,9	22
311	<2	2,2	12,9	<6	<0,6	<25	<20	<0,8	<0,9	0,8
312	<2	2,0	8,9	<6	<0,6	<25	<20	<0,8	<0,9	0,8
313	4	<2	6,1	<6	<0,6	<25	<20	<0,8	<0,9	0,8
314	18	<2	1,4	<6	<0,6	<25	<20	<0,8	<0,9	1,8
315	2	<2	0,4	<6	<0,6	<25	<20	<0,8	<0,9	3,8
316	29	<2	5,3	<6	<0,6	<20	<20	<0,8	<0,9	0,7
317	1520	<2	9,6	<6	<0,6	<20	<20	<0,8	<0,9	4,2
318	574	<2	10,4	<6	<0,6	<20	<20	<0,8	<0,9	4,9
319	110	<2	5,0	<6	<0,6	<20	<20	<0,8	<0,9	4,7
320	99	<2	10,0	<6	<0,6	<20	<20	<0,8	<0,9	3,7
321	11	<2	0,4	<6	<0,6	<20	<20	<0,8	<0,9	4,1
322	554	<2	3,6	<6	<0,6	<20	<20	<0,8	<0,9	5,6
323	361	<2	2,9	<6	7,0	<20	<20	<0,8	<0,9	110
324	<2	<2	8,2	<6	<0,6	<20	<20	<0,8	<0,9	0,2

TABLE 5.3(8) SEMI-QUANTITATIVE ANALYSES OF TSS RESIDUES

Sample	Mg%	Al%	Si%	P%
271	0,066	0,039	0,250	0,014
272	1,768	5,655	17,635	0,049
273	0,147	0,254	1,036	0,007
274	0,000	0,015	0,072	0,002
275	0,100	0,031	0,486	0,044
276	0,121	0,108	1,939	0,100
277	0,034	0,027	0,138	0,014
278	0,035	0,037	0,152	0,011
279	0,025	0,011	0,036	0,005
280	9,455	4,647	12,032	0,093
281	0,061	0,067	0,241	0,021
282	0,073	0,017	0,086	0,003
283	0,111	0,170	0,686	0,074
284	0,031	0,163	0,047	0,003
285	2,140	0,347	1,800	0,022
286	0,467	0,485	1,453	0,007
287	0,159	0,136	0,471	0,007
288	0,050	0,015	0,059	0,003
289	0,018	0,036	0,101	0,008
290	0,008	0,036	0,081	0,007
291	0,027	0,034	0,139	0,019
292	0,001	0,003	0,004	0,001
293	0,041	0,026	0,100	0,017
294	0,017	0,017	0,083	0,005
295	0,193	0,308	2,164	0,056
296	0,027	0,026	0,164	0,015
297	1,251	3,590	15,197	0,062
298	0,163	0,294	2,211	0,029
299	1,047	0,387	2,591	0,066
300	0,084	0,041	0,071	0,014
301	0,268	1,202	2,929	0,074
302	0,213	1,071	3,088	0,056
303	0,095	0,049	0,214	0,029
304	2,041	3,428	8,308	0,017
305	0,269	0,198	0,767	0,110
306	0,062	0,046	0,183	0,028
307	0,124	0,197	1,062	0,057
308	0,989	6,853	21,169	0,224
309	0,562	0,656	3,345	0,070
310	0,146	0,870	2,745	0,146
311	0,112	0,063	0,818	0,005
312	0,091	0,077	1,486	0,051
313	0,016	0,051	0,120	0,017
314	0,024	0,015	0,105	0,031
315	0,131	0,040	0,233	0,047
316	0,145	0,117	1,159	0,157
317	4,296	2,838	10,167	0,122
318	0,759	1,424	5,578	0,021
319	0,015	0,065	0,203	0,007
320	0,366	1,661	4,713	0,043
321	0,000	0,014	0,059	0,014
322	7,401	0,435	8,440	0,168
323	4,141	1,012	4,630	0,104
324	0,271	0,041	0,223	0,022

The data are purely nominal conversions of XRFS counts per second

TABLE 5.3(9) SEMI-QUANTITATIVE ANALYSES OF TSS RESIDUES

Arbitrary units of peak height

Sample	Pb	Cu	Zn	Fe	Mn	Ti	Ca	Other elements
271	---	---	---	30,0	---	---	1,25	
272	0,5	1,0	2,0	105,25	2,5	2,5	19,25	
273	1,0	0,5	0,5	9,5	---	---	1,0	
274	1,0	---	---	3,25	---	---	0,5	
275	1,25	---	2,0	84,0	---	---	2,25	Cr?
276	1,0	---	8,5	200,0	0,25	---	4,0	
277	---	0,25	0,25	11,5	---	---	1,5	
278	0,25	0,25	0,25	9,25	---	---	0,25	
279	0,5	0,25	0,25	4,25	---	---	0,5	
280	1,0	---	14,5	125,0	1,0	3,0	44,0	
281	0,25	0,5	0,5	28,25	---	---	2,0	
282	---	---	---	3,0	---	---	1,25	
283	---	0,5	0,5	159,5	0,25	---	3,0	
284	0,25	0,25	0,25	7,0	---	---	1,5	
285	0,75	---	3,0	98,25	0,25	---	15,0	
286	---	0,25	---	10,25	---	---	4,25	
287	1,0	---	---	7,5	---	---	2,5	
288	0,5	---	---	3,0	---	---	1,25	
289	1,0	0,5	---	3,0	---	---	1,25	
290	0,25	---	---	2,5	---	---	0,5	
291	---	0,25	---	3,0	---	---	2,5	
292	---	---	---	3,0	---	---	2,0	
293	---	---	---	7,0	---	---	2,0	
294	---	---	---	3,0	---	---	2,5	
295	0,25	0,5	12,0	156,25	---	---	6,5	
296	1,0	---	---	14,0	---	---	1,5	
297	1,25	---	93,0	212,5	1,0	1,25	88,0	
298	0,25	0,5	0,75	11,5	0,25	---	10,25	
299	0,25	---	2,0	25,0	0,25	---	22,5	
300	---	0,25	---	7,5	---	---	2,5	
301	1,25	0,75	2,0	71,5	0,25	0,25	0,75	
302	---	---	7,0	187,5	0,25	---	1,0	
303	---	---	---	32,0	---	---	2,0	
304	---	4,0	3,0	82,0	0,5	1,0	9,0	
305	1,5	4,0	12,0	87,5	0,25	---	3,25	
306	0,25	---	---	5,0	---	---	3,0	
307	---	4,5	47,0	400,0	0,5	0,25	6,5	
308	---	3,0	22,0	450,0	3,5	7,0	8,0	
309	15,5	88,0	>100,0	500,0	2,5	1,5	19,0	
310	1,25	6,0	>100,0	>625,0	0,5	0,25	8,5	
311	1,0	1,0	2,0	91,0	---	---	2,0	
312	1,0	1,0	2,5	42,0	0,25	---	1,5	
313	---	0,5	0,5	4,0	---	---	0,5	
314	1,0	0,5	0,5	38,5	---	---	1,0	
315	1,0	1,0	1,5	29,0	0,25	---	2,25	
316	---	---	1,0	12,5	---	---	5,0	
317	1,0	0,25	3,0	85,0	1,0	2,5	53,0	
318	1,0	0,5	1,0	28,5	0,5	1,0	15,0	
319	1,0	---	0,75	3,5	---	---	1,5	
320	---	0,25	4,0	69,25	0,5	0,5	3,75	
321	0,5	0,25	0,5	3,5	---	---	0,5	
322	---	0,5	0,5	19,5	1,5	0,25	89,0	
323	5,5	5,0	2,5	93,0	15,0	1,0	173,25	
324	1.0	0.5	---	4.0	0.25	---	6.25	

--- = no discernible peak. ? = dubious peak

The data are purely nominal conversions of peak heights, read to the nearest quarter block on the graph paper.

either (a) the writer was correct in suspecting that the distribution of the elements in the mine waters had been seriously disturbed by the activities of man, or (b) certain elements (notably cadmium, mercury and those with non-metallic tendencies), although present in the mine waters in ponderable amounts, are actually not very mobile in dolomitic formational waters and do not survive long enough in solution to migrate any appreciable distance beyond the immediate environment of the orebody. This phenomenon - which amounts to a very rapid decay of the aureole of secondary dispersion for certain species - is very well documented /53,55,1007,1080,91,93,115,121, 782/. Perel'man and Sharkov /344/ and Brodskii /345/, in particular, have recorded many examples were elements that are readily detectable in mine waters are not found in the normal groundwaters surrounding the orebody.

A detailed comparison of the data and conclusions of the first and second orientation surveys will not be included here, because such a comparison can contribute nothing of value to the second survey and thus will not further the aims of the project as a whole. Nevertheless, cognizance was taken of the results of the study of the mine waters and particular attention was paid in the second orientation survey to those (detectable) elements that the examination of the mine waters had shown to be "candidate" pathfinders.

The data for the interesting elements and ions were plotted by a computer and are presented as Maps 4c,4d...4z,4aa,4ab... etc. The computer program is listed in Appendix K. These computer-generated diagrams comprise plots of the raw data, ratios -such as Zn/TDS- and so on. The diagrams, together with various statistical information derived for the data with the BMDP76 statistical package /281/ formed the basis for the interpretation of the orientation information.

A great deal has been written about the definition and recognition of anomalies /51,803,1045,1073/ and it is accepted that powerful intuitive and subjective factors are involved. After two weeks of examining the orientation maps and BMDP printouts, and trying several "mathematical" or "geometrical" schemes for defining various anomalies and rating their importances, the writer came to the conclusion that the standard method of subjective visual assessment of anomalies could not be improved upon in this case. (This procedure is often informally termed "picking out the eyes", which is a rather good description of what is involved). It was anticipated that both positive (e.g. high [Zn]) and negative (e.g. low pH) anomalies might be encountered and the "most anomalous" values were therefore classified into four grades (I,II, -I and -II), with respective thresholds set as near as possible at >90%, >80%, <10% and <20% of the cumulative frequency distribution for a particular element. For example, in a population of 100 pH data the ten highest values would be assigned to Grade I and the next ten highest values to Grade II. The ten lowest values would constitute the Grade -I class and the following lowest ten samples would be Grade -II. The remaining 60 values would be considered to represent the "normal" or "background" range of pH values and would be ignored. Threshold data for the various chemical species are compiled in Table 5.4. The orientation maps were examined to establish whether any meaningful patterns were created by the distributions of background values and samples of various anomalous grades. Several elements produced patterns that may be interpreted as regional anomalies.

Hydrogeochemistry is intrinsically a tool for identifying regional rather than local anomalies. It is sometimes possible to "zero in" very closely on a hidden orebody by taking closely spaced samples (e.g. /819, 822,865/) but these cases are exceptions. In this orientation study, where samples were necessarily widely spaced and where the shallow bodies of groundwater right at the ore deposits are highly disturbed (or, as at Tsumeb, practically annihilated), there could be no question of pinpointing the "eye" of any regional anomaly. The principle objective was simply to reduce the target zone to as small an area as possible.

Whether the regional anomalies in the Otavi Mountainland represent old and diffuse secondary dispersions from central orebodies, or whether they are independent expressions of primary dispersion aureoles or local "metallogenic provinces" /880/ that are host to the central orebodies, is academic; there is no way at this stage of the project of telling the difference. There has certainly been a great deal of natural and anthropogenic secondary dispersion about the two mines, but both centres also have many of the hallmarks of an accompanying metallogenic province. There is important mineralization at Asis Ost and Asis West, quite close to Kombat, and numerous other small showings can be seen within a radius of a few kilometres of the mine. A similar situation prevails at Tsumeb, where the mineralization at Tsumeb West and Friezenberg and, somewhat further afield, at Uris and Karavatu, can be cited as examples.

What *is* important is deciding whether an apparent regional anomaly is a genuine reflection of an ore-bearing zone, or whether it is a spurious or fortuitous occurrence. Spurious anomalies can be either anthropogenic or natural /856/. An example of just how important manmade influences can be is found in the oilfields of Kentucky, where artifical dispersion trains for chloride that are over 100 km long have developed within the regional groundwater system as a result of the recirculation of briny wastes. The occurrence of waters containing chromium in the upper levels of the Tsumeb mine provides a probable example of a natural false anomaly. The chromium apparently comes from the kersantite dykes nearby and would still be present even were there no orebody. Thus the association of chromium with

TABLE 5.4 THRESHOLD DATA FOR VARIOUS GRADES OF ANOMALOUS ORIENTATION SAMPLES

Data	Map	Grade -I	Grade -II	Grade I	Grade II
		≈10% CF*	≈20% CF	≈90% CF	≈80% CF
PO4, µg/l	4Y	40	40	300	220
PO4/TDS	4BC	0,0328	0,0328	0,5778	0,4738
Sus P	4AJ	0,005	0,007	0,11	0,07
Sus P/TSS	4BN	0,0005	0,0013	0,35	0,233
F, µg/l	4X	40	50	280	210
F/TDS	4BB	0,0777	0,0978	0,6009	0,4528
Si, mg/l	4V	2,9	3,6	12,9	9,6
Si/TDS	4AZ	0,0048	0,0084	0,0222	0,020
Sus Si	4AI	0,071	0,101	8,44	3,088
Sus Si/TSS	4BH	0,0100	0,071	0,785	0,4709
Al µg/l	4U	2	7	1520	253
Al/TDS	4AY	0,0043	0,0133	2,045	0,6280
Sus Al	4AH	0,017	0,031	2,838	0,870
Sus Al/TSS	4BL	0,0049	0,0079	0,2550	0,115
Sus Ti	4AE	0,2	0,2	1,3	0,3
Sus Ti/TSS	4BI	0,0034	0,0034	0,613	0,0091
Ni, µg/l	4T	0,3	0,5	2	1,3
Ni/TDS	4AV	0,0006	0,0009	0,0036	0,0024
Co, µg/l	4S	0,1	0,1	0,5	0,3
Co/TDS	4AU	0,0001	0,0001	0,0008	0,0006
Fe, µg/l	4R	7,8	10	2700	750
Fe/TDS	4AT	0,0164	0,0222	3,7406	1,7717
Sus Fe	4AC	3,2	4	200	105,2
Sus Fe/TSS	4BG	0,260	1,670	37,98	26,04
Mn, µg/l	4Q	0,5	0,7	51	16
Mn/TDS	4AS	0,0011	0,0016	0,1150	0,0411
Sus Mn	4AD	0,2	0,2	1,0	0,5
Sus Mn/TSS	4BH	0,0116	0,0116	0,0893	0,0431
Sr, µg/l	4P	61	91	664	464
Sr/TDS	4AC	0,1528	0,2339	1,32	0,8511
K, mg/l	4O	0,3	0,5	1,4	1,0
K/TDS	4AQ	0,0004	0,001	0,0033	0,0022
HCO3, mg/l	4I	484	529	706	645
HCO3/TDS	4AM	0,6958	1,1057	1,5083	1,3835
Na, mg/l	4K	1,8	2,3	63	16,2
Na/TDS	4AP	0,0035	0,0058	0,0829	0,0299
Mg, mg/l	4G	27	35	91	78
Mg/TDS	4AK	0,0552	0,0768	0,1738	0,1372
Sus Mg	4AG	0,016	0,027	2,041	0,562
Sus Mg/TSS	4BK	0,0025	0,0086	0,1550	0,1003
Ca, mg/l	4H	52	76	172	152
Ca/TDS	4AL	0,1028	0,1328	0,3314	0,3115
Sus Ca	4AF	0,8	1,3	22,5	9,0
Sus Ca/TSS	4BJ	0,0690	0,2680	4,167	2,50
Cl, mg/l	4E	11	15	85	36
Cl/TDS	4AN	0,0222	0,0320	0,1297	0,0925
SO4, mg/l	4D	0,4	1,0	60	27
SO4/TDS	4AO	0,0007	0,0021	0,0748	0,0402
SO4/Cl	4BO	0,0055	0,0222	5,0	1,1667
Zn, µg/l	4J	8,2	15	1900	710
Zn/TDS	4AX	0,0137	0,0295	3,625	1,4449
Sus Zn	4AB	0,2	0,2	14,5	3,0
Sus Zn/TSS	4BF	0,0068	0,0068	2,069	1,0714
Pb, µg/l	4M	0,7	0,9	11,7	7,6
Pb/TDS	4BA	0,0011	0,0018	0,0217	0,0150
Sus Pb	4Z	0,2	0,2	1,3	1,0
Sus Pb/TSS	4BD	0,0415	0,0415	0,7813	0,4545
Cu, µg/l	4L	1,0	1,5	24	10,1
Cu/TDS	4AW	0,0019	0,0031	0,0317	0,0245
Sus Cu	4AA	0,2	0,2	4,0	0,8
Sus Cu/TSS	4BE	0,0061	0,0061	0,625	0,3879
Cu + Pb, µg/l	4BP	2,4	3,4	34	16,1
Temperature ^{0}C	4N	19	22	27	26,2
pH	4F	6,4	6,7	7,65	7,58
TDS, mg/l	4C	350	400	802	598
TSS, mg/l	4W	0,2	0,4	61,2	10,8

Sus = suspended, i.e. data from XRFS analysis of TSS residues.

CF = cumulative frequency value taken as a criterion of threshold.

Cu-Pb-Zn ore is meaningless except in the improbable event that all such deposits in the Tsumeb area are cut by kersantite dykes. The literature contains many reports of natural false anomalies /140-1,888,992,998,1143/.

In subsection B of this chapter the characteristics of each of the orientation maps will be discussed in detail. The reader should note the following features of these maps:

(1) There are typically two maps per element - one showing the raw data for "dissolved E" and one showing the ratio dissolved E/TDS. In most cases this dissolved E is actually an approximation of total (i.e. suspended and dissolved) E, since the sample aliquot was acidified on site without filtration. For certain elements there are four maps - dissolved E, dissolved E/TDS, suspended E (SusE) and SusE/TSS. Note particularly that it does *not* follow that dissolved E minus SusE equals the amount of E in true solution. The XRFS method for the determination of the composition of the suspended solids was semi-quantitative and there are a number of other legitimate complications that have been discussed at length in Appendixes B and J.

(2) Multiplication factors have been applied to some of the data in order to avoid the unnecessary irritation of coping with strings of zeros in the values plotted on the maps. For example, absolute values for Ni/TDS typically lie around n x 10^{-5} and would normally be plotted as 0,000n. The whole set of values for nickel has therefore been multiplied by 10^5 to given plotted values of between 0,n and 1,n. Obviously, where multiplication has been applied, the threshold values have also been multiplied. *However*, it must be noted that the element/TDS ratios calculated from the orientation data are *not* regarded as being unitless ratios; instead they are held to retain the units of the original measurements constituting the numerator and denominator of the ratio. Thus the sulphate/TDS ratio is in mg/mg but the Ni/TDS ratio is in µg/mg. The multiplication factor for Ni/TDS is therefore shown on the map as 10^2 and not 10^5, since there is an implied multiplication of 1000 within the Ni/TDS data already.

(3) Anomalous values are shown in colour on the maps. Positive anomalies are indicated by symbols in red, negative anomalies by symbols in green and background values by symbols in black. Also, rounding has been applied to the data. Thus in some maps a value that was read by the computer as 1,4 mg/l, for example, will be plotted as "1", whereas a value read as 1,6 mg/l will be plotted as "2". But the program selects anomalies *before* rounding and this produces occasional apparent inconsistencies in the data on the maps. Take for example a situation where, for a given element, the background/positive threshold value calculated by the BMDP program is 8,7 µg/l and two analytical values of 8,6 and 8,8 µg/l are read by the plotting program. The

program will flag the first value as "background" and the second value as "positive anomaly", but will then round them both to "9" before plotting them. A "black" 9 and a "red" 9 may therefore appear side by side. In a few cases - for example suspended manganese - there are so many values of zero that the concept of a "negative anomaly" becomes meaningless. This, of course, will in no way deter the computer from attempting to create one. In these cases, which are always quite obvious and self-explanatory, the rash of green values should simply be regarded as the "bottom end" of the range of values in the background distribution.

(4) Inequalities cannot be shown on the maps. Values read as <n are plotted as zero. Values read as >n are plotted as n, but these are very uncommon and restricted to the XRFS data.

(5) The computer will not tolerate attempts to perform certain arithmetic operations with zeros. Thus any calculated ratio of the form n/zero (overflow error) or zero/n (underflow error) will be plotted as zero. Zeros resulting from underflow are common but zeros resulting from overflow are extremely uncommon or absent in these maps.

(6) The plotter cannot draw the symbol μ and this is therefore represented by u.

(7) The data from the application study (Chapter 6) that followed the orientation work discussed here are also shown, where available, on these maps, because it is handy to have all the analytical information on one diagram. Nevertheless, the application data obviously did not exist when the orientation was performed and will therefore be ignored for the present.

(B) *SYSTEMATIC EXAMINATION OF THE ORIENTATION MAPS*

(1) *TDS and TSS (Maps 4C and 4W)*

The concentration of TDS in the waters of the orientation area varies through an order of magnitude but there does not appear to be much of a correlation between dissolved solids and the lithology of the bedrock. Most of the peak values occur near to either Tsumeb or Kombat. High levels of TDS have previously been noted in the vicinity of weathered orebodies /782, 873/ but there have been few if any proposals to use TDS *per se* as a prospecting criterion, because there are too many other possible causes for changes in the mass of TDS. The importance of this parameter lies rather in the fact that the concentrations of several elements often exhibit a high degree of correlation with TDS /904/. In other words a TDS anomaly, whatever its cause, will tend automatically to generate sympathetically anomalous concentrations of certain other elements or ions; sodium, chloride, magnesium, vanadium and uranium are well-known examples. The data of Section II of this thesis give us reason to believe that the TDS anomalies at Tsumeb and Kombat may be partly anthropogenic and it follows that any anomalies defined by elements that are strongly associated with relatively brackish waters may also be partially "manmade". At the very least we may expect to find that some anomalies have been exaggerated by man's disturbance of the natural groundwater regime /512,541/. It will therefore be necessary to consider very carefully both the raw data and element/TDS ratios before deciding upon the potential usefulness as pathfinders of the various chemical species that have been studied in the waters of the Otavi Mountainland.

Much of what holds for TDS can be applied, *mutatis mutandis*, to TSS (Map 4W). There is a weak TSS anomaly at Tsumeb, while at Kombat there is a strong one, which extends somewhat to the northwest of the mine. It is notable that the size, shape and locus of this anomaly are very similar to those of several of the trace elements that are described below. The suspended matter in groundwater has not really been given the attention it deserves by exploration geochemists /527,819,997/. It is, however, generally agreed that a significant proportion of many of the microcomponents of groundwaters are not in true solution /902/ and the potential importance of suspended metals has been pointed out by many authors - including Agricola in 1546 /689/. There is a *prima facie* case for expecting that certain TDS anomalies around ore deposits will be accompanied by high TSS values. The accelerated dissolution and subsequent hydrolysis or precipitation of elements such as iron, manganese and calcium would tend to enhance the concentrations of suspended materials in these waters. These elements, together with trace elements such as copper, lead, cobalt etc. that are normally co-precipitated with them /997/, will tend to be concentrated wherever TSS levels are higher than average. It is for this reason that each of the maps showing the concentrations of various elements in suspension (SusE) is matched by a corresponding map showing the values of SusE/TSS.

(2) *Silicon (Maps 4V, 4AZ, 4AI and 4BM)*

Silicon is probably too ubiquitous to be a pathfinder but, *ipso facto*, its distribution can often reveal features of the overall hydrogeochemical pattern that will not be brought out by the trace element data. This it does in the orientation area presently under consideration, where there are two "total" silicon "anomalies" (overlay Map 4V on Map 4). In the south the Otavi phyllite is marked by a line of three high values. In the north the Grade I and Grade II values are associated with the large patches of Mulden quartzite that lie to the northeast of Tsumeb, and several of the remaining high values in the north occur in waters that lie fairly near to other outcrops of these arenites. (An exception is a pair of Grade II values in the dolomitic region immediately north of Tsumeb. The possible significance of these will become more apparent when the data for SusSi are discussed in due course). It appears that the concentration of dissolved silicon is directly related to the lithology of the host rocks and that the Otavi dolomites, like most carbonate aquifers (Siever, in /35/), contain waters that are comparatively poor in the element. The differential accumulation of silicon in carbonate and non-carbonate formations is of course a specific example of a general principle that is widely recognized in all branches of groundwater hydrogeochemistry - that adjacent rock units of contrasting lithologies generally contain waters of contrasting compositions /544,783/. If this phenomenon is the chief cause of the pattern of distribution of dissolved silicon in the Otavi Mountainland, then two interesting consequences follow :

(i) There appears to be little active exchange of groundwater in the area. i.e., the siliceous bodies of groundwater are more or less co-extensive with the outcrops of siliceous rocks. There is no massive lateral displacement of identifiable bodies of water and insufficient strong movement and mixing to blur the distinctions between "dolomitic" and "arenaceous" waters. This is in keeping with what is known about the general hydrology of the region and with the data collected during the study of seasonal fluctuations in the compositions of the local waters (Appendix J). A sluggish water--exchange tends to favour the development of small regional anomalies and reduces the degree of lateral displacement in them /782,645,717,783/. This is naturally not always desirable in exploration programs, but under the circumstances prevailing in this particular study small anomalies are to be regarded as highly favourable attributes.

(ii) It will be necessary to watch very carefully for abnormalities in the distributions of those elements that could be influenced significantly by changes in lithology. For instance, it is conceivable that a hypothetical (say) rubidium anomaly at Kombat could have been caused by active fluids from the ore reacting with rubidium-bearing minerals in the Mulden phyllite, and not by a release of the element from within the orebody. Furthermore, it will be necessary to watch for changes in background concentrations, caused by changes in lithology, that could disguise anomalies by altering the contrast ratio between local peak values and the local background.

The Si/TDS map shows a distribution very similar to that of the unratioed data.

The SusSi map provides a good example of the aforementioned influence that TSS may have on the distributions of certain elements. Note that the pattern of anomalies for SusSi is practically a duplicate of the anomalies on the TSS map, with clearly-defined groupings at Tsumeb and at Kombat. Interestingly, these two oval, "TSS-weighted" anomalies are transformed upon division by TSS (4BM) into two remarkably linear anomalies at more or less the same sites. The one in the south is, like the one for "dissolved" silicon, apparently related to the trend of the outcrop of the Mulden phyllite. The one in the north is suspiciously parallel to the major faults in the region. Many of the boreholes in the area immediately north of Tsumeb are drilled along northeasterly structural features. These features are generally prolific yielders of water and are, in places, occupied by subcropping kersantite dykes of Karoo age /52/. It must be considered possible that this northeasterly trend in the distribution of the SusSi/TSS peaks is due to the presence of these dykes and/or faults; this possibility would account for the singular but otherwise unexplained occurrence in the dolomitic terrane north of Tsumeb of the group of three samples with high levels of "total" silicon (*vide supra*). The evidence is circumstantial and tenuous but cannot safely be ignored. It will be necessary to bear in mind that any trace element anomaly that appears just to the north or northeast of Tsumeb could be a false anomaly caused by the kersantite rather than by the ore or its associated regional dispersion aureole.

(3) *Physical data (Maps 4N and 4F)*

Trost and Trautwein /1080/ have shown that some sulphidic deposits are surrounded by groundwaters that are slightly warmer than the background value. At Kombat there is no evidence of a similar phenomenon. Anomalously warm waters do occur at Tsumeb, but they are not distinguishable from a broad band of warm waters that stretches over a very wide area from Tschudi in the west to Colombo in the northeast.

The depression of pH values in the vicinity of some types of ores is very well-documented /49/ but it is also well known that such anomalies may be neutralized in carbonate terranes. Two low pH values occur well to the west of the Kombat mine and may be related to local conditions within the carbonate-poor phyllite. The other -I values are scattered widely. There is no reason to anticipate a great concentration of Grade I values in any particular location and none is observed.

It is concluded that temperature and pH are not successful indicators of mineralization in the Otavi Mountainland.

(4) *Phosphate (Maps 4Y, 4BC, 4AJ and 4BN)*

The use of phosphate as a pathfinder is practically unknown. There are many reasons for this, including the fact that the concentration of phosphorus, even in groundwaters, can be radically influenced by biological factors /1187/. The distributions of the values for both "total" phosphate and phosphate/TDS are practically random and no unique anomalies can be identified at either mine. The SusP map shows a strong anomaly at Kombat only. This provides a further illustration of the bias introduced by the "scavenging" effect mentioned in foregoing subsections. Note that the SusP and TSS (4W) anomalies are practically co-extensive and that the strong positive anomaly at Kombat is converted into a rather weak, negative one when the raw SusP data are divided by TSS (4BN). This negative anomaly cannot be regarded as significant because it is not repeated at Tsumeb and is offset by a wide scattering of grade -1 values in background areas. It does not appear that this element could be a useful pathfinder in the Otavi Mountainland.

(5) *Fluorine (Maps 4K and 4BB)*

Fluorine is a fairly useful pathfinder for deposits of several types, including some kinds of base metal deposits /1099/. Dissolved fluorine shows a strongly regional distribution in the orientation area, with high values in the north and low values in the south. The cause of this pattern is not known. The clustering of negative values at Kombat and positive values at Tsumeb must be seen as part of the respective sub-regional trends and are therefore probably not significant. If one considers the northern and southern zones separately, and examines the distribution of values in terms of (local peak/local background), then there is a fair anomaly at Kombat but none at Tsumeb, where even the best values nearest to the mine are not amongst the highest in the northern sub-region. The F^-/TDS ratios also reflect the existence of the two sub-regions, but less clearly. There is a small anomaly, including one rather high value, at Kombat but this is not convincing, especially in view of the fact that a similar value occurs at Otavifontein, an unmineralized spring many kilometres to the west.

Fluoride ion is probably not a pathfinder for the type of mineralization occurring at Tsumeb and Kombat.

(6) *Nickel (Maps 4T and 4AV)*

Nickel is not a popular pathfinder for Cu-Pb-Zn mineralization because its "track record" has been poor /345/. It does sometimes concentrate to a degree in mineralized zones /344/, but according to Shvartsev *et al.* /1102/

its contrast ratio tends to be poor and comparable to those of slightly mobile elements such as barium, tin and zirconium. There is a small but well-defined "dissolved" nickel anomaly at Kombat that includes an extreme value at Asis West. Most of the exceptional nickel values occur in the north, but there is no particular clustering at Tsumeb and if the pattern of peak values does indeed represent a regional anomaly then it is so extensive and vapid that it is practically useless. The Ni/TDS ratio does not change this picture greatly.

In summary, it appears that nickel has performed inconsistently in this orientation. The "fingerprint" at Kombat is very interesting but the lack of any focus at Tsumeb, the poor historical record of the element and the real problems involved in achieving precise, routine determinations at such low levels (70% of the observed concentrations are below 1 µg/l) tip the scales against using this metal routinely as a pathfinder in the Mountainland.

(7) *Strontium (Maps 4P and 4AR)*

Strontium is a pathfinder for its own ores /954/ but has little other application in hydrogeochemical exploration. There is a remarkable concentration of dissolved strontium in the Tschudi-Bobos area, well to the west of Tsumeb, but the cause of this anomaly is not apparent. Low strontium values are scattered widely in the southern part of the orientation area. In the Sr/TDS map the Tschudi-Bobos anomaly is even stronger and the Grade -I values are dotted along the Otavi valley on both sides of Kombat. The (local peak/local background) contrast at Kombat is not remarkable. There has been no indication whatsoever in this study that the distribution of strontium is associated in a rational manner with the presence of mineralization.

(8) *Potassium (Maps 4O and 4AQ)*

The use of potassium as a pathfinder is virtually unknown. There is no positive potassium anomaly at either Tsumeb or Kombat and little else about the distribution of this metal is remarkable. Like strontium, potassium is more abundant in the northern part of the orientation area. Four of the grade I values occur in groundwaters exposed to the atmosphere - i.e. springs, lakes or pits - and this suggests that some biological controls may have been operative. On the other hand, three of the peak values (near Olifantsfontein) are amongst the few samples that were collected from localities reasonably close to outcrops of the Abbabis granite. It is conceivable - but in the writer's opinion improbable - that these samples have been influenced by potassium from these leucocratic rocks.

The K/TDS map is very similar to the potassium map. It is concluded that this metal will definitely not be an aid in this exploration program.

(9) *Aluminium (Maps 4U, 4AY, 4AH and 4BL)*

No one uses aluminium as a pathfinder because it is too ubiquitous and too readily hydrolyzed /415/;the distribution of this element, like the distribution of silicon, is of potential interest only because it may reveal important regional hydrogeochemical features. Note that (i) All four aluminium maps suggest the existence of "anomalies" of some kind at both Tsumeb and Kombat. These are generally quite well marked. (ii) A comparison of the "total" aluminium and SusAl maps suggests that most of the aluminium is present in these samples in suspension. This is quite in keeping with the hydrogeochemical properties of this element (Hem, in /35/). The relationship between the dissolved, colloidal and suspended fractions of aluminium in natural waters is very complicated, but it is clear that the concentration of the metal in true solution is likely to be less than one microgram per litre at moderate pH values. It is almost impossible to determine what is truly dissolved because not all of the light colloidal fraction can be removed by filtration. The "total" aluminium peaks are so pronounced that they are scarcely modified by division of the raw data by TDS. (iii) There are marked similarities between the respective relevant maps for aluminium, silicon and TSS. This suggests that the "anomalies" indicated by these parameters may be congeneric. Again, this is hardly amazing, since aluminium silicates are one of the commonest components of natural suspensions.

It therefore seems likely that the distribution of aluminium, like that of silicon, is strongly influenced by lithological factors. Many of the peaks in the south can perhaps be attributed to aluminium silicates from the phyllite and some of those in the north to similar materials from the kersantite. This possibility is underscored particularly by the SusAl/TSS map, which suggest - albeit not so clearly - the same development of linear anomalies at Tsumeb and Kombat that were apparent from the SusSi/Tss map.

The distribution of aluminium therefore tends to support the hypothesis that changes in lithology, rather than the presence of ore *per se*, may be responsible in a large measure for the "anomalies" at Tsumeb or Kombat. Even if this theory is incorrect, it remains true that the distribution of aluminium is closely correlated with TSS and the metal is suspect as a pathfinder unless a convincing connection can be shown to exist between the concentration of total suspended solids and the natural influences of the orebodies at Tsumeb and Kombat.

(10) *Titanium (Maps 4AE and 4BI)*

There are many similarities between the distributions of titanium and aluminium in the orientation samples. Titanium is also readily hydrolyzed and the content of dissolved Ti in natural waters is of the order of 1 µg/l (Correns, in /35/). The determination by AAS of such minuscule amounts of this element is impracticable and therefore XRFS data only have been presented. The SusTi map shows anomalies at both Tsumeb and Kombat that are almost identical to the TSS anomalies that occur there. The SusTi/TSS anomalies are essentially similar to the anomalies produced by the raw data; there is but a weak tendency to transform into the strike-orientated linear anomalies that are to be seen in the corresponding maps for aluminium and silicon. It is concluded that titanium is too closely correlated with TSS to be of real use in this project.

(11) *Iron (Maps 4R, 4AT, 4AC, 4BG)*

Many of the factors that need to be considered in an examination of the distribution of iron in the orientation area have already been discussed (cf. paragraphs dealing with aluminium and silicon). Iron is exceedingly insoluble in the presence of free oxygen at pH >2 (Berner, in /35/) and most of what is termed "dissolved iron" in the literature is really very finely colloidal iron. "Suspended " iron (>0,5 µm) is very common in fresh water. Like many other elements, iron tends to be concentrated in waters around sulphidic orebodies but is never regarded as a pathfinder - the most obvious problem in a borehole sampling program being the mass of steel in contact with every sample.

The distribution of "total" iron in the orientation area shows no startling features. There is the expected anomaly at Kombat, which reflects the influence of the TSS anomaly and/or the presence of the iron-rich phyllites. There are two ferruginous samples at Tsumeb but they lie well south of the TSS peaks that occur north of the mine. A weak anomaly occurs in the Accra-Colombo area well to the east of the town. The cause of this is not apparent; it is difficult to imagine that it is related to the underlying lithology. The Fe/TDS map shows patterns essentially identical to those just described.

As expected, the SusFe map also shows this basic pattern of distribution of peak values, but with a tendency to form a weak, symmetrical, regional anomaly around Tsumeb. The SusFe/TSS map is rather interesting; the familiar linear "phyllitic" anomaly appears once more along the Otavi valley (cf. Si and Al), the anomaly at Accra-Colombo disappears and Tsumeb is ringed by four widely-spaced peak values. Isolated peak values appear in the central, background regions.

From the foregoing it appears that the determination of iron is of little interest to the hydrogeochemical prospector and that the study of the distribution of the metal has added practically nothing to our knowledge of the groundwater regime in the Otavi Mountainland.

(12) *Manganese (Maps 4Q, 4AS, 4AD and 4BH)*

There are very few examples of the use of manganese as an indicator of mineralization; the oxides and hydroxides of this metal are not very soluble in oxidizing waters (Wedepohl, in /35/). Nevertheless Shima /127/ gives examples of the use of manganese in hydrogeochemical prospecting for ores containing the metal as a major component.

Like iron, manganese is more likely to occur in natural waters in suspension than in solution. It is a major component of the suspended fraction of fresh waters. Furthermore manganese is, like iron, an important component of steel /41/. It is therefore not surprising to note strong similarities between the "total" manganese and "total" iron maps, viz. the strong anomaly at Kombat, the two high values on either side of Tsumeb and the small cluster of peak values at Accra-Colombo. The Mn/TDS and Fe/TDS maps are also similarly matched, except that the Accra-Colombo manganese anomaly is not as clearly demonstrated.

The SusMn and SusFe maps are not quite so alike. The iron anomaly in the south is repeated in the SusMn values in the central Otavi valley but the regional anomaly at Accra-Colombo is considerably smaller. None of these contrasts seems to have any important significance. Predictably, the SusMn/TSS map is almost a copy of the corresponding map for iron.

Manganese and iron apparently follow each other very closely in the orientation samples and it is concluded that manganese is therefore of no further interest to us in this exploration project.

(13) *Cobalt (Maps 4S and 4AU)*

Cobalt is a rare element in natural waters and is not regarded as a useful pathfinder /345,1102,55/. Udodov and Parilov /792/ considered cobalt to be approximately as immobile as Be, Ti, Sn, Zr and tungsten. Cobalt is very readily absorbed onto clay particles and manganese and iron precipitates. For example, cobalt correlates well with iron in most soil profiles (Turekian, in /35/). There is a strong "total" cobalt anomaly at Kombat and a weak one at Tsumeb. They correspond partially with, but not exactly to, the TSS and SusFe anomalies at these two mines. A diffuse but important cobalt anomaly occurs to the east of Tsumeb in the Accra-Colombo area (cf. iron and manganese). This anomaly, again, corresponds only partially to the SusFe anomaly that occurs in this eastern region. The Accra-Colombo cobalt anomaly is practically co-extensive with the large outcrop of quartzite in this area but this must be taken to be fortuitous as there is no other evidence of any correlation between high concentrations of dissolved cobalt and the outcrops of this arenite. The Co/TDS map shows rather similar features.

There is not enough evidence in these maps to convince the writer that the TSS and cobalt anomalies are congeneric. There appears to be a fair possibility that the cobalt anomalies - and especially the Co/TDS anomalies - at Tsumeb and Kombat are real, independent features, perhaps related to the metallogenic aureoles of the two ore deposits. This is by no means certain, however, and there are several other factors that militate against the use of cobalt as a pathfinder: the fact that the metal occurs in some steels /41/, its poor historical record, the extremely low threshold values (90% of the observed concentrations are below 0,5 µg/l) and, most especially, the large anomaly at Accra-Colombo that appears to be totally spurious. Cobalt is therefore relegated to the ranks of the "second class" pathfinders in this project. One would reconsider the possible usefulness of the metal only if the more conventional pathfinders (*vide infra*) failed to perform satisfactorily.

(14) *Bicarbonate (Maps 4I and 4AM)*

Bicarbonate is a very important ion in uranium hydrogeochemistry /904/ but not as far as exploration for base metals is concerned. Negative bicarbonate anomalies are sometimes noted near sulphide ores /1034/. In the orientation area the distribution of the bicarbonate ion appears to be related partly to lithology. Several peak values occur in the northeast, on the border of the sand-covered areas, whereas bicarbonate-poor waters are most common along the edge of the phyllite in the Otavi valley. The HCO_3^-/TDS map is rather ambiguous. There is a regional negative anomaly at Tsumeb but at Kombat both high and low values cluster together. The low bicarbonate/TDS values can in any case not be regarded as independent indicators of the existence of a regional anomaly, since bicarbonate is a major component of TDS and bicarbonate/TDS values will be depressed wherever ions other than

HCO_3^- have accumulated. Note that the bicarbonate/TDS "lows" (Grade -1) form virtually a "negative print" of the positive (Grade 1) TDS peaks. The same logic explains why most of the bicarbonate/TDS "lows" correspond exactly with the highest sodium values (*vide infra*). Bicarbonate analyses are therefore of little direct interest in this orientation study.

(15) *Sodium (Maps 4K and 4AP)*

Sodium is one of the most mobile elements and is scarcely removed from natural waters by any process other than evaporation /1048-50/. The metal will often show some tendency to accumulate around an orebody and such an anomaly will most readily be seen if the country rock is a carbonate or some other sodium-poor formation. However, it was shown earlier in this thesis that sodium may be accumulating at Tsumeb and Kombat because of anthropogenic interference with the groundwater rather than as a result of natural processes of dispersion. Moreover, the sodium and Na/TDS anomalies at Kombat show clear signs of being related to the Mulden phyllite. Another unwelcome sign is the occurrence of high sodium values on the border of the sand-covered areas; any buildup of the metal in the flat areas as a result of "metamorphism" of the groundwater /1048/ will make it almost impossible to recognize genuine sodium anomalies. For these reasons it is necessary to be extremely circumspect about attaching any great significance to the sodium anomalies at the two mines.

(16) *Magnesium (Maps 4G, 4AK, 4AG and 4BK)*

Magnesium is a major component of the carbonate rocks of the Otavi Highland and the distribution of the metal can be expected to reveal, if anything, only major trends within the groundwaters of the orientation area. Thus we find that there is a good correpondence between magnesium peaks and TDS peaks, giving "anomalies" at both mines, but when the bias is modulated by plotting Mg/TDS the peak values appear as a rather more random sprinkling of points. The corresponding sets of lowest values for magnesium form no interesting patterns.

Similarly, one notes a fair correlation between high values of SusMg and TSS peaks. However, the ratioed data do not randomize the pattern of peaks as strongly as Mg/TDS did for the "dissolved" magnesium values. Only a small anomaly remains at Kombat, but in the north there appears to be an alignment of peaks running past Tsumeb and parallel to the strike of the major lineaments in the area (cf. silicon). The cause of this pattern is not apparent. There is no known reason why an abundance of magnesium should be related to the fault line. The only perceivable factor that may tend to produce elevated concentrations of magnesium near either mine is a possible acceleration of the rate of corrosion of dolomite owing to increased recycling of groundwater /23/, or the release of sulphuric acid from decomposing sulphide minerals (cf. Section I). Nevertheless it is not clear how this could affect suspended magnesium without being reflected in the values for dissolved magnesium.

(17) *Calcium (Maps 4H, 4AL, 4AF and 4BJ)*

Calcium, like magnesium, is not expected to show any important local features. There is some clustering of calcium-poor waters in the Otavi valley and a group of calcium-rich waters occurs on the edge of the sand-covered tracts northeast of Tsumeb. The calcium/TDS values produce interesting negative values both at Tsumeb and at Kombat and there is a good correlation between Ca/TDS and TDS. This provides a good example of a negative anomaly due to mathematical closure /1192/. The concentration of calcium is fixed by the carbonic system and, as the concentrations of other ions such as sodium and magnesium build up, so calcium becomes a proportionately less dominant component of the TDS. The high-TDS waters around the mines therefore appear on the Ca/TDS map as "lows".

The picture presented by the SusCa data is confused, with high and low values occurring side-by-side at both mines. There is, as one would expect, a fairly good correlation between the SusCa peaks and the TSS peaks. The distribution of the SusCa/TSS peaks is essentially random, except for a weak negative anomaly in the central Otavi valley.

In Chapter 5 it was mentioned that there was, in theory, a slight possibility of using very high Mg/Ca ratios as a prospecting criterion for sulphidic ores emplaced in dolomite. A comparison of the data in Table 5.3(ii) with Map 4A shows that there is some tendency for samples with very high Mg/Ca ratios to occur at either Tsumeb or Kombat. However, very high values also occur in background areas, for instance at Lake Otjikoto and at Lucas Post. Furthermore, it was shown in Chapter 4 that high Mg/Ca ratios will also result from active recirculation of groundwater and of course it is near the two mines that this kind of recycling is most active. Moreover, the Mg/Ca ratio, if it is to have any use at all, must be utilized in a dolomitic terrane, because it is a prospecting sign related not to the products of the orebody *per se*, but to the chemical interaction of these products with these specific host rocks. The Kalahari beds are not dolomitic (Chapter 6) and have variable concentrations of magnesium. It therefore seems highly improbable that an orebody emplaced in buried dolomite could have any meaningful influence on the Mg/Ca ratio of the formational waters in the overlying superficial materials.

(18) *Chloride (Maps 4E and 4AN)*

Chloride is not a popular pathfinder but it is released during the weathering of sulphidic ores /1072/. It is a mobile element that can be expected to follow sodium (*vide supra*) closely in the orientation samples. This it does, and the significance of the chloride "anomalies" at the two mines is therefore as much suspect as the "anomalies" produced by sodium.

(19) *Sulphate (Maps 4D and 4AO)*

Sulphate and the sulphate/chloride ratio are amongst the most important pathfinders for base metal mineralization /351,495,1100,873,1037/. There is a small but sharp sulphate anomaly in the central Otavi valley and a strong but unfortunately rather wide anomaly at Tsumeb. If one includes all the Grade II sulphate values then this northern anomaly broadens out into a very wide regional feature stretching from Tschudi in the west to Aarhus in the east. The substitution of sulphate/TDS values results in a convincing although still rather broad regional anomaly around Tsumeb, but in the south the smaller anomaly is considerably weakened. The sulphate/chloride ratio does not offer any improvement; the Kombat anomaly remains weak and the broad anomaly at Tsumeb persists, but with the main concentration of Grade I values displaced strongly to the southeast. (It is some consolation to know that others have had problems with this much-celebrated ratio. Belyakova /783/ was particularly iconoclastic about it and cited instances where the ratio *dropped* significantly as one approached the orebody!).

Sulphate has not performed outstandingly well in this orientation study. Nevertheless it is clearly the most important anion that has been examined in either of the two orientation surveys and will undoubtedly be of some value in hydrogeochemical exploration in this region.

(20) *Zinc (Maps 4J, 4AX, 4AB and 4BF)*

Zinc is undoubtedly the most important hydrogeochemical pathfinder for Cu-Pb-Zn deposits /356,537,782,345,55,527,819,1119,1030,1035,45,48,970/. It can also have high and erratic background concentrations in carbonate formational waters /45,48/. It is a common contaminant of samples taken from boreholes with galvanized casings /49,99,1101/; this chronic problem has been discussed at length in Appendix J. There is essentially no sure way of telling whether the peak values observed in the orientation samples are more-or-less genuine features or whether they are merely the result of contamination, but there is some evidence that certain of the waters (e.g. at Kranzberg East) are heavily laced with zinc derived from the borehole hardware. Isolated extreme values, such as those at Welcome Post and Cork, must therefore be regarded with suspicion at this stage. Zinc is very mobile and it is of course just possible that these extreme values represent real examples of secondary dispersion from undiscovered mineralization within the vicinity of these anomalous boreholes. However, this cannot be assumed in assessing the results of an orientation study and we will delay further consideration of this point until the following sub--section of this Chapter.

Even allowing that the Kranzberg East sample may be contaminated, there is at Kombat a good "total" zinc anomaly, which is displaced somewhat to the west of the mine. Unfortunately there is no indication whatsoever of a zinc anomaly at Tsumeb. The Kombat anomaly appears again in a somewhat weakened form in the Zn/TDS map, which also reveals a small cluster of zinc peaks well to the west of Tsumeb.

The SusZn map is practically a duplicate of the total zinc map, which makes one suspect that the anomaly at Kombat may have been enhanced by the partial correlation of zinc with TSS. This doubt is reinforced by the waning of the Kombat anomaly when the SusZn/TSS ratios are substituted for the raw data.

The performance of zinc in this orientation study has been below expectation. However, it has produced anomalies of some form at Kombat, has an outstanding historical reputation and is easy to determine, and for these reasons ought to be retained as a possible pathfinder.

(21) *Copper (Maps 4L, 4AW, 4AA and 4BE)*

Copper is, after zinc, the most popular metallic pathfinder for deposits of base metals /99,106,140-1,185,344/. It is not as mobile as zinc /121,782,345,537/ but on the other hand contamination from hardware affects copper to a far lesser degree than it does zinc /53/. There is a strong "total" copper anomaly at Kombat and a smaller but important one at Tsumeb. A very important aspect of this map is that all of the Grade I values and most of the Grade II's are confined to these two anomalies; there are no important copper peaks in background areas.

A different pattern is shown by the data for Cu/TDS: the Tsumeb anomaly is significantly weakened, while the Kombat anomaly becomes very strong indeed and covers most of the central Otavi valley. On the debit side, one must note a fair correlation between the values for "total" copper and TSS and also that the anomaly at Tsumeb is located in the vicinity of the kersantite dykes to the northwest of the mine. Nevertheless, copper is apparently *not* in suspension in the anomalous samples in the north, since there is no more than one Grade II SusCu peak in the area. Furthermore, the SusCu anomaly at Kombat is very powerful and is displaced but not destroyed by ratioing the raw data against TSS. The correction does, however, produce spurious anomalies in background areas.

On balance, copper seems to have performed rather well in this study. It certainly appears to be a more promising pathfinder than zinc in the Otavi Mountainland. The reason for this state of affairs is at this juncture a matter of speculation. It may be due to the combined effects on the distribution of zinc of contamination and an unstable background value. Because zinc is very mobile it will be more susceptible to these influences than copper will be.

(22) *Lead (Maps 4M, 4BA, 4Z and 4BD)*

Lead is a rather immobile element and is not given to forming broad anomalies /49/. Many workers (e.g. /792,782,1094,1033/) have nevertheless noted that the element can be a very useful "short range" pathfinder for base metal sulphides. If lead values are very high then the chances are that the deposit is close at hand. Under most circumstances the metal is relatively unaffected by contamination.

"Total" lead and Pb/TDS, like the corresponding data for zinc, reveal good anomalies at Kombat (with an extreme value at Kranzberg East) but no sensible clustering of peak values at Tsumeb. There is, once again, a fair correlation between these lead anomalies and areas of high TSS, so it is not surprising to find a strong SusPb anomaly at Kombat. There is only one peak value near Tsumeb.

The SusPb/TSS map creates a very different picture. Here the Kombat anomaly is greatly weakened and displaced but an important anomaly appears at Tsumeb. Unfortunately a number of peak values also crop up in background areas and they detract rather heavily from the significance of the new anomaly at the northern mine.

Lead has proved to be not nearly as useful as copper in this study but there are enough encouraging signs to justify its inclusion, with zinc, as a supplementary pathfinder for mineraliztion in the Otavi dolomites.

(23) *Copper plus lead (Map 4BP) and Copper plus lead plus zinc (Map 4BQ)*

Many writers, particularly in the USSR, have emphasized that a wide range of elements is commonly encountered at somewhat elevated concentrations within hydrogeochemical dispersion haloes in groundwaters /1102,1133/. This is obviously true at Tsumeb and especially at Kombat (cf. data for the mine waters in Chapter 4). It does not follow that each of these species will be a useful pathfinder. Some have limited mobility, others are too prone to contamination or to fluctuations due to lithological changes, and so on. Nevertheless, many authors have pointed to the possibility of using the sums of concentrations of metals to reveal gross features that are not emphasized by the patterns of distribution of the individual elements /792/. Some of these proposed "summed indices" are quite straightforward, e.g. (Zn + Cu + Pb) /1097/. Others are quite bizarre, e.g.

$$((Fe+Pb+Ag+Zn+Mn+Ba)/TDS) \quad /1030/.$$

There is obviously no point in including metals like iron and manganese in any potential summed index for the Otavi Mountainland. Zinc must also be excluded because it is usually relatively abundant and therefore tends to swamp the index (Map 4BQ). Cobalt and nickel, on the other hand, are present in such small amounts that they effect no sensible "leverage" on the index. The only potentially interesting index for this orientation project appears to be ("total" copper plus "total" lead); the distribution of these values is shown in Map 4BP. It reveals a massive anomaly at Kombat but only a very half-hearted one at Tsumeb. If one recalls the very poor development of anomalies for individual base metals at Tsumeb, then it is logical to deduce that the process of summation is unlikely to improve matters much.

(C) *SUMMARY, CONCLUSIONS AND RECOMMENDATIONS*

(1) The data of Appendix J show that the problem of contamination from borehole hardware is generally not serious in the orientation area. Zinc is the only metal that may be seriously affected in some samples, but the orientation results show that it is nevertheless possible to identify some real zinc anomalies (cf. points 10 and 14 below).

(2) Appendix J also shows that contamination of samples by the high-density polyethylene containers that they were stored in was minimal. It was also shown that the samples were quite stable when thus stored.

(3) It was further shown in Appendix J that seasonal variations in the compositions of the groundwaters in the Otavi Mountainland are slight. Specific sampling programs, such as the second orientation study and the Application phase (Chapter 6), were completed rapidly and seasonal drift

could therefore be ignored.

(4) Analytical data were collected for pH, temperature and some forty chemical species. The following species showed so little variation in concentration or were generally present in such small amounts that no meaningful assessment could be made of their distributions: Li, Rb, Cs, V, Cr, Mo, Ag, Au, Cd, Hg, Tl, Ge, As, Sb, Bi, Se and Te.

(5) The distributions of the remaining species were studied with the aid of maps and basic statistical calculations, both of which were produced by computer. Maps drawn by the computer are very useful and time-saving.

(6) The geographical distribution of the sampling points makes contouring of the data impossible. Various formal mathematical and geometric methods were applied to the data but failed to yield good results. The location and significance of anomalies were therefore judged subjectively "by eye".

(7) For each element (X) one or more of the following distributions were studied:

(a) Total X; i.e., dissolved X plus acid-soluble suspended X.

(b) Total X/TDS

(c) Suspended X

(d) Suspended X/TSS

(8) The following factors had to be taken into account in order to explain the observed patterns of distribution of values, to decide which of them constituted anomalies and to assess the importance of those anomalies:

(a) the individual characteristics of the different chemical species

(b) contrast values and the detection limit of analysis

(c) variations in the local value of the background concentration

(d) the influence of lithology of the host rocks

(e) the correlations between TDS, TSS and the concentrations of certain species

(f) the postulated "metallogenic zones" or "aureoles of dispersion" at Tsumeb and Kombat

(g) disturbances of the groundwater systems at the two mines by the activities of man.

(9) It was found that meaningful anomalies could be recognized and that pathfinders could be identified with some confidence. This result stands in contrast to those of the first orientation study of the waters of the Tsumeb mine, in which it was found that the effects of recycling of groundwater made it practically impossible to achieve these goals with any confidence. Accordingly it is recommended that the second orientation survey should be followed up by an attempt to apply the hydrogeochemical technique in exploration in a selected area of Kalahari terrane (Chapter 6 following).

Despite this positive result, it must be noted that the anomalies at Tsumeb are much poorer than those at Kombat. This may be due to dewatering or other local effects but it is not possible to identify any definite cause. It is also impossible to say to what extent these observations will affect the relative probability of detecting a buried orebody of the "Kombat" type as opposed to one of the "Tsumeb" type. The original patterns of dispersion around these two deposits may have been the same, or they may have been quite different. We have no way of knowing, because we simply cannot tell to what extent those original patterns have been altered by the process of exploitation of the ore.

(10) It is obviously highly desirable to limit the number of pathfinders that are to be determined in a hydrogeochemical survey involving large numbers of samples. It is therefore recommended that only the four most promising species - copper, lead, zinc and sulphate, including the sulphate/chloride ratio and species/TDS ratios - be adopted as potential pathfinders for the application phase of this project. The remaining species or measurements were not shown to be prime candidates for admission to the class of potential pathfinders and, with the exception of those elements and ions required for purposes set out in paragraph (13), should be disregarded.

(11) A considerable proportion of the total mass of copper, lead and zinc in the orientation samples is in suspension. There is, however, no decisive advantage in filtering out and separately analyzing the suspended material; indeed, it would probably be disadvantageous to do so. This procedure would in any case be extremely tedious in the application phase of the project and might increase the probability of contamination of the samples during collection. It appears that the method of determining "total" metal after acidification of the sample is both efficient and efficaceous, and is accordingly recommended.

(12) The abovementioned four pathfinders produce very different anomalies at the Kombat and Tsumeb mines. There can therefore be no question at this stage of setting any realistic orientation parameters such as threshold values, sampling densities or anticipated diameters of anomalies. Nevertheless, it seems certain that the anomalies will be regional rather than local ones. One may anticipate that these regional anomalies will be quite small under most circumstances. Although most of the anomalies observed during orientation consisted of clusters of peak values within a few kilometres of one another, the possibility of encountering "single point" anomalies during the application phase must be borne in mind.

(13) The statement in (10) above notwithstanding, there are many obvious advantages in being able to examine the relationship between the concentrations of the selected pathfinders and the major element chemistry of the samples.

This is especially important in view of the fact that one may expect that the groundwaters of the Kalahari areas will not have the same bulk chemistry as the dolomitic waters (Section I). For this reason it is recommended that the following supplementary measurements and determinations be made during the application study : pH, bicarbonate, calcium, magnesium and sodium.
(14) Several samples collected during the orientation study proved to have extremely high concentrations of zinc and, in one case, lead. Kranzberg East and Welcome Post are examples of boreholes that yielded exceptionally metalliferous waters. It seems probable that contamination from borehole hardware is the cause of some of these high values but it remains possible that one or more of these holes may have intersected a real anomaly associated with unknown mineralization at depth. It is suggested that this observation may provide a starting point for further profitable research work, but it must also be stressed that such an undertaking has definitely never been included in the terms of reference of this thesis.

Chapter 6. Application experiment in the Withdrawal Area northeast of Tsumeb

6.1 Introduction

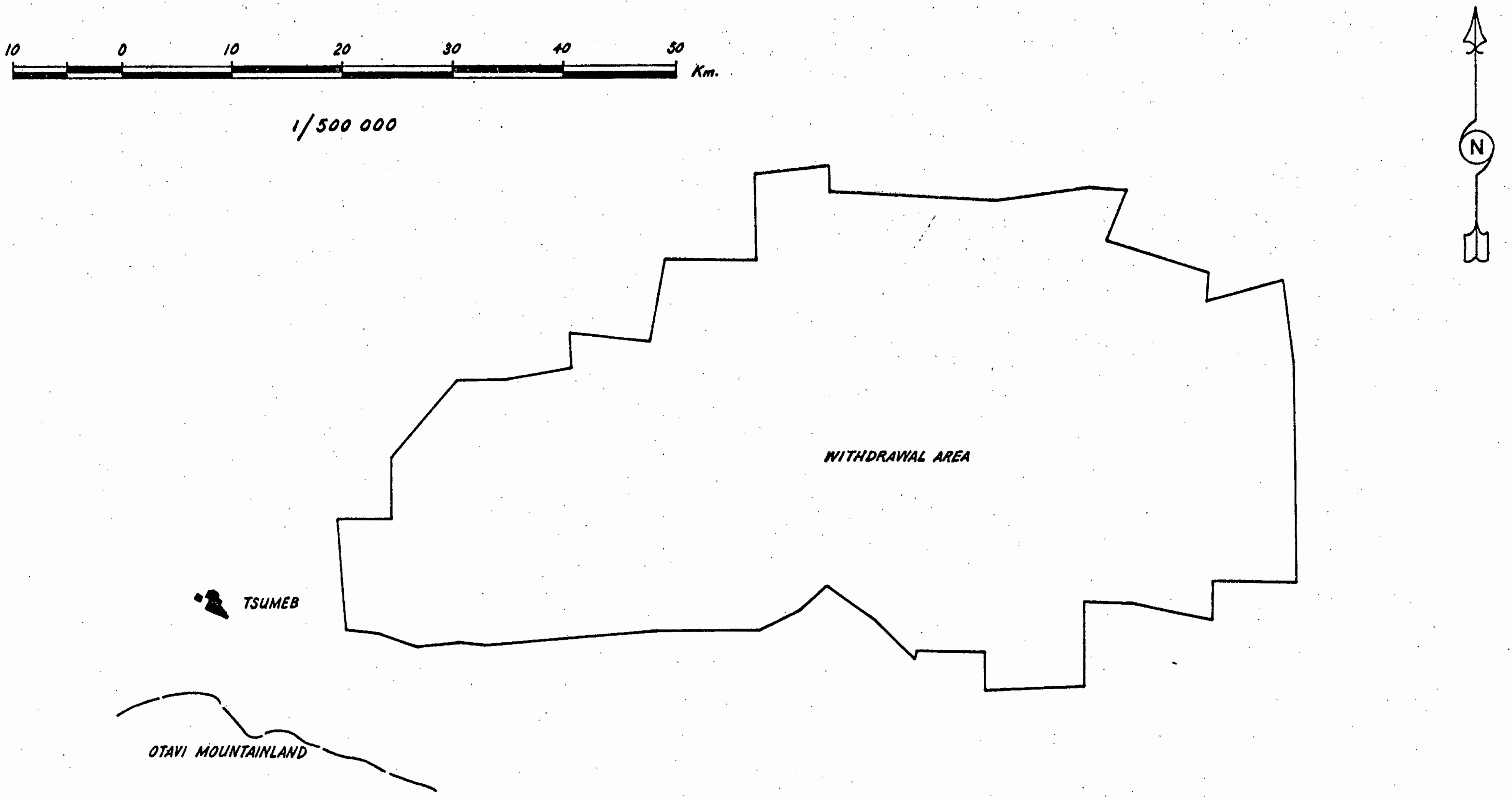
The results of the second orientation study were encouraging enough to justify applying the hydrogeochemical technique in a selected area on the pediplain northeast of Tsumeb. The block of farms chosen for this purpose has been described in Section I and was withdrawn from pegging by the Administration in favour of Tsumeb Corporation Limited (TCL) in April 1974 (Withdrawal Order numbers 261, 262 and 263). This "Withdrawal Area" is shown overleaf (Fig. 6.1) and on most of the versions of Map 4 in Vol. II, and covers about 200 000 ha.

The Withdrawal Area consisted of a few dozen cattle farms, with a total of perhaps 200 boreholes or other potential sources of water samples, not all of which were operational or accessible at any given time. During May to July 1974 all the usable sources (170-odd) of groundwater in this area were sampled and analyzed for pathfinders and major components. The collection and analysis of these samples was very kindly undertaken on behalf of and under the direction of the writer by Tsumeb Corporation Limited.

6.2 Sampling, analysis and results

The sampling procedures used were essentially the same as those described in Chapter 5. Appendix L is a copy of the typed instructions followed by the field personnel responsible for the collection of the samples. The footnotes to this appendix list the small changes made during the sampling program

Fig. 6.1



Map showing the Withdrawal Area (Nos 261, 262 & 263) relative to Tsumeb Town & the Otavi Mountainland.

as a result of practical experience. The most notable was the substitution of perchloric acid for nitric acid as the preserving acid. Perchloric acid has the advantage of improving the precision of MIBK/APCD extraction of trace metals (Koirtyohann and Wen, 1973 /34/), a fact we were unaware of at the time of the orientation sampling. There was no reason to suppose that the substitution of perchloric acid would have any adverse effects and indeed none were noted at any stage of the program.

The following analyses and measurements were undertakem: pH, methyl alkalinity, phenolphthalein alkalinity (allowing the calculation of the concentration of bicarbonate), total hardness, calcium hardness (allowing the calculation of the concentrations of magnesium and calcium ions), sulphate, chloride, copper, lead, zinc and sodium. The methods and all associated tests of precision are described in Appendix B5. The analytical results are compiled in Table 6.2, following. (The data are given in the units in which they were reported by the TCL laboratories. The calculations necessary to convert these numbers into the same units as those used for the representation of the orientation data were performed automatically by the computer that plotted the data on the hydrogeochemical maps in Vol. II).

6.3 Initial interpretation

(A) *INTRODUCTION*

The interpretation of the data followed lines broadly similar to those of the second orientation study. The data are plotted on the same maps 4C, 4D ... etc. described in Chapter 5, and the threshold values used (computed by the BMDP routines referred to in that chapter /281/) are compiled in Table 6.3A. In addition, it was possible to construct computer-generated contour maps and "three dimensional" perspective projection diagrams of the chemical data from the Withdrawal Area. (This had not been feasible for the unequally and thinly distributed orientation data). The "3D" diagrams are labelled 6a, 6b, 6c, 6d ... etc. and the corresponding contour maps are labelled 6ac, 6bc, 6cc, 6dc ... etc. Note the following features of these maps and perspective projections and the programs that produced them:

(i) The computer programs responsible for these illustrations are contained in the SACLANT graphics package at UCT /1197/. The bulk of the programming is in ALGOL and is so transparent to the user that it would be pointless to reproduce in this thesis the control cards selected to construct the particular figures shown.

(ii) The contour map is orientated in the conventional manner, with north towards the top of the diagram. The 3D projections are always viewed from a

TABLE 6.2 RESULTS OF ANALYSES OF BOREHOLE WATERS FROM THE WITHDRAWAL AREA

	pH	$SO_4^=$	CaH	MgH	TH	TDS	Cl^-	PA	MA	Cu	Pb	Zn	Na
1	6,8	5	240	314	560	584	49	nil	565	<1	3	748	7
2	6,8	4	200	356	556	604	36	nil	555	<1	3	7	5
3	6,8	7	68	508	576	648	36	nil	590	<1	3	14	6
4	7,0	9	88	440	528	604	36	nil	500	<1	2	27	7
5	6,9	9	112	380	492	560	36	nil	490	3	1	62	2
6	6,8	111	108	444	548	776	24	nil	455	4	<1	712	30
7	6,8	20	336	344	680	620	109	nil	495	<1	<1	24	10
8	6,7	31	340	330	670	556	74	nil	540	1	4	22	9
9	6,8	6	276	314	590	404	32	nil	570	<1	5	10	9
10	6,8	37	464	566	1030	1292	306	nil	605	3	<1	184	130
11	6,7	9	288	392	680	544	34	nil	590	<1	16	2600	18
12	6,9	15	276	374	650	492	30	nil	615	<1	6	43	13
13	6,8	2	384	436	820	672	190	nil	525	<1	4	15	11
14	7,0	2	312	338	650	480	72	nil	570	2	<1	91	15
15	6,90	3	304	136	440	476	6	nil	460	5	3	378	17
16	6,85	23	244	316	560	584	6	nil	555	<1	9	7820	6
17	7,10	5	208	152	360	428	7	nil	370	4	5	94	5
18	6,90	6	252	238	490	508	7	nil	520	<1	2	220	5
19	6,90	10	252	268	520	516	6	nil	540	4	<1	410	5
20	6,85	6	252	268	520	540	7	nil	545	7	2	75	5
21	6,85	6	252	288	540	540	8	nil	570	2	2	20	6
22	7,00	3	228	162	390	440	8	nil	404	9	4	48	6
23	6,90	5	244	196	440	460	19	nil	415	50	2	200	3
24	6,9	5	272	358	630	512	21	nil	605	3	4	12	7
25	6,7	2	276	324	600	436	17	nil	595	3	<1	128	5
26	6,8	18	312	348	660	800	41	nil	610	2	5	25	19
27	6,9	8	252	398	650	568	46	nil	600	24	<1	200	9
28	6,9	64	564	1336	1900	2524	854	nil	500	18	<1	514	220
29	6,9	24	252	298	550	444	33	nil	475	2	3	80	16
30	6,9	6	232	348	580	456	7	nil	585	14	3	360	7
31	7,1	43	284	556	840	1512	318	nil	590	5	6	34	220
32	6,9	10	272	338	610	612	53	nil	590	2	16	23	34
33	7,0	5	260	400	660	744	73	nil	550	3	<1	340	14
34	6,9	32	324	266	590	640	49	nil	475	7	2	266	24
35	7,0	7	276	334	610	624	42	nil	605	5	<1	218	30
36	6,9	5	304	256	560	564	39	nil	550	4	<1	139	13
37	6,9	3	276	304	580	528	30	nil	575	5	<1	42	13
38	7,0	6	276	334	610	528	76	nil	500	<1	<1	71	11
39	6,9	202	352	1058	1410	2444	685	nil	475	4	<1	291	280
40	7,0	181	260	450	710	816	53	nil	525	2	<1	67	40
41	7,3	15	280	420	700	880	99	nil	570	9	<1	84	30
42	7,2	9	292	428	720	844	102	nil	530	1	<1	102	19
43	7,2	3	252	528	780	856	102	nil	590	2	<1	100	10

Values for sulphate, total dissolved solids , chloride and sodium in mg/l.

Values for copper, lead and zinc in micrograms per litre.

Values for calcium hardness, magnesium hardness, total hardness, methyl alkalinity and phenolphthalein alkalinity in ppm calcium carbonate.

TABLE 6.2 RESULTS OF ANALYSES OF BOREHOLE WATERS FROM THE WITHDRAWAL AREA

(continued)

	pH	$SO_4^=$	CaH	MgH	TH	TDS	Cl^-	PA	MA	Cu	Pb	Zn	Na
44	7,8	3	228	372	600	656	15	nil	605	4	<1	101	5
45	7,1	80	452	628	1080	1692	331	nil	545	9	<1	58	120
46	7,4	27	316	894	1210	1520	349	nil	480	4	<1	78	50
47	7,6	24	252	308	560	840	69	nil	460	<1	<1	9	60
48	7,3	4	240	310	550	628	15	nil	545	8	<1	47	9
49	7,8	22	232	198	430	436	21	nil	420	1	<1	53	15
50	7,4	22	280	270	550	608	74	nil	500	<1	<1	23	30
51	7,5	21	164	366	530	612	40	nil	560	1	16	17	60
52	7,5	10	216	234	450	560	55	nil	395	<1	7	12	40
53	7,5	9	212	228	440	444	24	nil	455	3	14	27	20
54	7,5	48	272	568	840	1008	125	nil	555	10	12	17	60
55	7,4	9	68	422	490	524	33	nil	485	4	4	90	20
56	7,3	316	844	1376	2220	4176	864	nil	545	24	<1	44	400
57	7,4	5	224	266	490	464	28	nil	480	3	1	101	13
58	7,3	14	140	460	600	600	41	nil	580	<1	6	30	20
59	7,9	185	304	816	1120	4064	770	nil	455	7	<1	59	400
60	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
61	7,7	55	192	338	530	724	33	nil	525	8	<1	56	20
62	7,9	48	192	318	510	964	85	nil	545	4	<1	29	60
63	7,8	28	100	500	600	952	121	nil	605	5	1	18	60
64	8,2	46	108	442	550	800	89	nil	515	29	36	2790	60
65	7,9	38	124	386	510	728	33	nil	555	31	<1	60	40
66	7,6	36	76	454	530	784	48	nil	545	2	<1	124	40
67	7,4	275	668	932	1600	4904	1431	nil	570	25	<1	140	700
68	8,1	137	268	332	600	1184	148	nil	530	25	<1	420	120
69	7,4	184	260	380	640	1388	173	nil	440	2	<1	48	160
70	7,3	332	136	954	1090	2436	311	nil	460	13	5	53	280
71	7,4	37	56	514	570	748	89	nil	460	5	<1	32	20
72	7,2	107	104	1376	1480	3572	885	nil	490	3	<1	880	600
73	7,3	4	52	398	450	424	14	nil	460	7	<1	124	6
74	7,5	617	56	684	740	1868	207	nil	645	1	<1	110	340
75	7,4	8	172	458	630	432	17	nil	640	ND	ND	ND	ND
76	7,1	205	160	2410	2570	4512	1185	nil	450	13	1	560	400
77	7,5	213	56	434	490	1024	101	nil	475	300	2	230	140
78	7,4	42	216	464	680	792	52	nil	685	3	2	32	60
79	7,3	29	240	240	480	556	24	nil	480	17	<1	12	14
80	7,2	20	236	354	590	728	46	nil	650	23	<1	120	40
81	7,4	37	196	394	590	788	72	nil	545	8	<1	10	40
82	7,3	30	216	324	540	636	30	nil	595	5	<1	182	40
83	7,2	45	268	252	520	608	30	nil	505	24	<1	32	42
84	7,3	119	384	836	1220	2016	295	nil	530	300	7	163	220
85	7,3	136	388	832	1220	2040	323	nil	530	6	<1	50	220
86	7,3	24	200	250	450	496	20	nil	470	9	<1	43	13

ND = not determined

TABLE 6.2 RESULTS OF ANALYSES OF BOREHOLE WATERS FROM THE WITHDRAWAL AREA

(continued)

	pH	$SO_4^=$	CaH	MgH	TH	TDS	Cl^-	PA	MA	Cu	Pb	Zn	Na
87	7,4	16	164	236	400	504	24	nil	445	5	<1	86	40
88	7,3	45	168	322	490	696	107	nil	440	3	<1	42	40
89	7,2	35	280	330	610	1028	145	nil	430	3	<1	255	100
90	7,5	113	140	250	390	760	67	nil	525	9	<1	60	100
91	7,9	10	44	76	120	552	18	nil	410	20	<1	667	140
92	7,4	103	272	588	860	1472	319	nil	455	12	<1	126	100
93	7,6	27	224	276	500	560	40	nil	485	7	<1	9	15
94	7,4	31	160	410	570	684	67	nil	580	17	<1	51	60
95	7,4	7	172	308	480	500	24	nil	500	1	<1	25	10
96	7,5	5	224	226	450	476	18	nil	470	3	<1	87	8
97	7,3	34	92	408	500	568	30	nil	515	1	<1	90	30
98	7,4	27	104	396	500	512	22	nil	490	4	<1	49	16
99	7,8	38	164	326	490	588	65	nil	480	2	<1	8	30
100	7,3	182	124	336	460	1060	188	nil	495	9	<1	415	220
101	7,2	9	164	256	420	532	32	nil	470	14	<1	268	30
102	7,3	91	96	174	270	720	52	nil	500	9	<1	1300	120
103	7,2	9	188	262	450	652	46	nil	445	1	<1	83	30
104	7,2	5	160	170	330	360	11	nil	360	140	10	6	5
105	7,3	131	140	270	410	1244	284	nil	615	<1	<1	629	320
106	7,2	409	148	412	560	1708	312	nil	640	14	<1	601	340
107	7,4	96	76	144	220	828	80	nil	535	15	<1	171	220
108	7,3	16	124	276	400	472	24	nil	420	9	<1	50	20
109	7,5	95	84	186	270	828	116	nil	470	27	<1	66	120
110	7,4	1697	60	610	670	5052	441	nil	1730	32	<1	190	1500
111	6,9	12	296	314	610	880	160	nil	455	9	<1	96	50
112	7,1	115	304	736	1040	2644	470	nil	435	14	<1	87	240
113	7,3	122	144	706	850	1936	506	nil	595	53	<1	112	280
114	7,1	197	208	352	560	696	19	nil	415	<1	<1	27	20
115	7,2	247	204	616	820	1308	160	nil	490	9	<1	12	140
116	6,9	181	612	1758	2370	4148	1320	nil	430	5	<1	550	400
117	7,3	48	152	228	380	548	31	nil	450	2	<1	220	60
118	7,3	60	328	752	1080	1560	258	nil	550	11	<1	142	120
119	7,1	59	316	744	1060	1464	253	nil	550	17	<1	85	120
120	7,0	24	280	370	650	792	158	nil	515	3	<1	65	50
121	7,0	141	336	394	730	1368	317	nil	485	5	<1	48	87
122	7,1	134	616	894	1510	3088	475	nil	370	8	<1	70	200
123	7,2	187	600	1230	1830	3708	561	nil	355	15	<1	42	300
124	7,1	46	312	358	670	856	111	nil	415	36	<1	175	50
125	7,3	63	160	260	420	644	83	nil	400	5	<1	105	40
126	7,2	174	304	486	790	2000	351	nil	555	25	<1	6	220
127	7,1	116	260	470	730	1364	227	nil	485	7	<1	179	120
128	7,2	6	148	352	500	612	43	nil	475	4	<1	88	30
129	7,2	27	140	290	430	624	53	nil	495	<1	<1	6	70

TABLE 6.2 RESULTS OF ANALYSES OF BOREHOLE WATERS FROM THE WITHDRAWAL AREA

(continued)

	pH	$SO_4^=$	CaH	MgH	TH	TDS	Cl^-	PA	MA	Cu	Pb	Zn	Na
130	7,2	20	236	224	460	628	44	nil	425	3	<1	98	20
131	7,3	14	172	348	520	684	47	nil	525	9	<1	112	40
132	7,3	8	164	416	580	616	31	nil	590	67	<1	132	19
133	7,0	12	292	228	520	748	41	nil	510	2	<1	22	18
134	6,9	5	316	174	490	572	14	nil	510	1	<1	100	4
135	6,9	8	280	260	540	680	25	nil	450	4	<1	67	18
136	7,6	13	124	306	430	560	29	nil	455	2	<1	6	17
137	7,4	17	196	144	340	544	30	nil	415	102	1	204	40
138	7,4	9	200	270	470	600	20	nil	530	1	<1	23	20
139	7,1	31	296	334	630	1132	218	nil	495	1	<1	37	120
140	7,3	101	264	636	900	1628	229	nil	565	7	<1	6	100
141	7,1	10	220	410	630	884	140	nil	500	4	<1	22	100
142	7,3	8	208	332	540	664	18	nil	585	46	<1	28	14
143	7,1	13	224	436	660	908	124	nil	515	9	<1	5	30
144	7,2	23	176	314	490	680	48	nil	490	3	<1	14	40
145	7,2	29	188	392	580	648	25	nil	625	5	<1	64	20
146	7,1	19	192	348	540	576	19	nil	585	12	<1	9	16
147	7,1	53	412	708	1120	1600	478	nil	480	11	<1	132	180
148	7,0	10	292	278	570	692	100	nil	495	14	<1	12	30
149	7,3	40	284	376	660	928	105	nil	575	28	6	24	50
150	7,1	17	260	330	590	688	43	nil	555	31	<1	48	20
151	7,0	3	248	252	500	496	15	nil	510	28	<1	77	7
152	7,0	20	324	526	850	940	163	nil	520	5	<1	26	20
153	7,0	5	312	158	470	512	18	nil	505	5	6	694	6
154	6,9	5	324	166	490	560	13	nil	520	14	<1	458	5
155	6,9	40	236	194	430	704	50	nil	555	9	<1	256	80
156	6,9	5	264	216	480	566	18	nil	515	31	<1	70	12
157	7,1	6	228	222	450	528	26	nil	445	21	<1	48	8
158	6,9	3	256	214	470	524	19	nil	475	12	<1	48	5
159	6,8	37	496	134	630	988	145	nil	420	10	<1	81	40
160	6,9	8	208	342	550	596	41	nil	510	20	<1	170	10
161	7,0	6	196	414	610	688	21	nil	630	12	<1	144	20
162	7,0	28	476	244	720	940	140	nil	480	28	<1	10	30
163	6,8	5	288	222	510	548	19	nil	545	16	<1	84	9
164	6,9	22	280	320	600	760	63	nil	530	23	<1	131	30
165	7,0	91	432	438	870	1756	242	nil	420	28	<1	5	100
166	7,0	91	320	500	820	1576	218	nil	525	28	<1	165	160
167	7,2	66	204	276	480	578	29	nil	480	4	<1	22	30
168	7,1	13	228	282	510	592	53	nil	500	4	<1	38	12
169	7,2	4	280	170	450	468	14	nil	495	4	<1	5	6
170	7,0	4	300	160	460	480	23	nil	495	40	<1	48	9
171	7,0	23	328	582	910	1084	175	nil	590	9	<1	172	50
172	7,1	10	244	326	570	544	24	nil	590	<1	<1	156	10

TABLE 6.3A THRESHOLD DATA FOR VARIOUS GRADES OF ANOMALOUS APPLICATION SAMPLES

Data	Map	Grade -I ≈10% CF*	Grade -II ≈20% CF	Grade I ≈90% CF	Grade II ≈80% CF
pH	4F	6,9	7,0	7,5	7,4
TDS, mg/l	4C	480	532	1936	1308
$SO_4^=$, mg/l	4D	5	6	181	95
$SO_4^=$/TDS	4AO	0,0089	0,0114	0,1053	0,0599
$SO_4^=/Cl^-$	4BO	0,1227	0,1835	1,2083	0,819
Cl^-, mg/l	4E	15	21	331	207
Cl^-/TDS	4AN	0,0302	0,041	0,1955	0,1538
Mg, mg/l	4G	48	61	179	121
Mg/TDS	4AK	0,0677	0,0806	0,1534	0,1393
Ca, mg/l	4H	45	64	141	122
Ca/TDS	4AL	0,0461	0,074	0,2102	0,1873
HCO_3^-, mg/l	4I	518	555	725	695
HCO_3^-/TDS	4AM	0,3656	0,4755	1,25	1,1672
Zn, μg/l	4J	12	23	360	179
Zn/TDS	4AX	0,0156	0,0249	0,3915	0,2196
Cu, μg/l	4L	1	2	28	17
Cu/TDS	4AW	0,0005	0,0025	0,0362	0,0211
Pb, μg/l	4M	1	1	5	1
Pb/TDS	4BA	0,0002	0,0002	0,0068	0,0021
Cu + Pb, μg/l	4BP	2	3	28	20
Na, mg/l	4K	6	10	220	120
Na/TDS	4AP	0,0128	0,0187	0,1149	0,0973

CF = cumulative frequency value taken as a criterion of threshold.

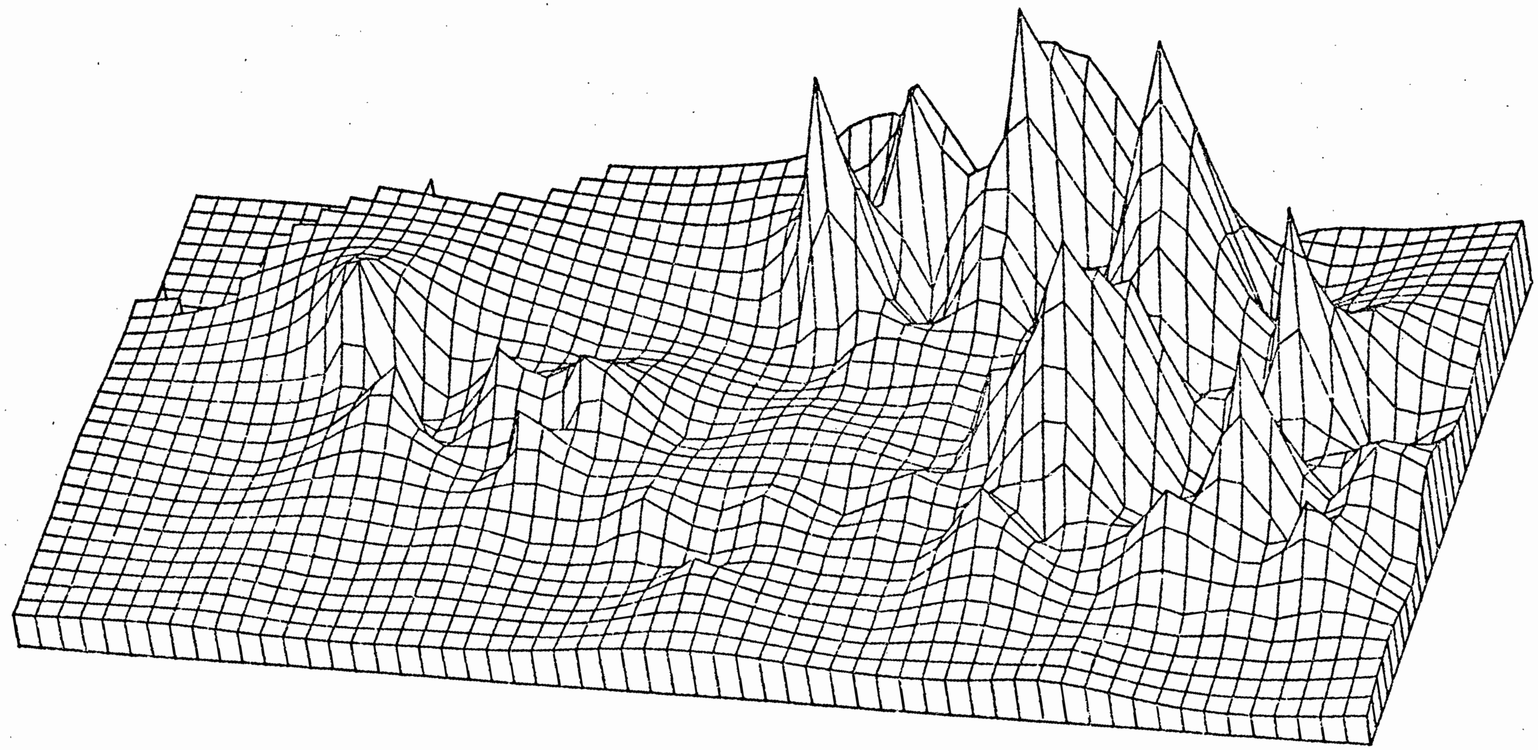


FIG.6A TDS

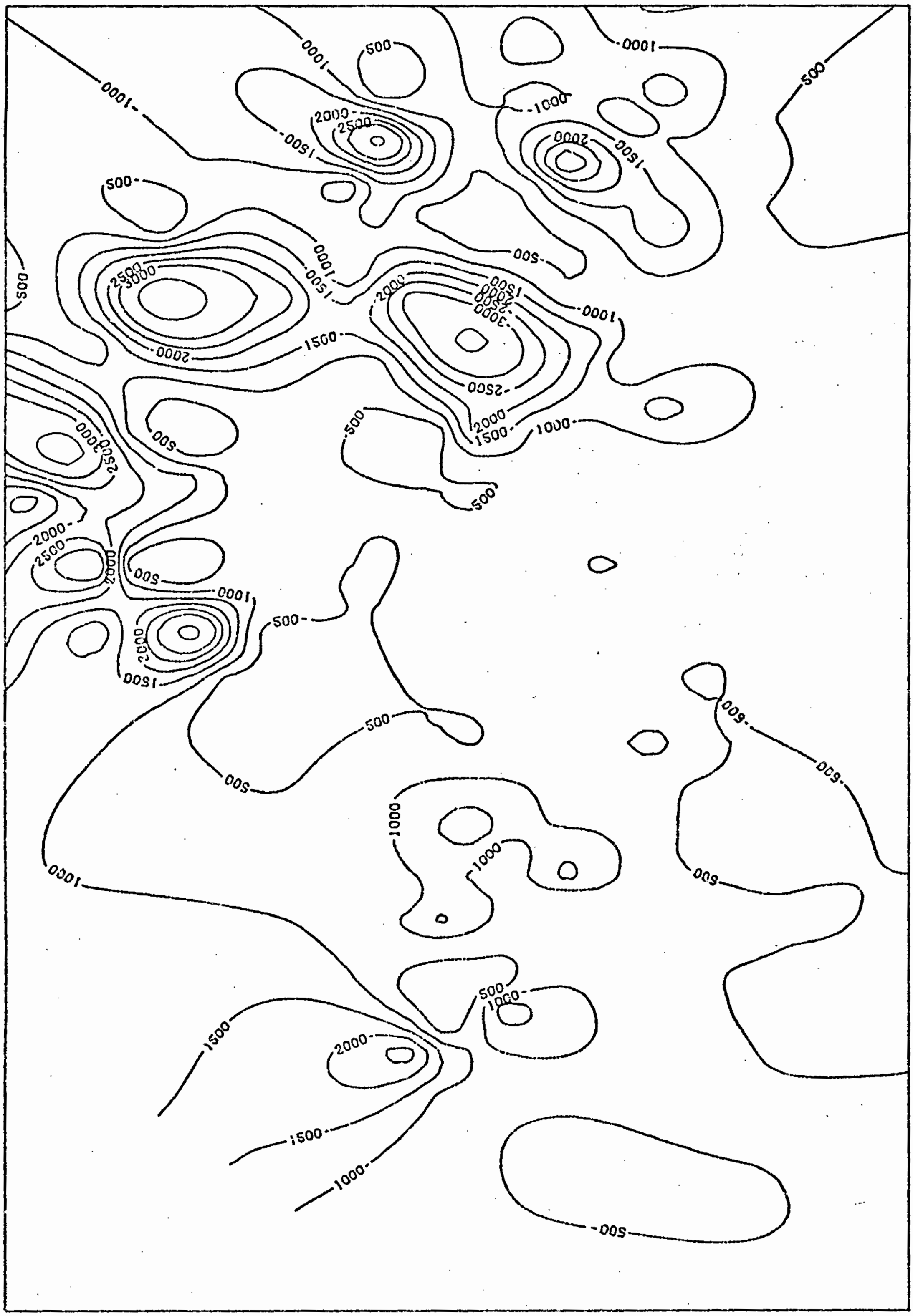


FIG.6AC TDS

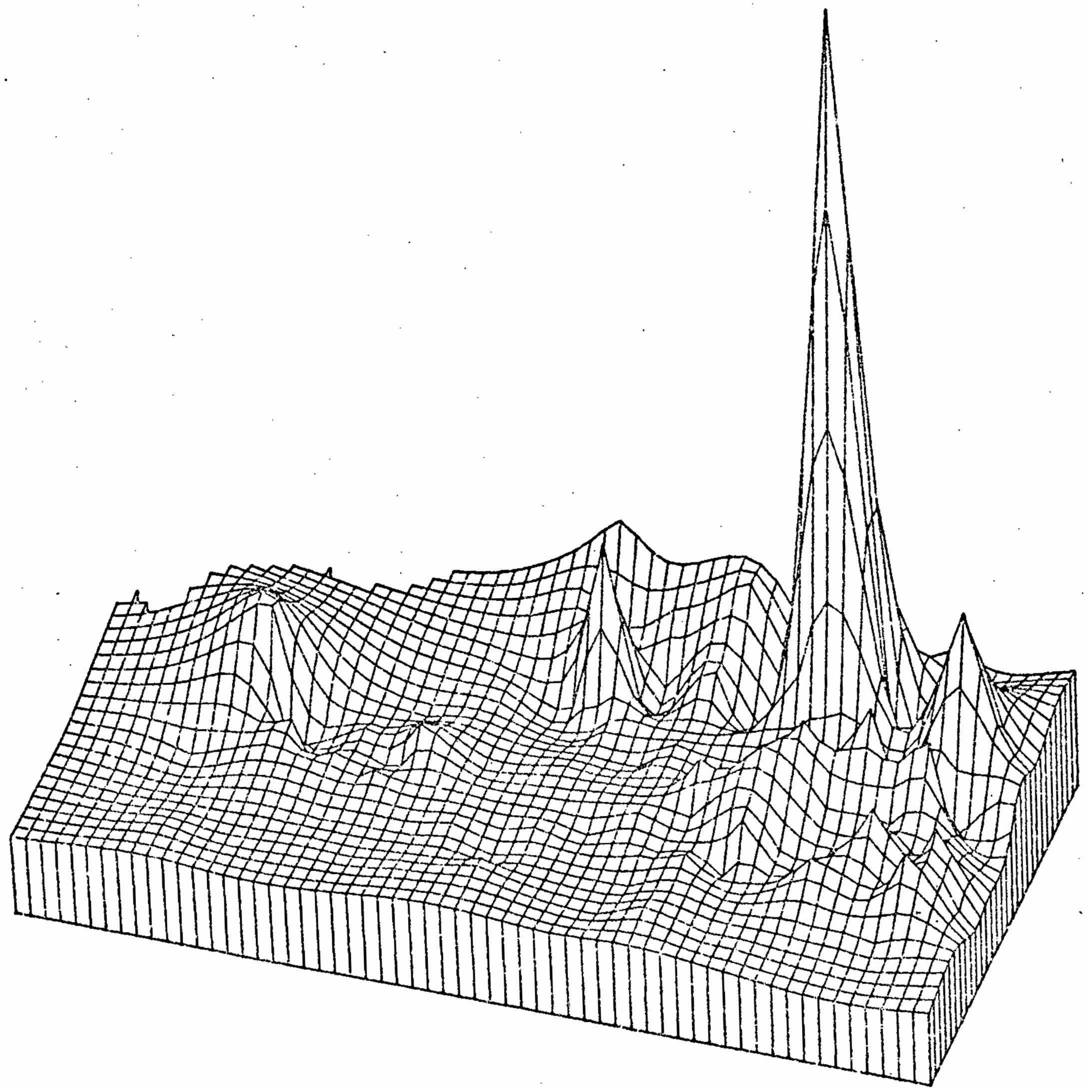


FIG.6B S04

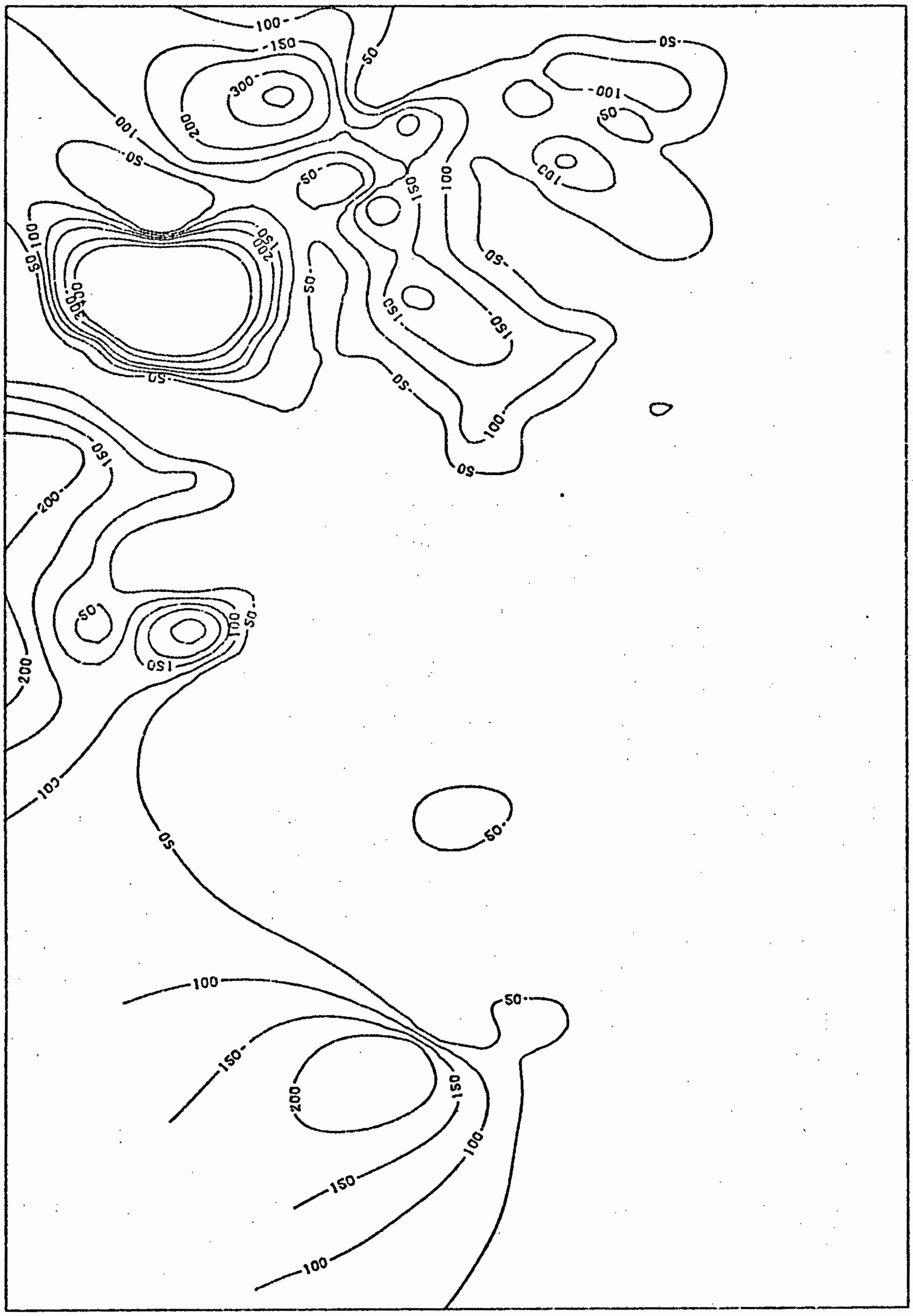

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FIG.6BC S04

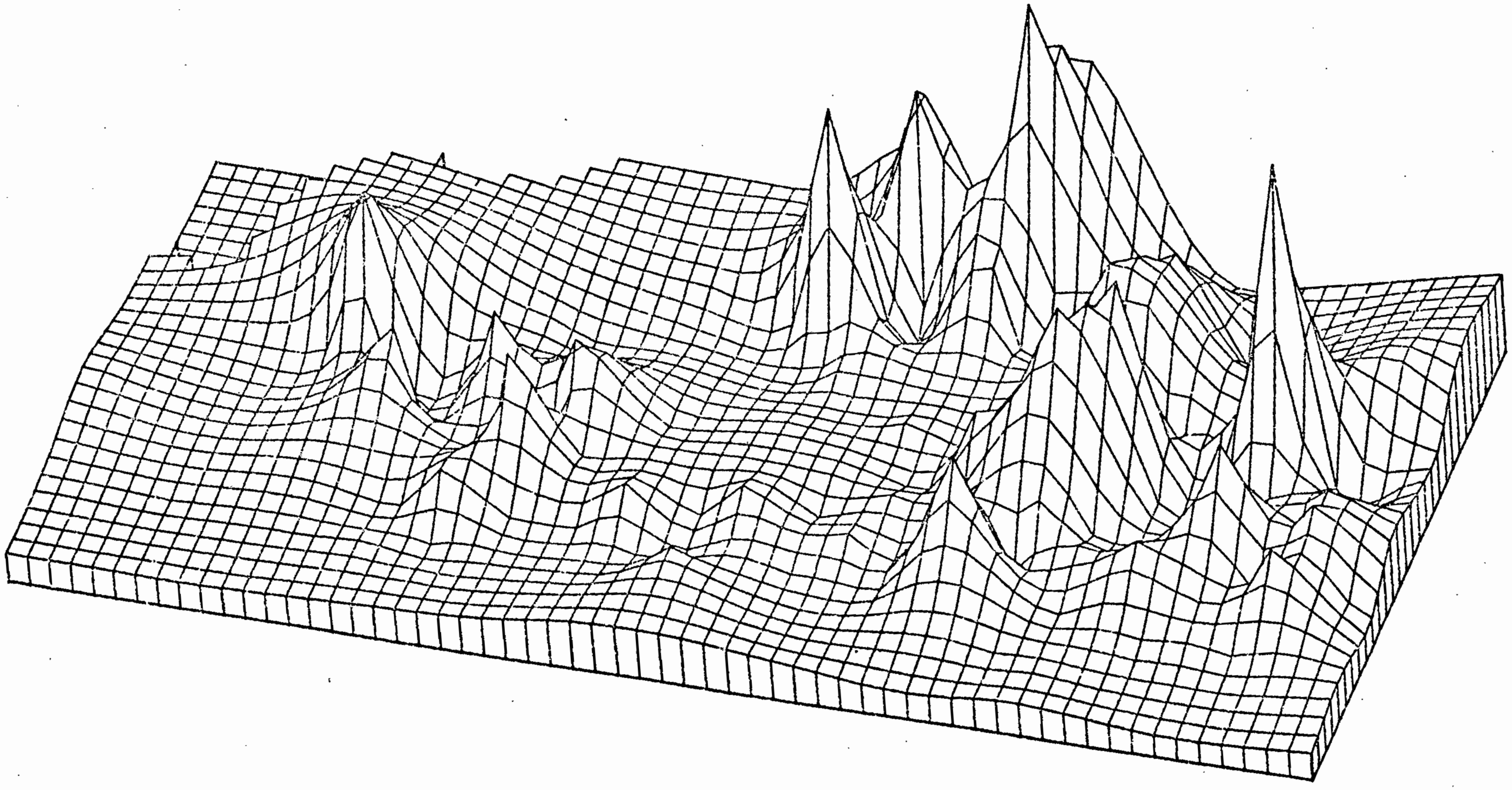

FIG.6C CL

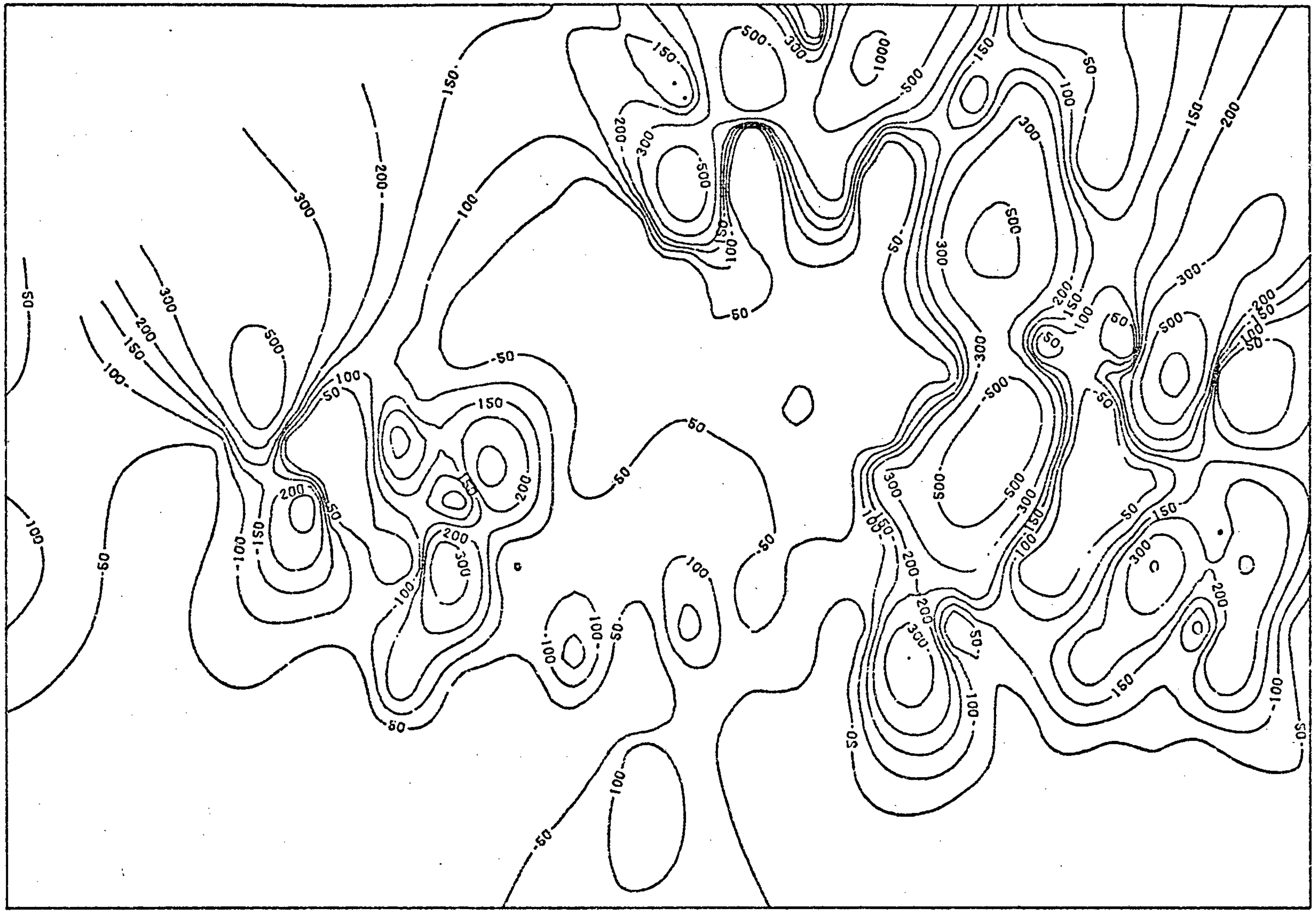

FIG.6CC CL

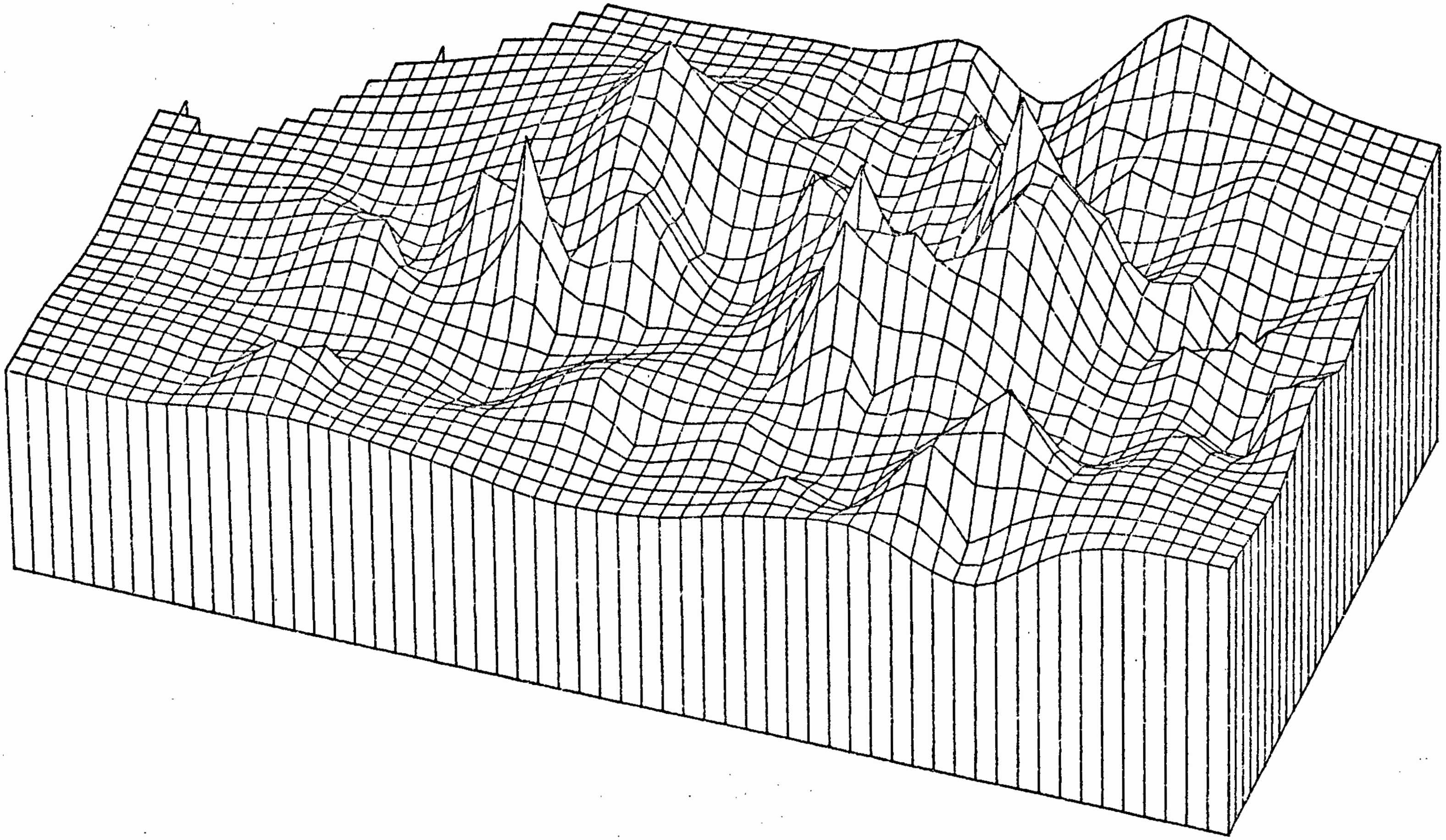

FIG.6D PH

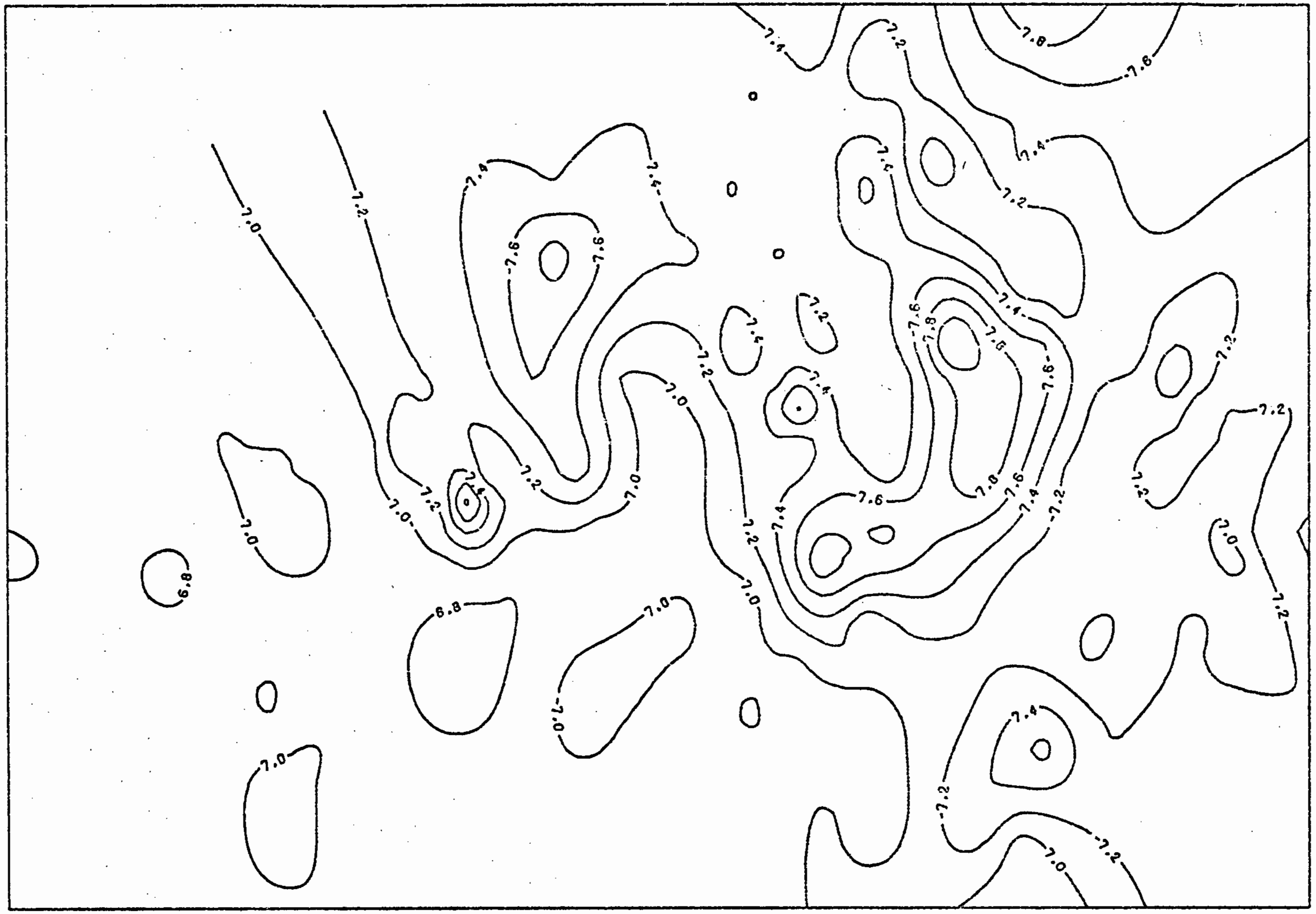

FIG.6DC PH

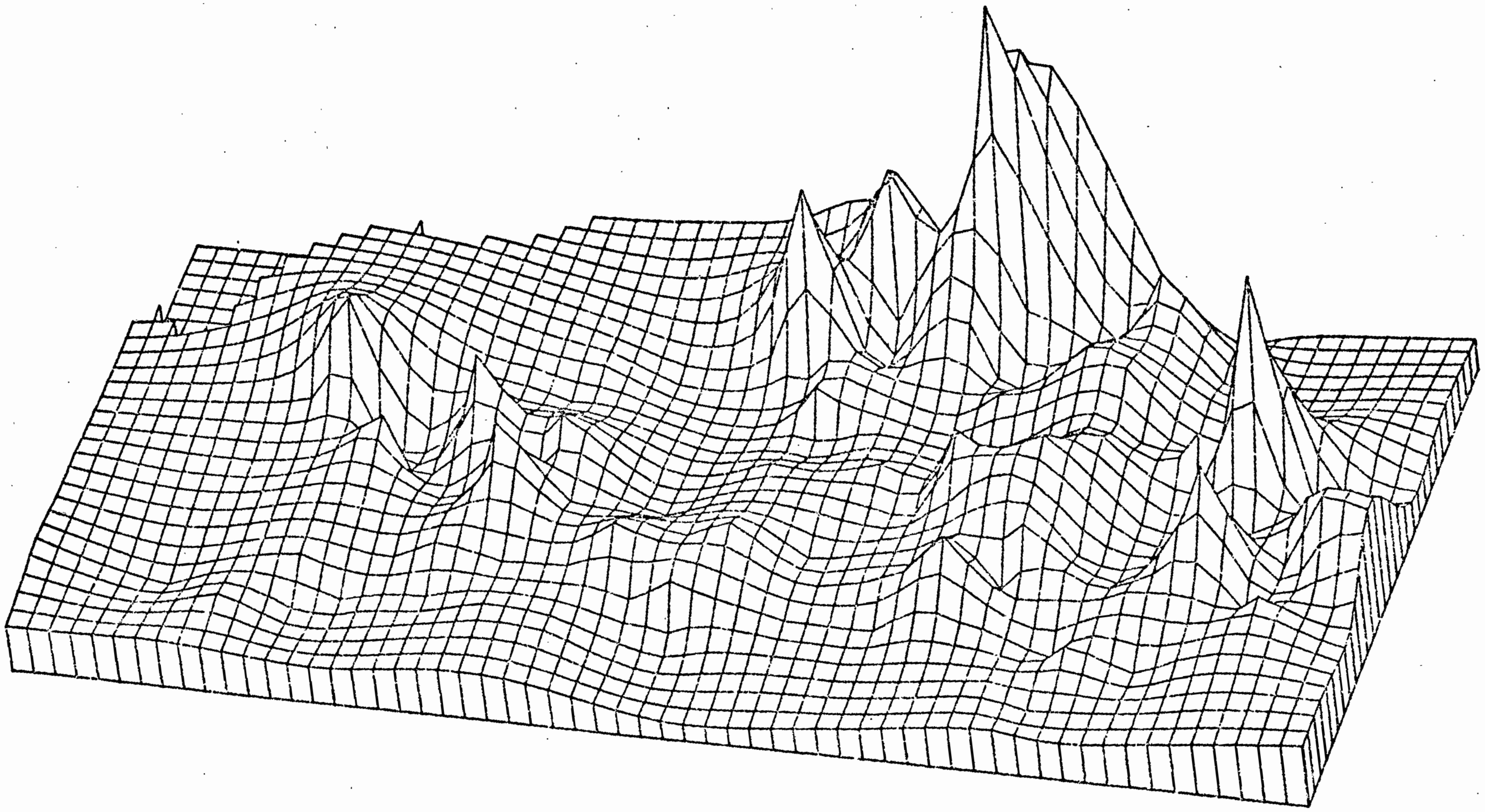

FIG.6E MG

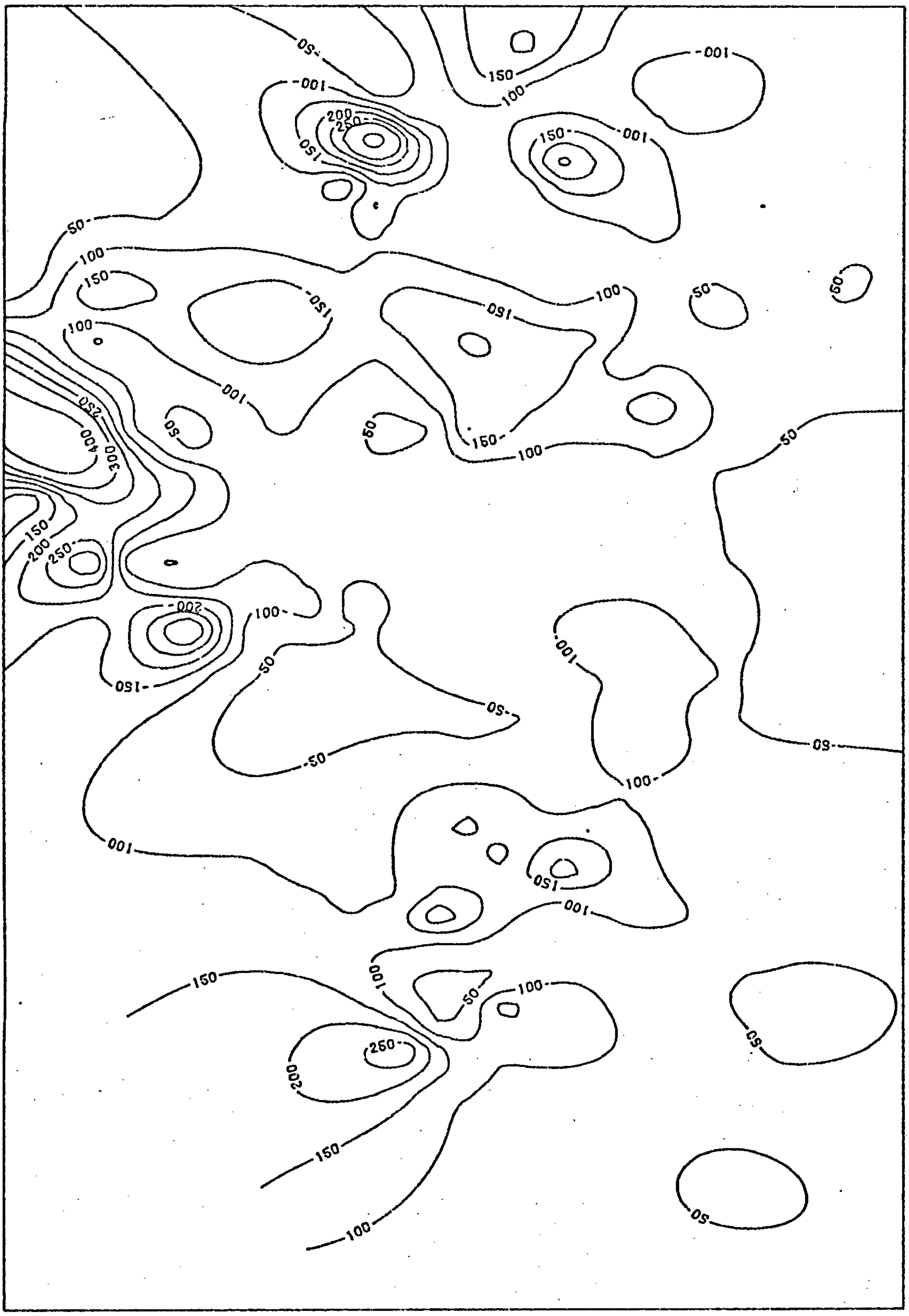
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FIG.6EC MG

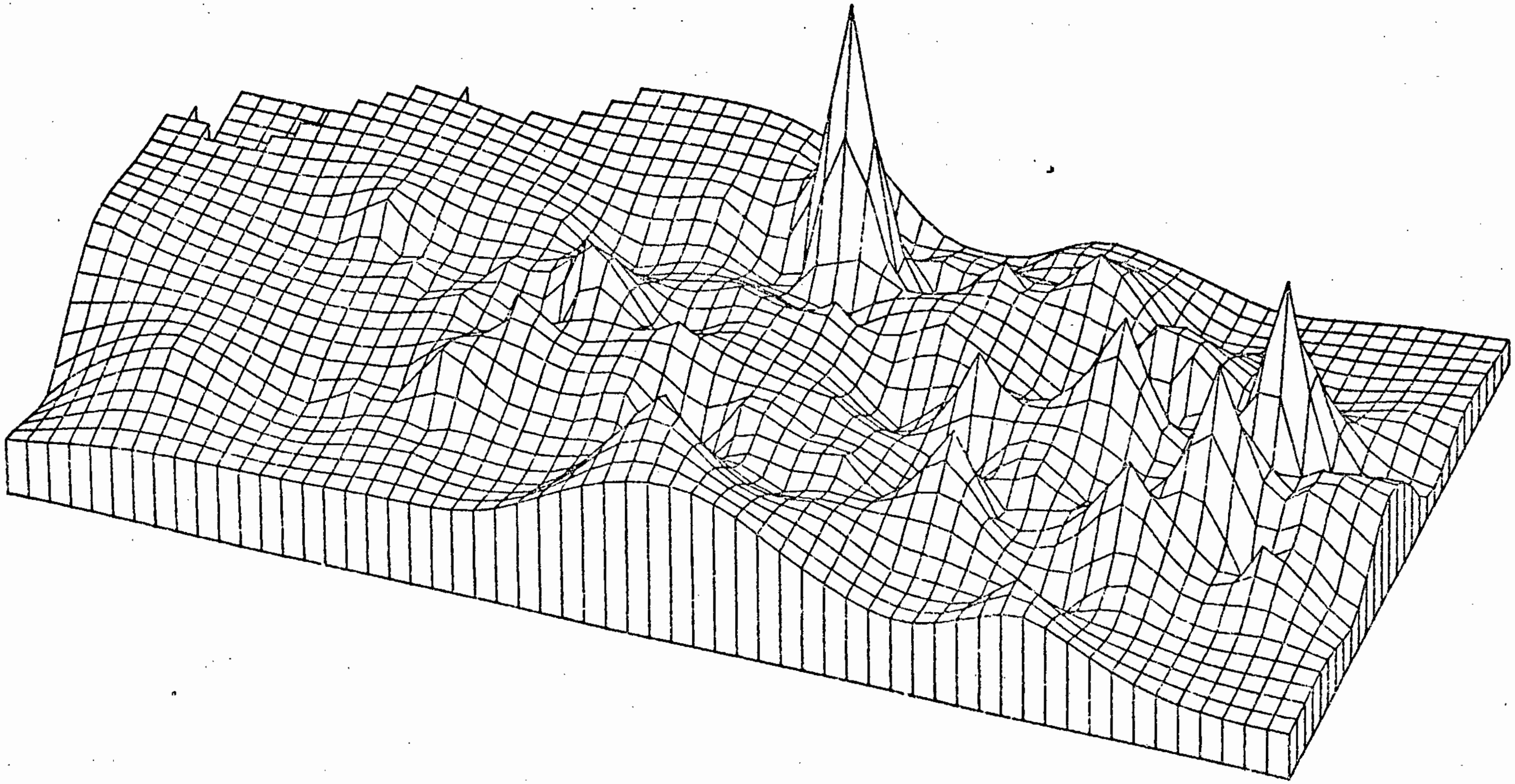

FIG.6F CA

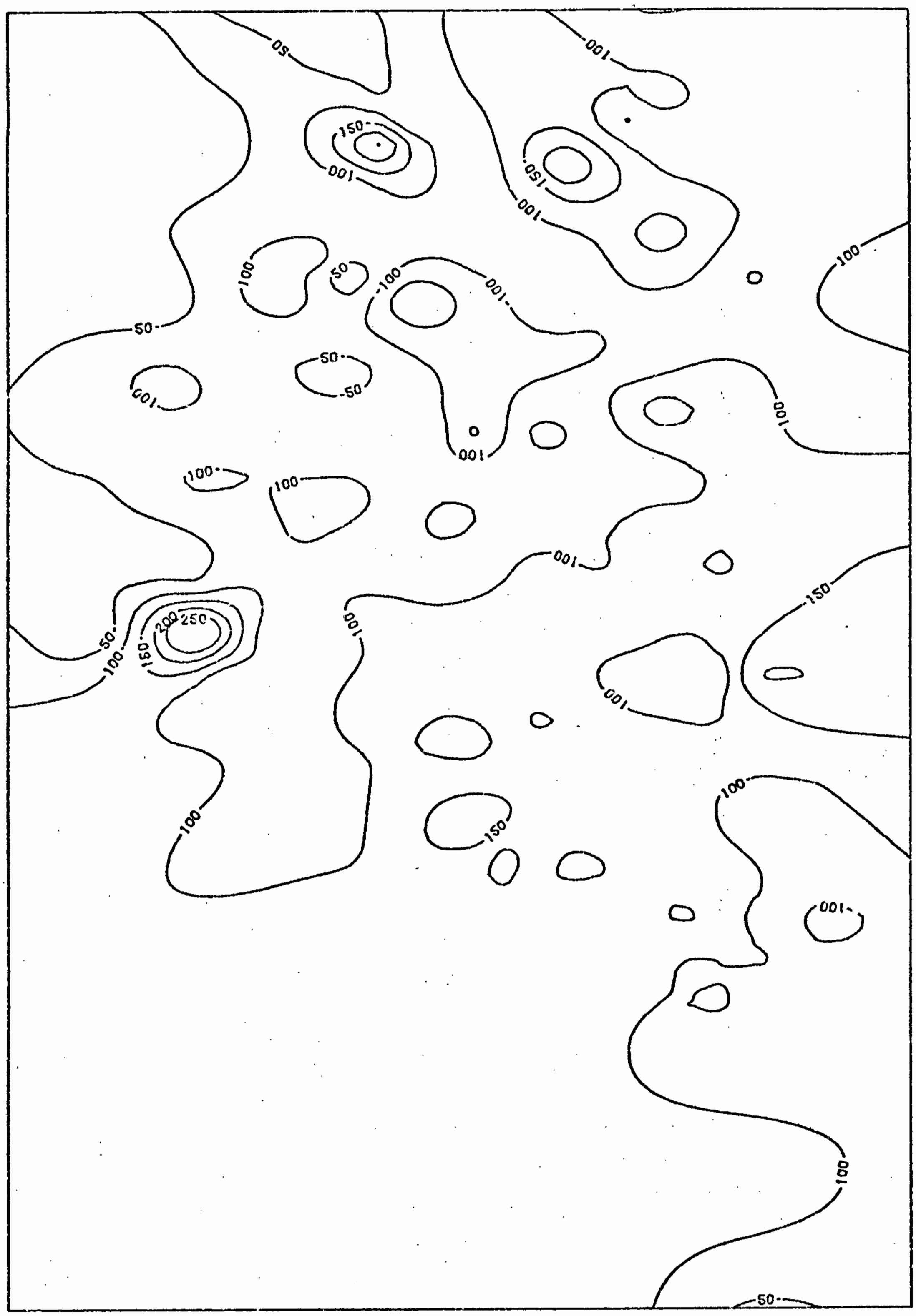
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FIG.6FC CA

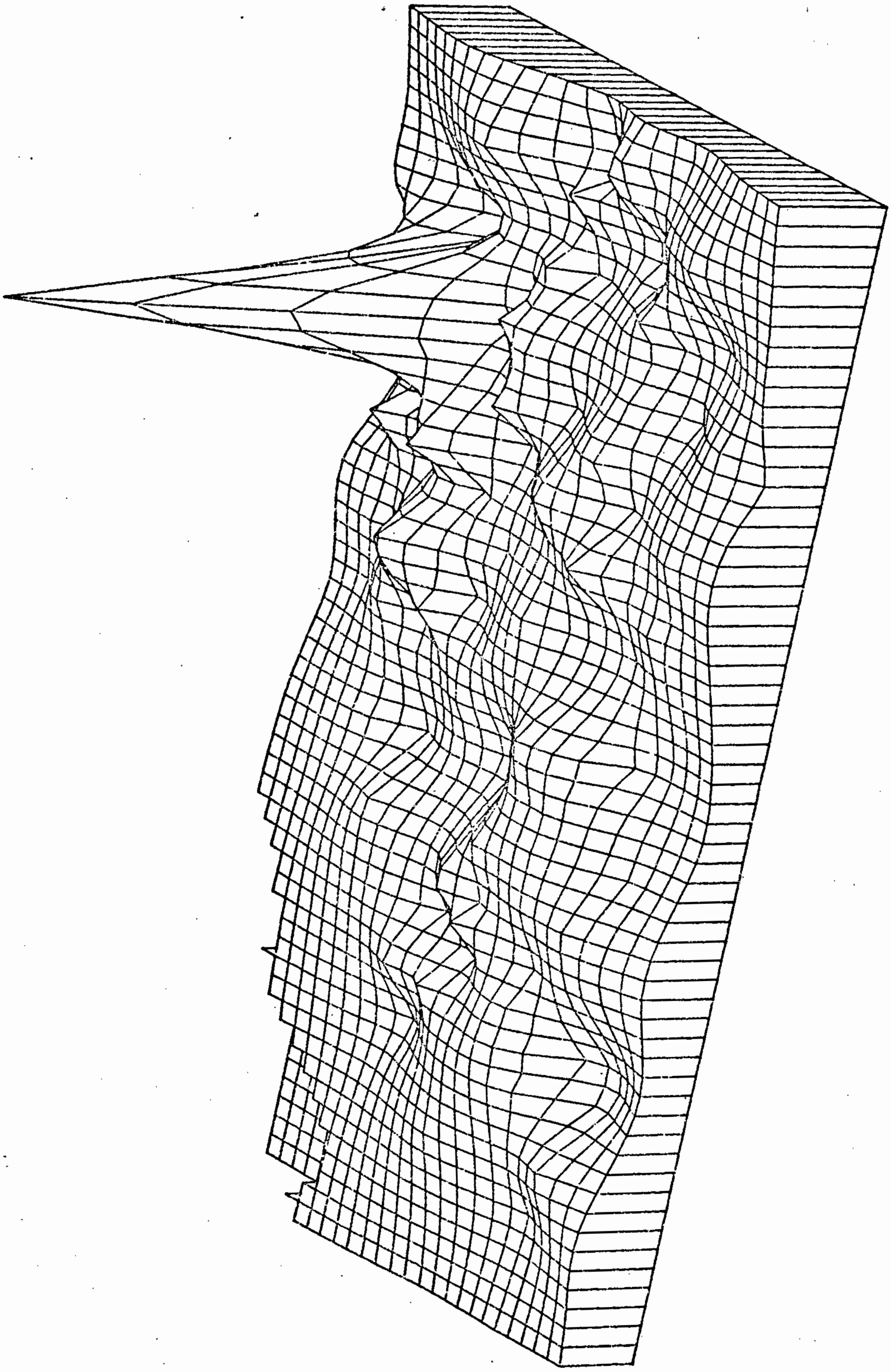

FIG.6G HC03

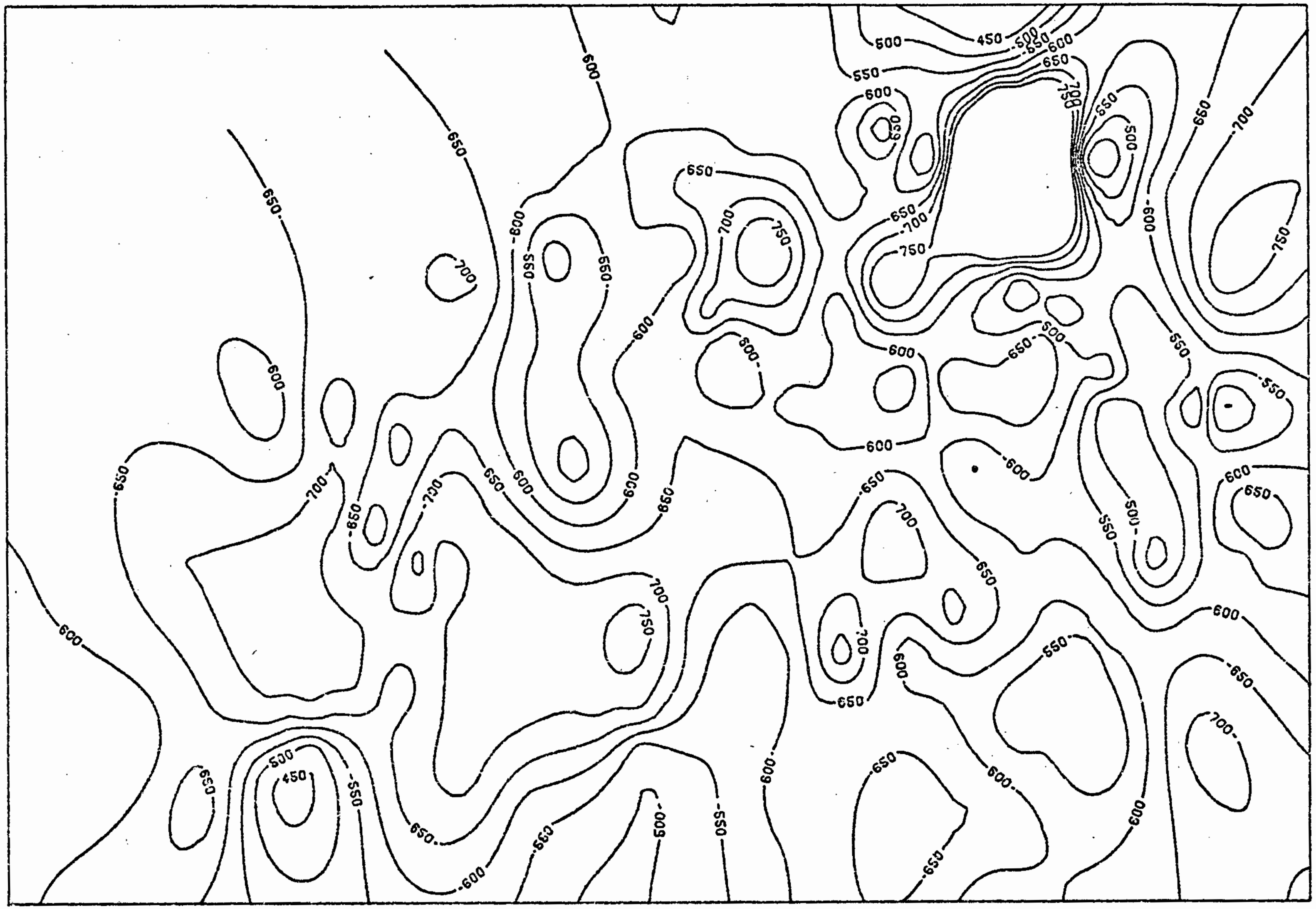

FIG.6GC HC03

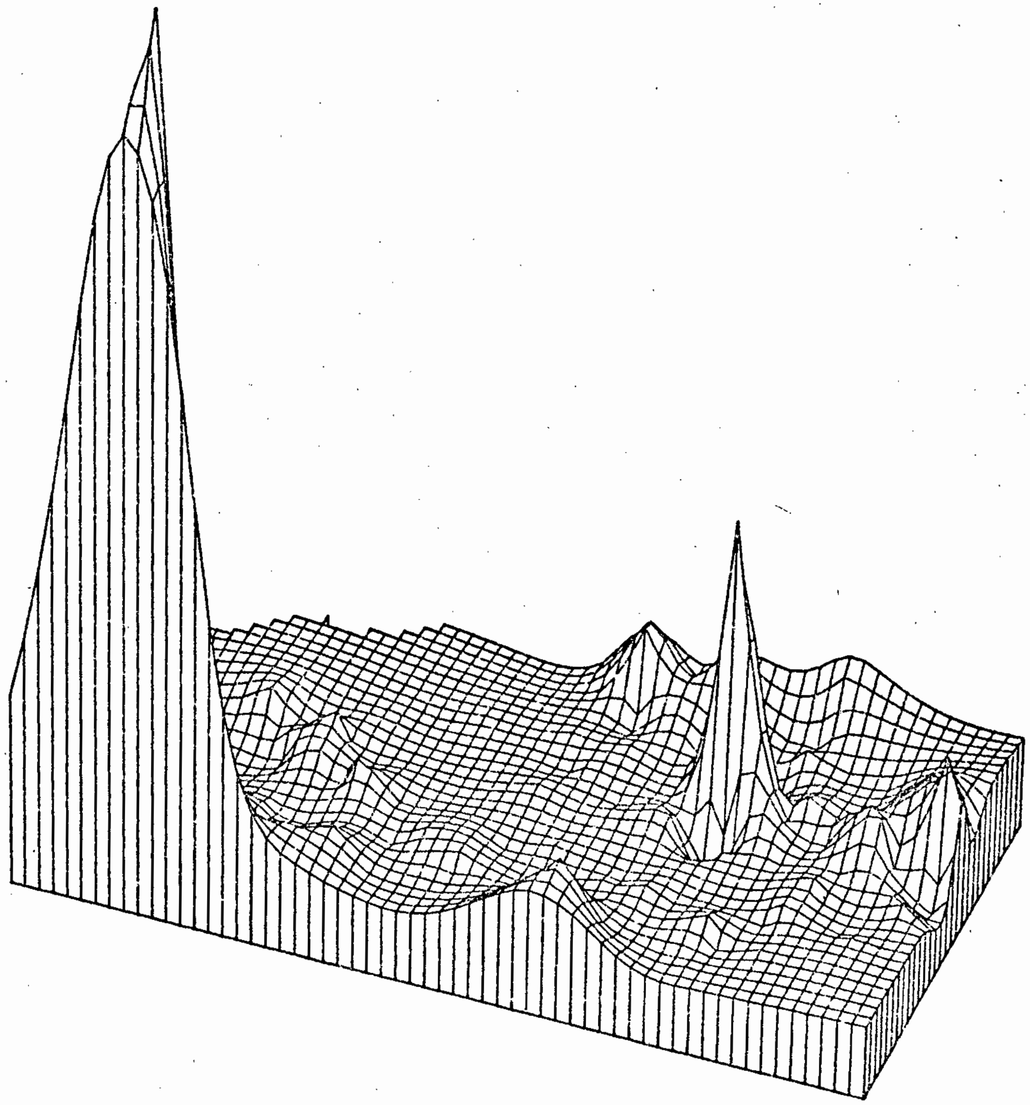

FIG.6H ZN

FIG.6HC ZN

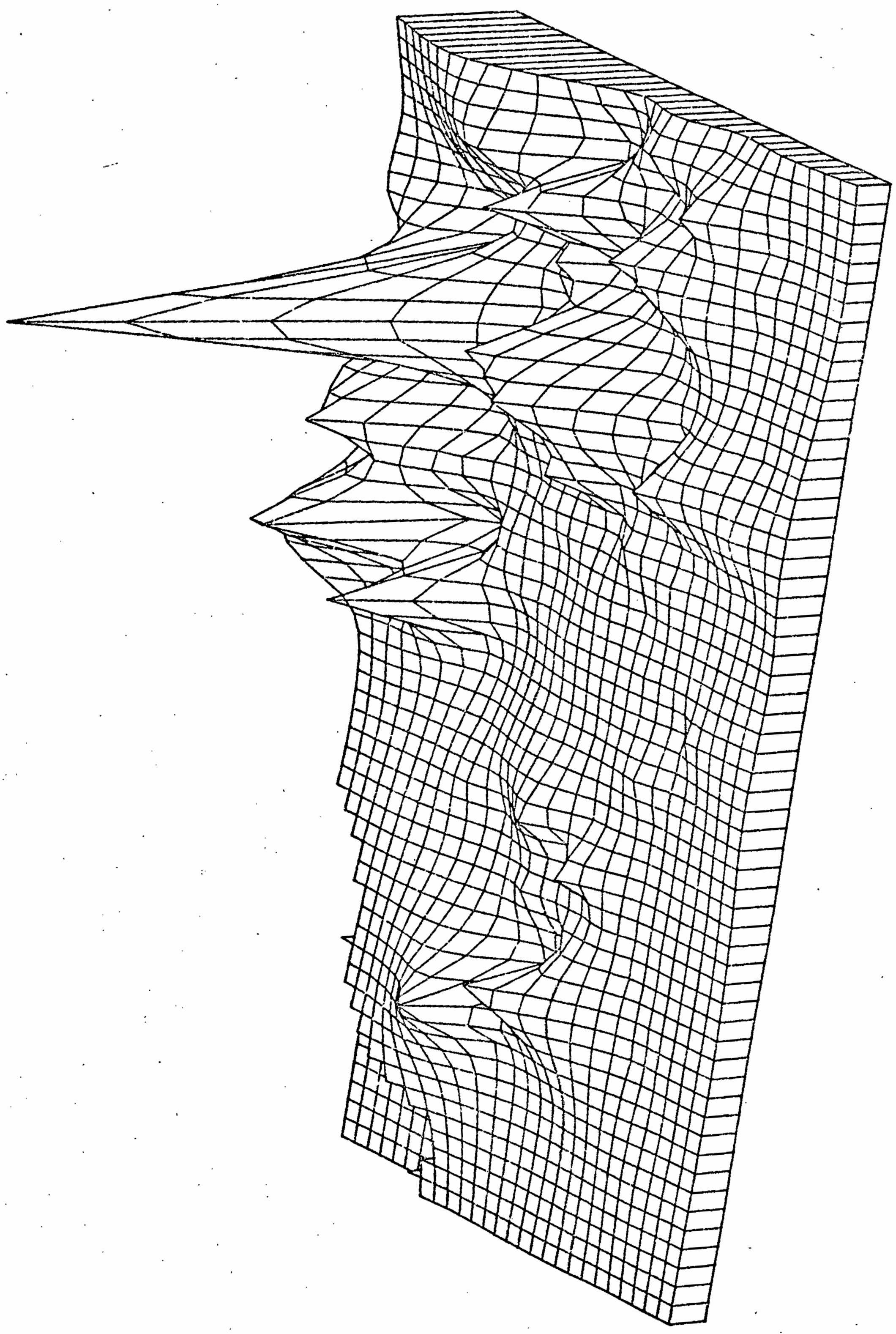

FIG.61 NA

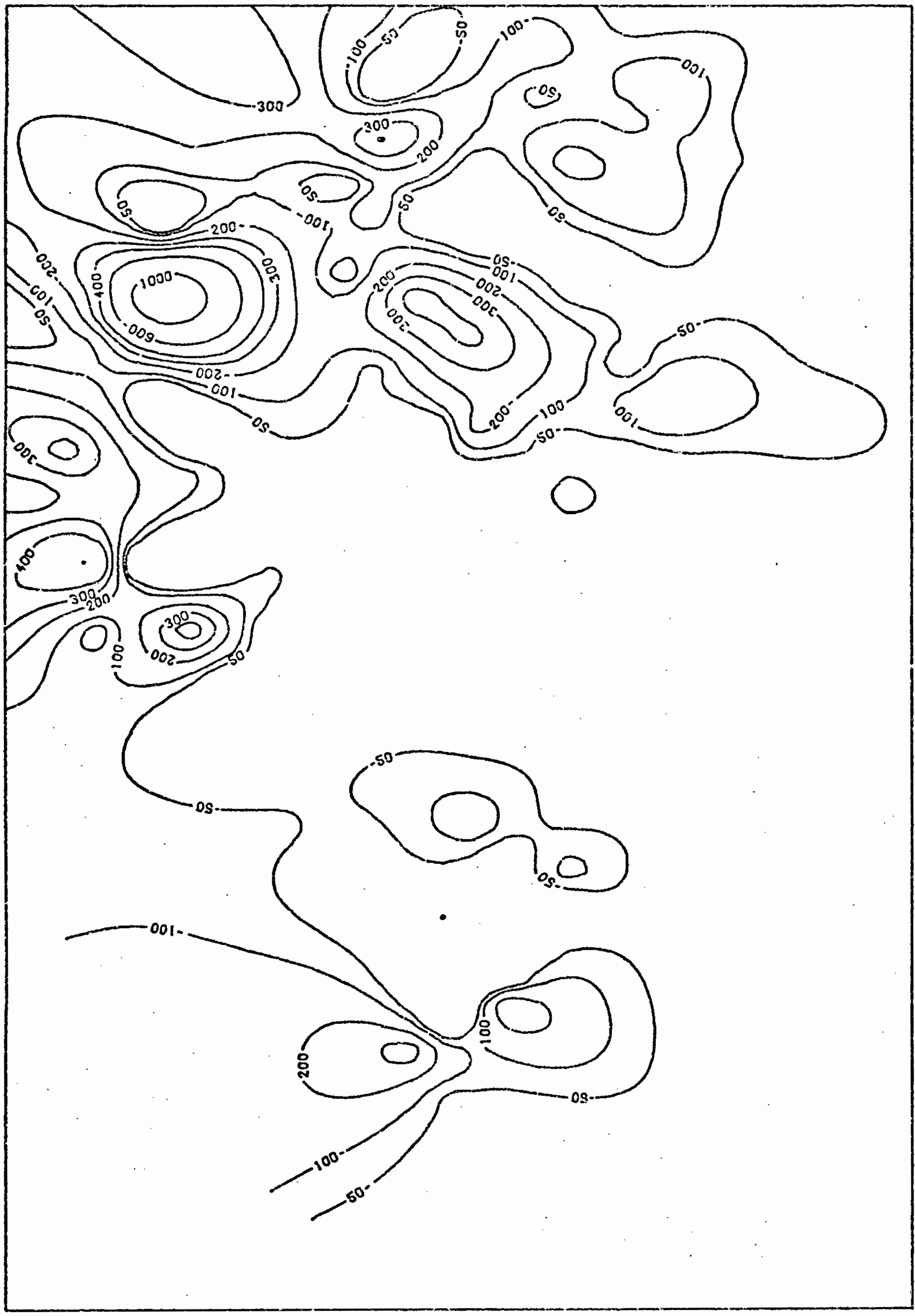
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FIG.61C NA

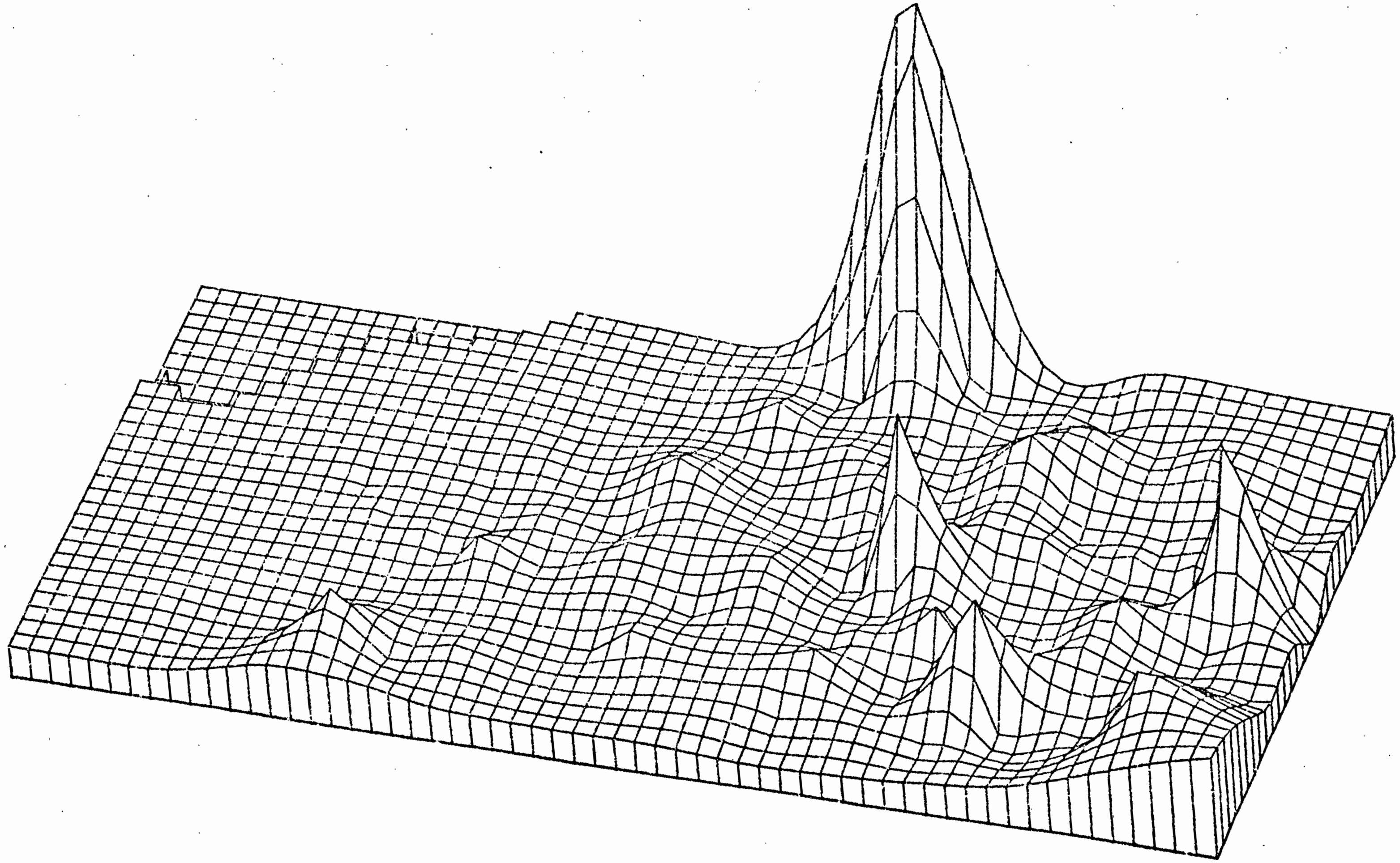

FIG.6J CU

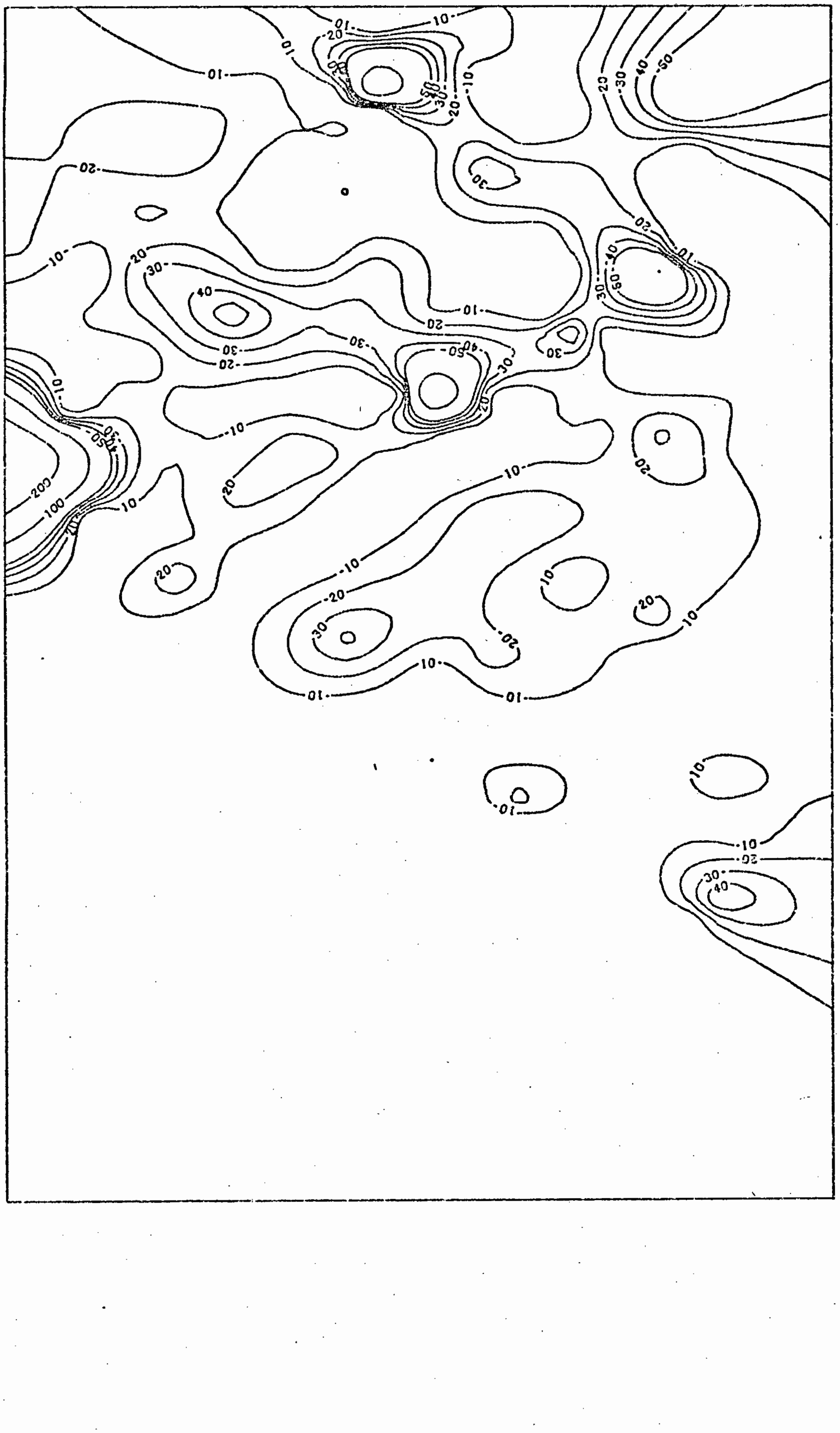

FIG.6JC CU

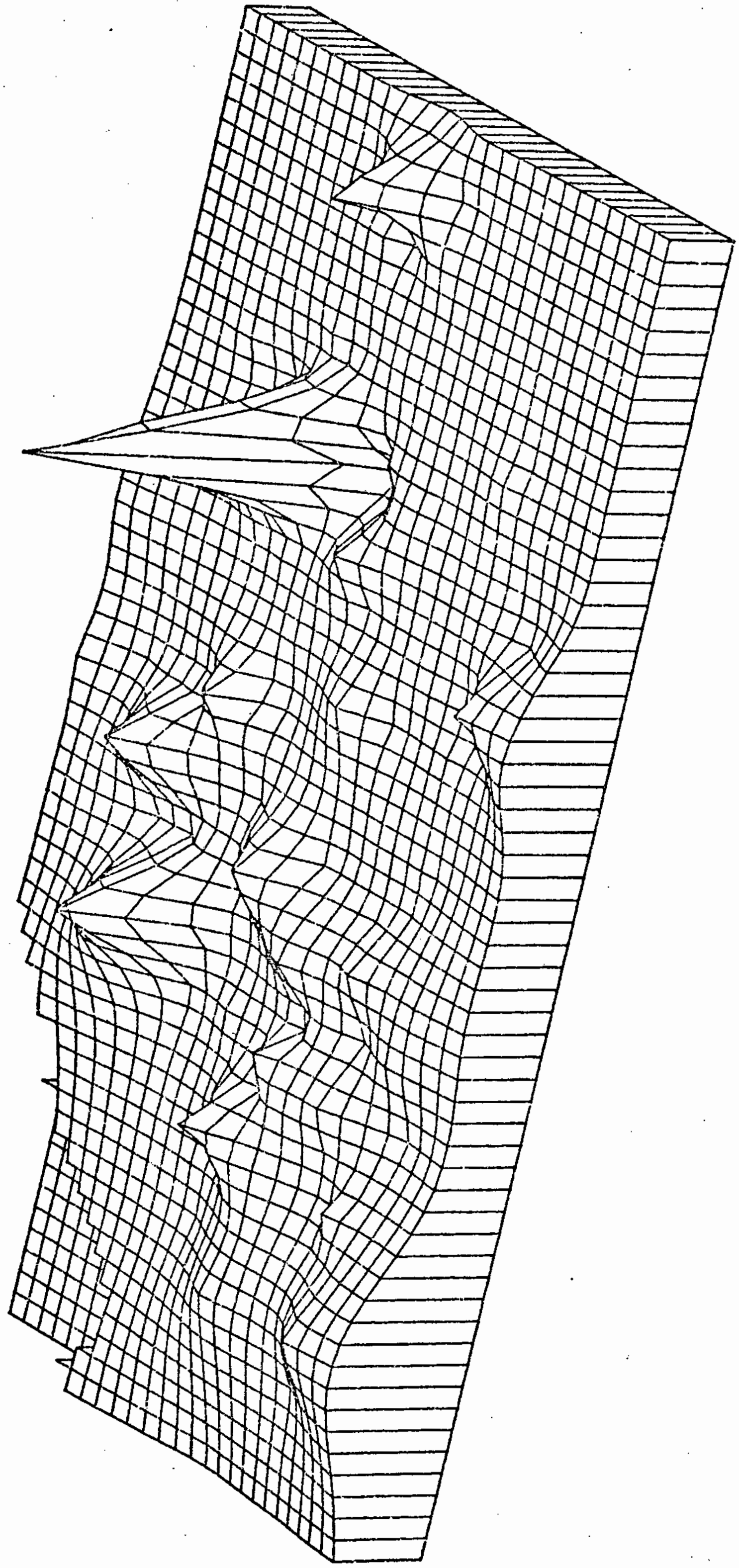

FIG. 6K PB

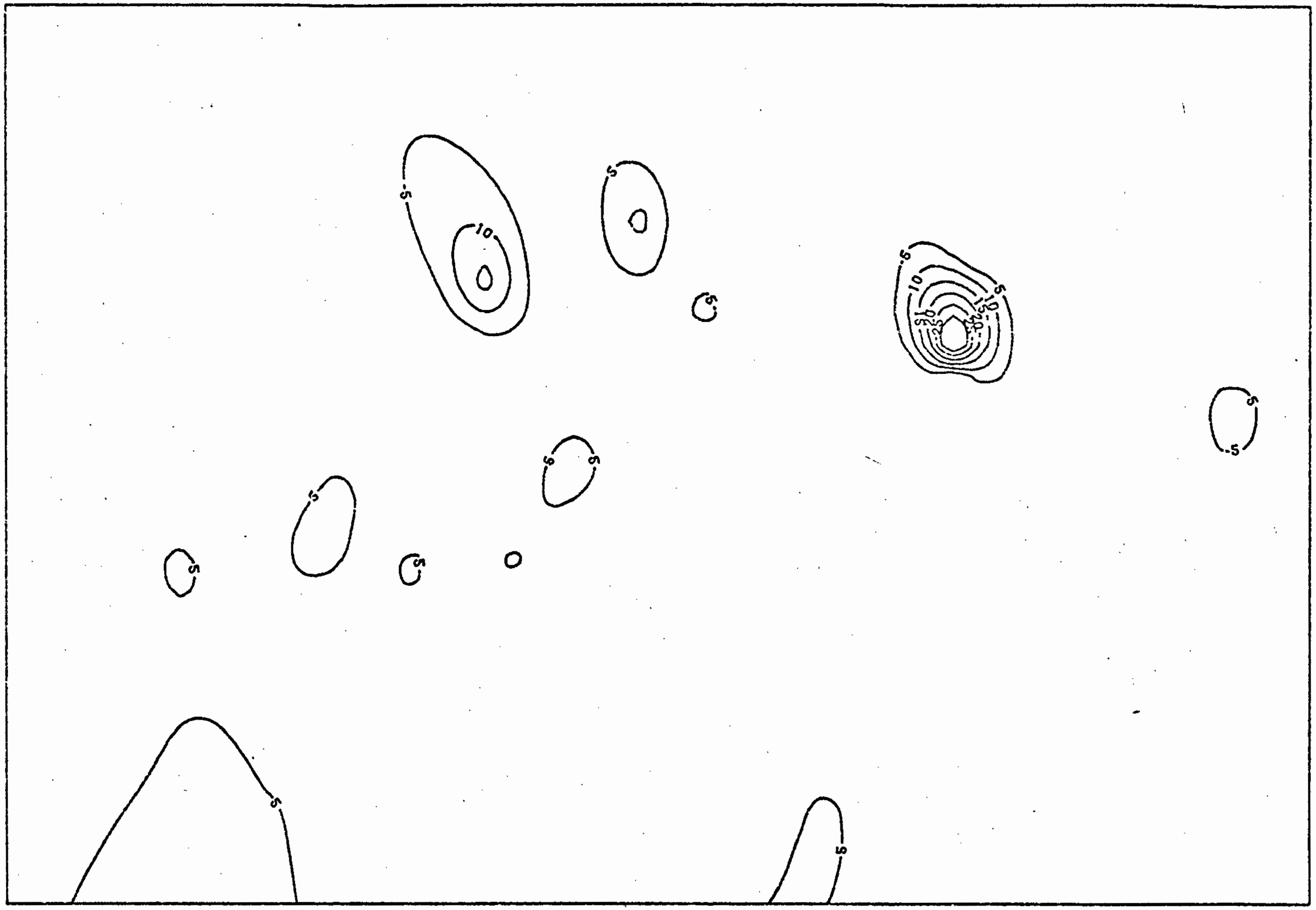

FIG.6KC PB

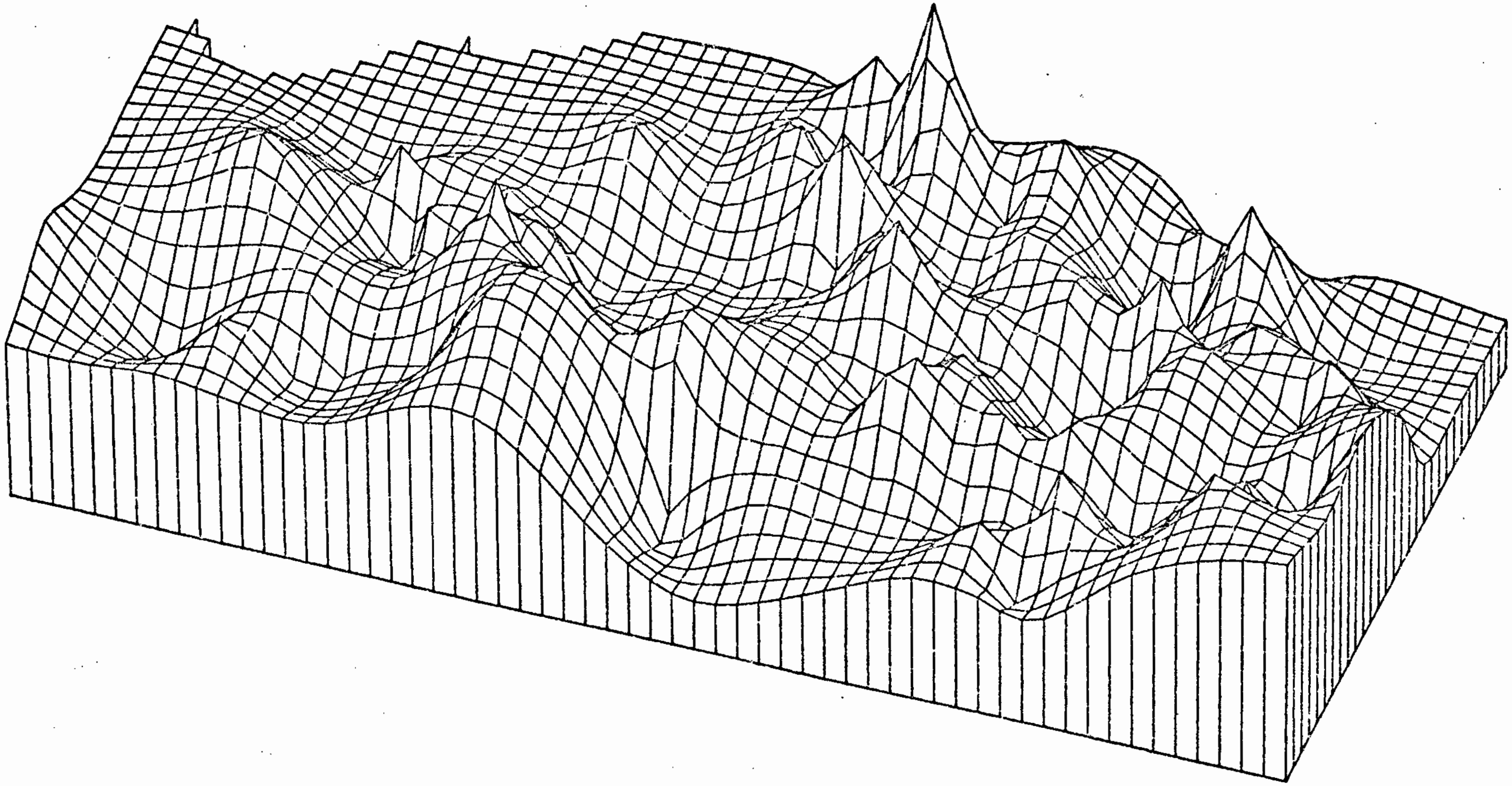

FIG.6L MG/TDS

FIG.6LC MG/TDS

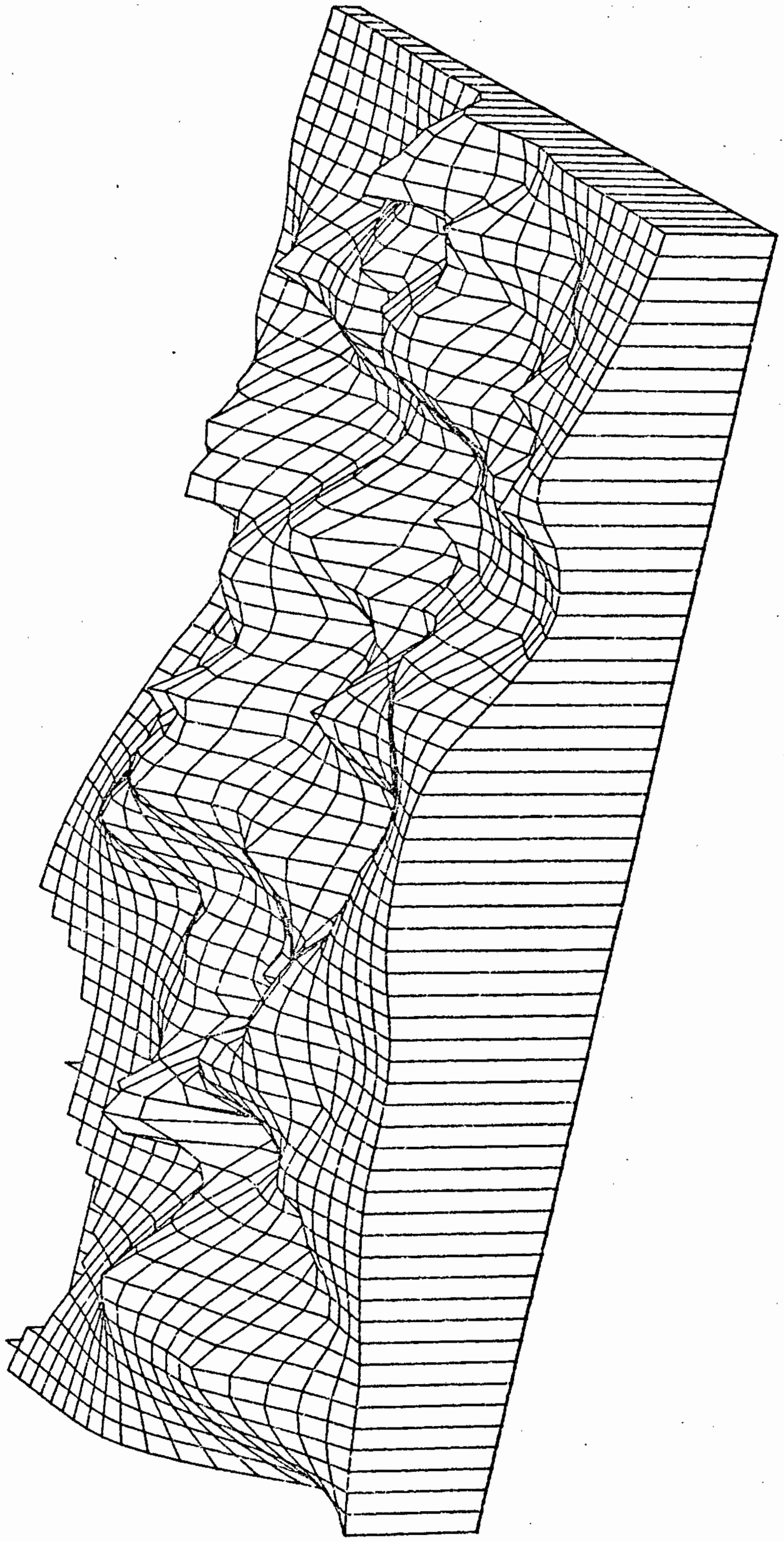

FIG.6M CA/TDS

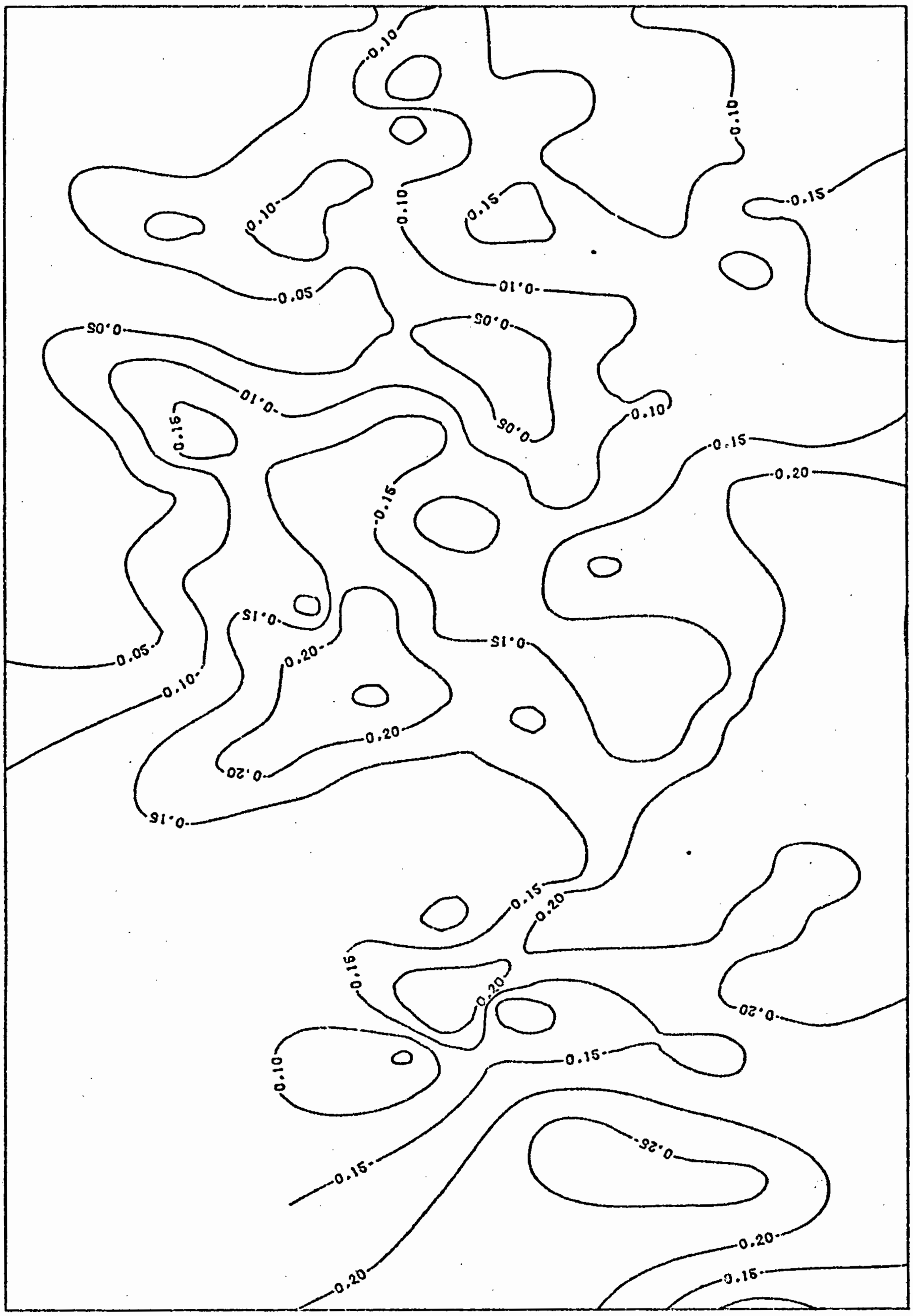

FIG. 6MC CA/TDS

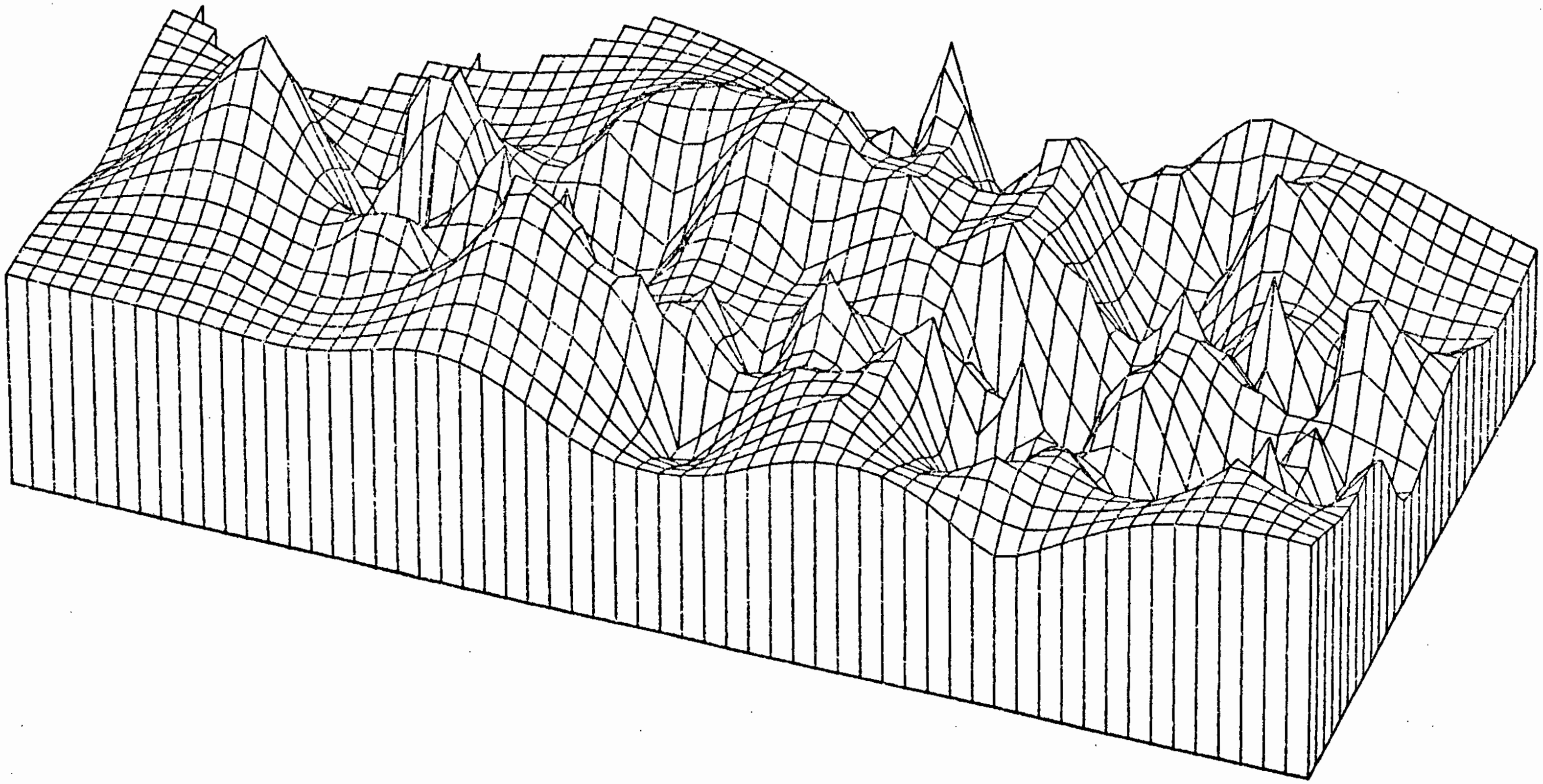

FIG.6N HC03/TDS

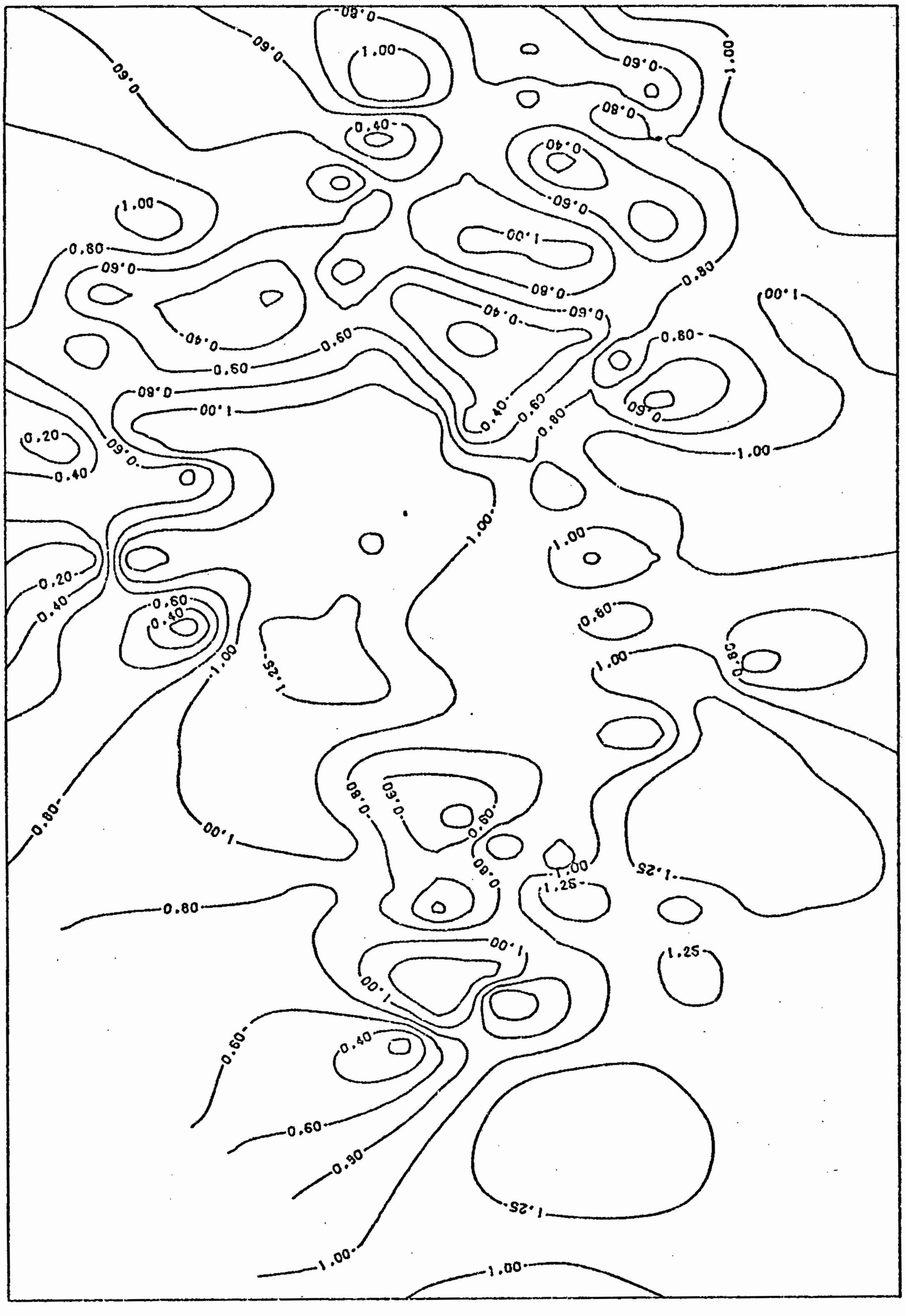

FIG.6NC HCO3/TDS

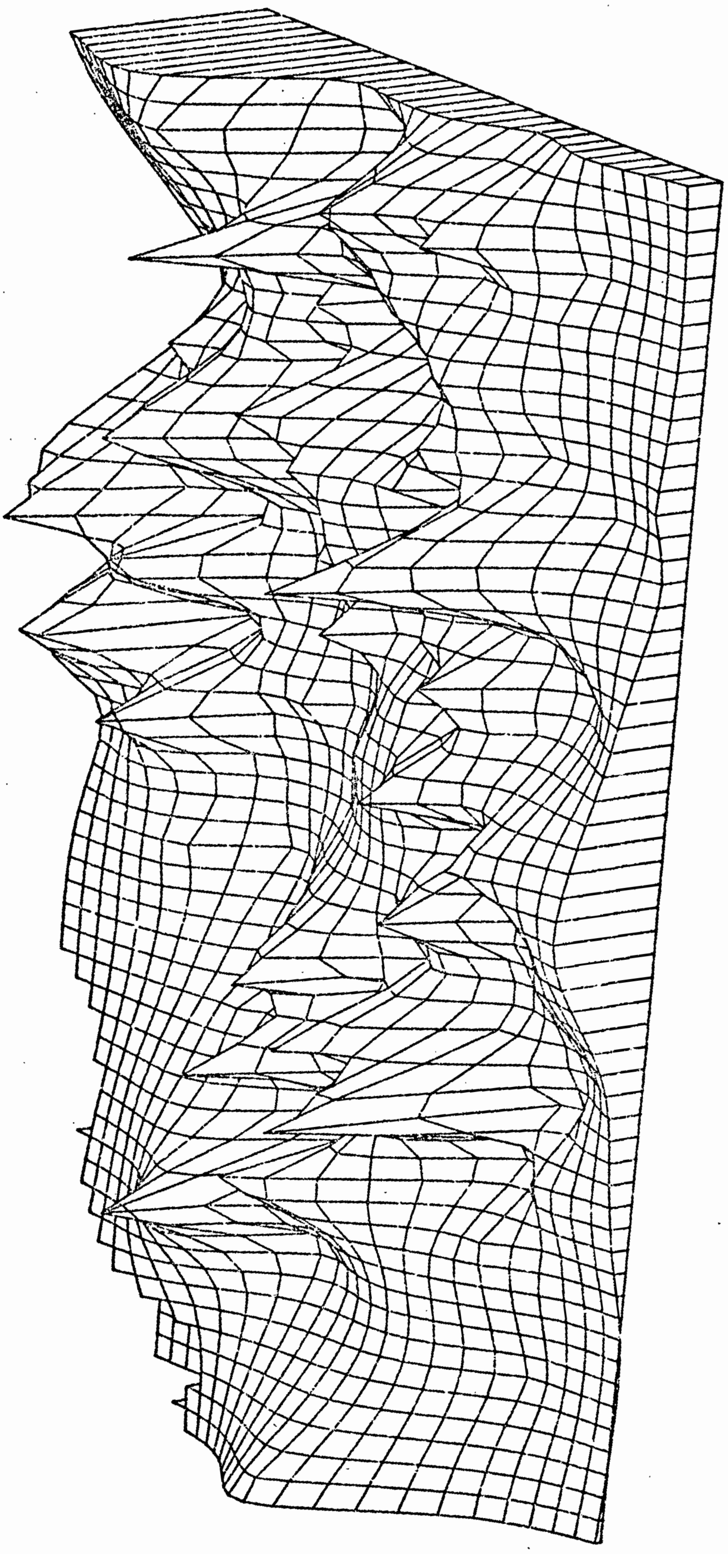

FIG.60 CL/TDS

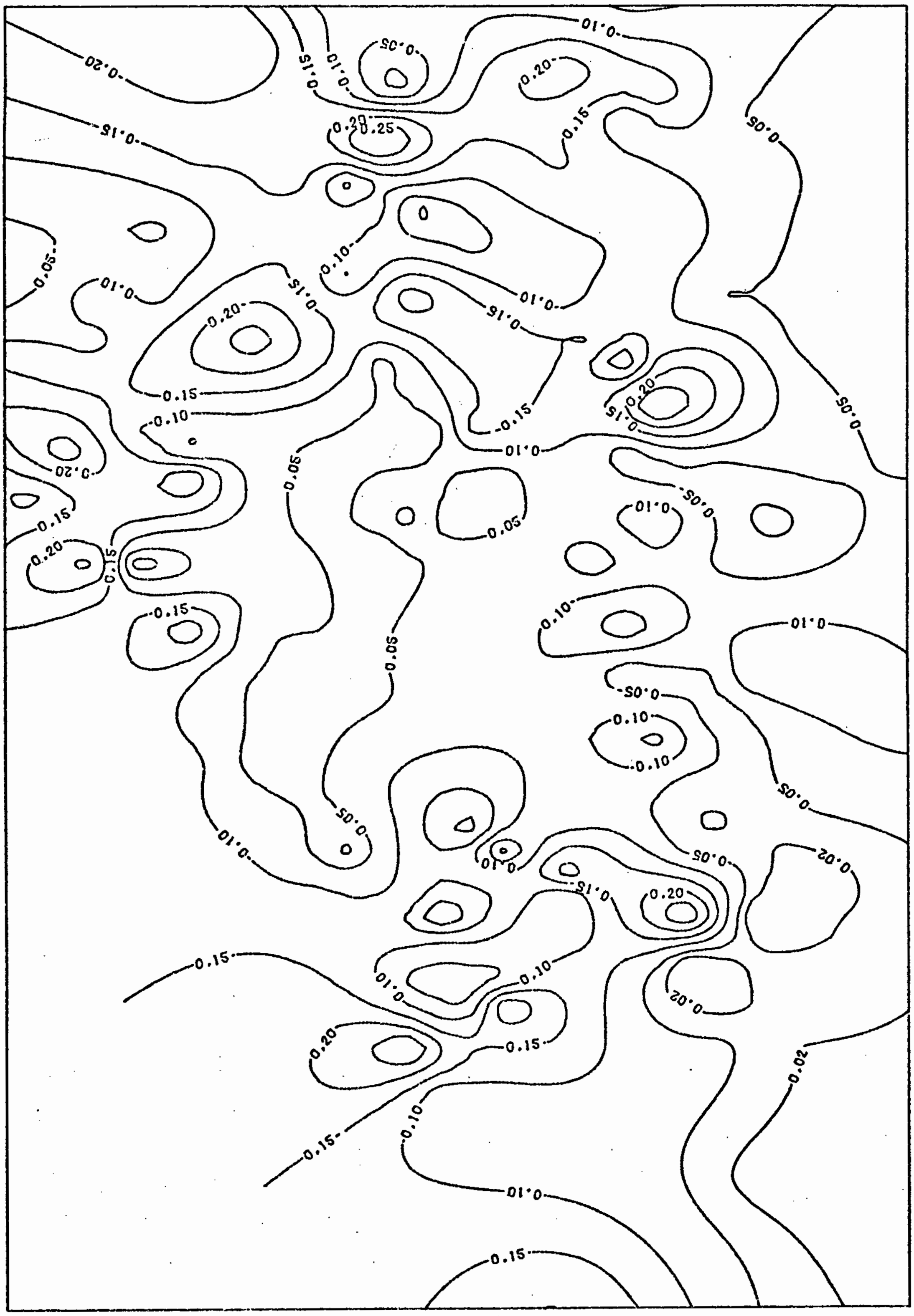

FIG.60C CL/TDS

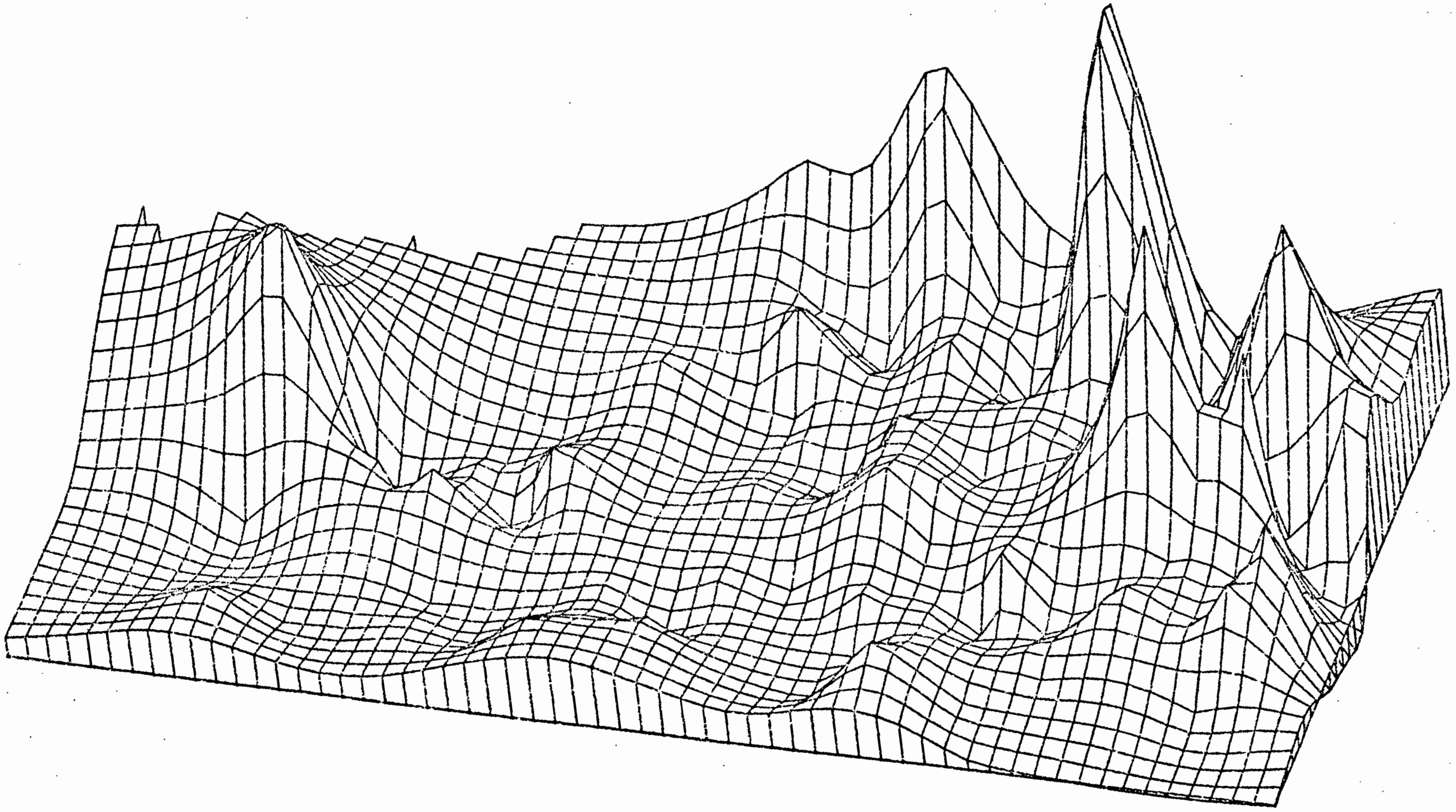

FIG.6P S04/TDS

FIG.6PC S04/TDS

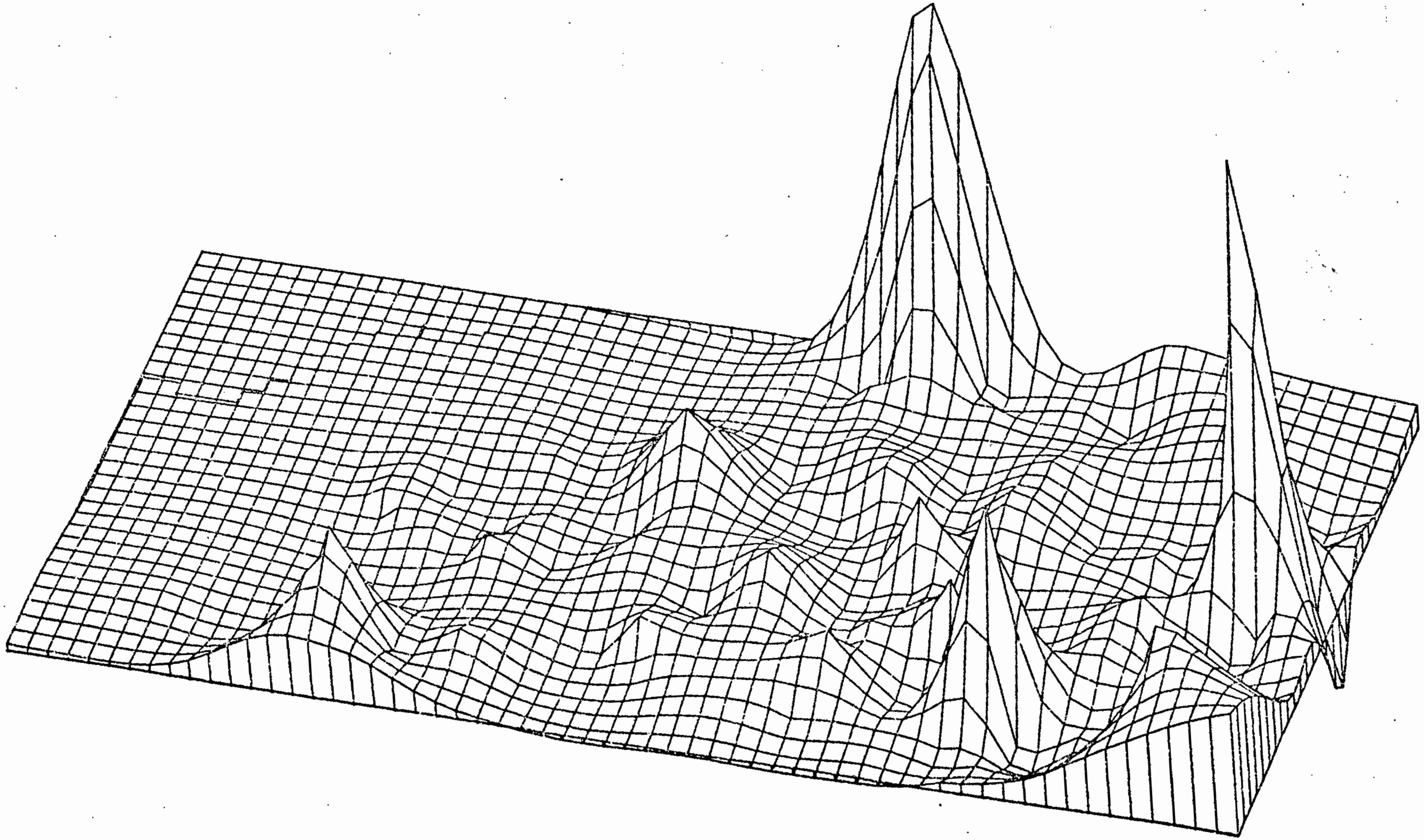

FIG.6Q CU/TDS

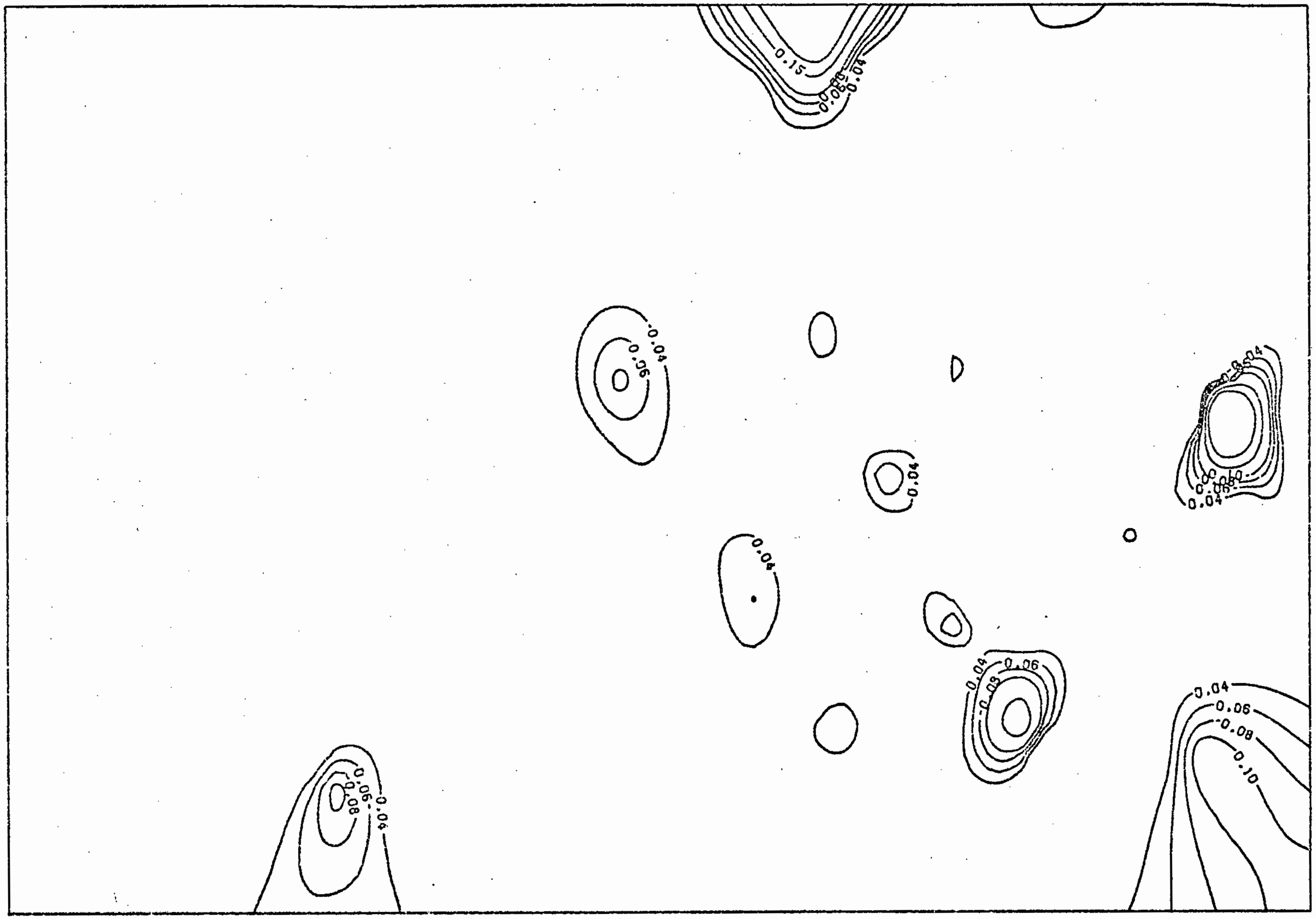

FIG.6QC CU/TDS

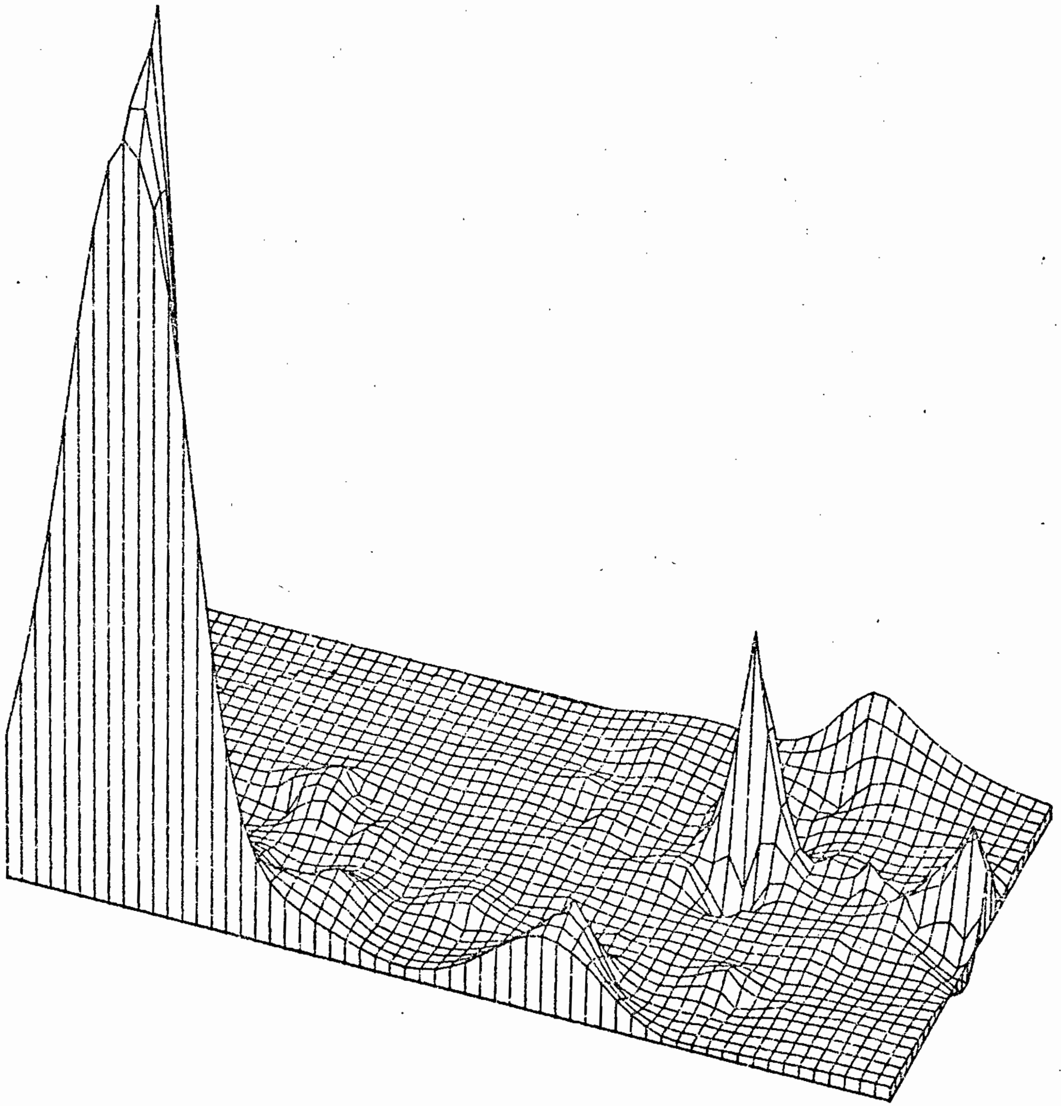

FIG.6R ZN/TDS

FIG.6RC ZN/TDS

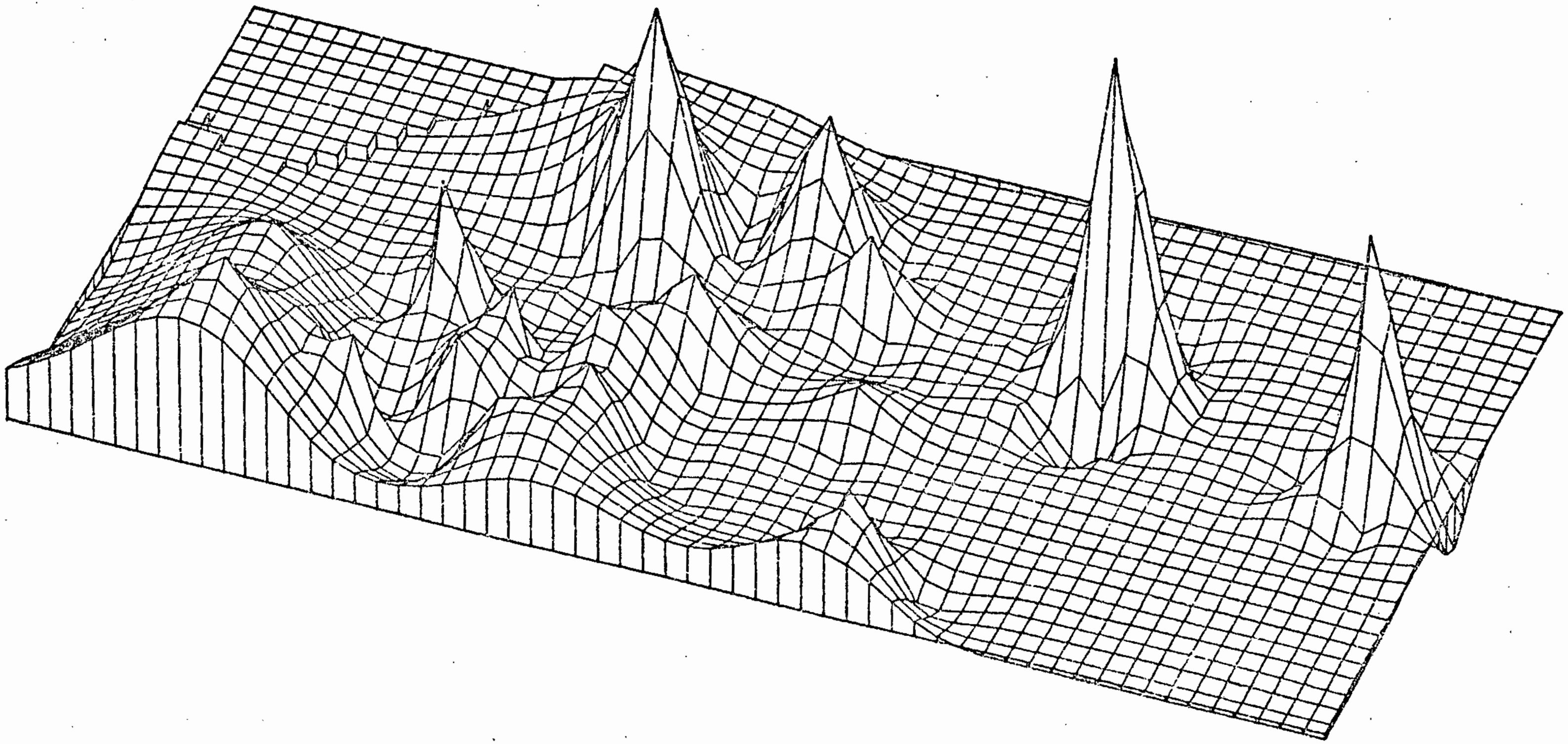

FIG.6S PB/TDS

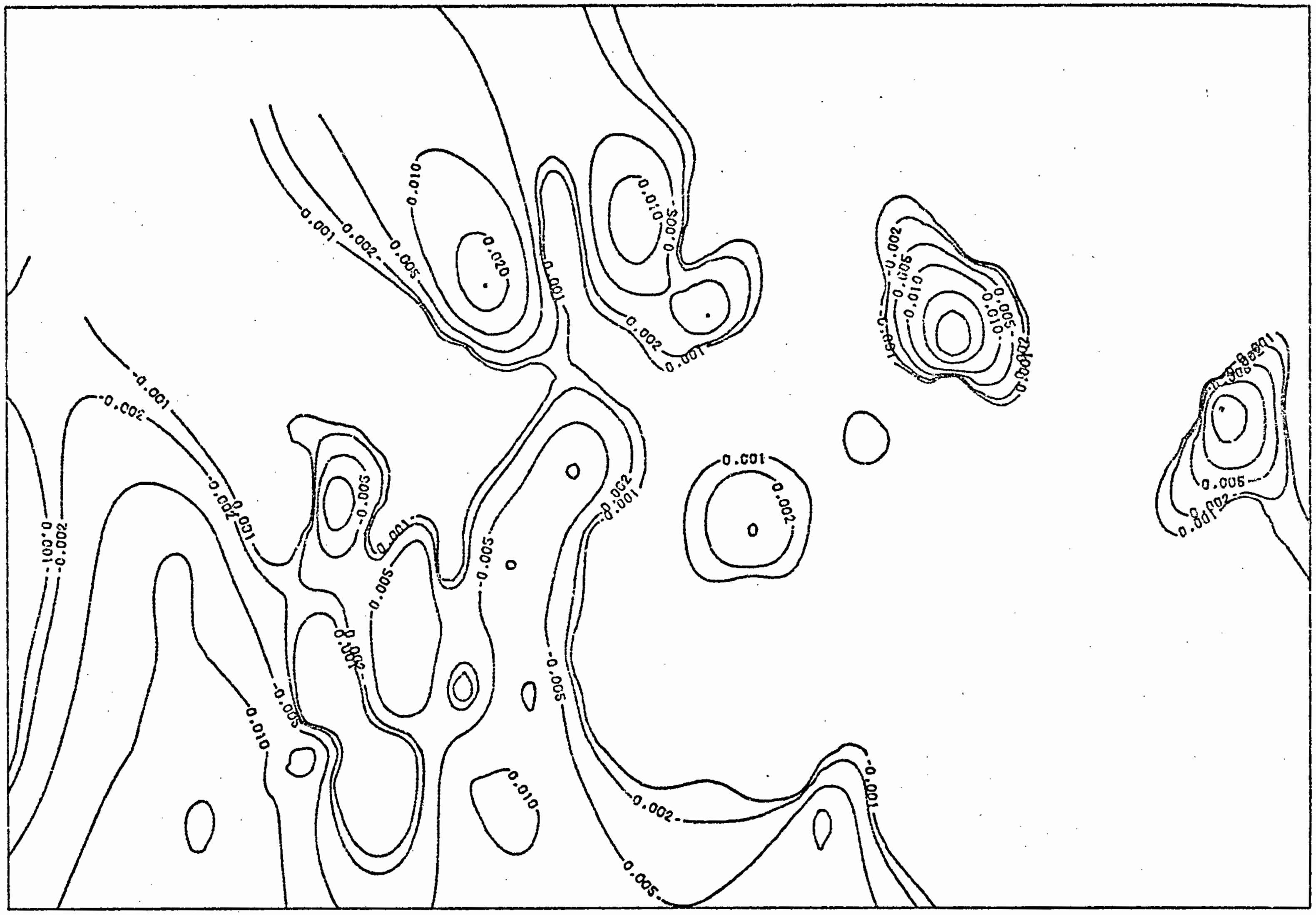

FIG.6SC PB/TDS

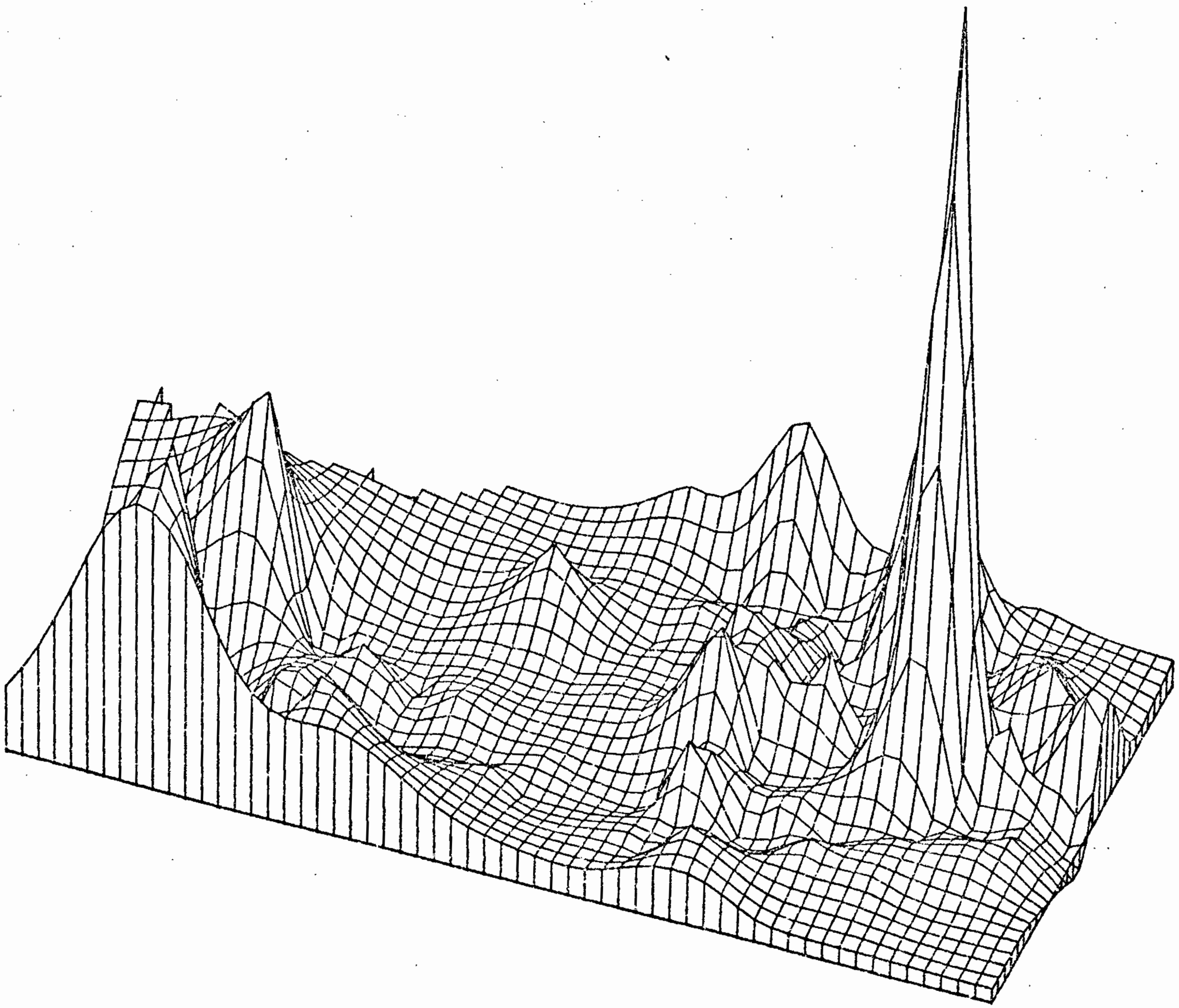

FIG.6T S04/CL

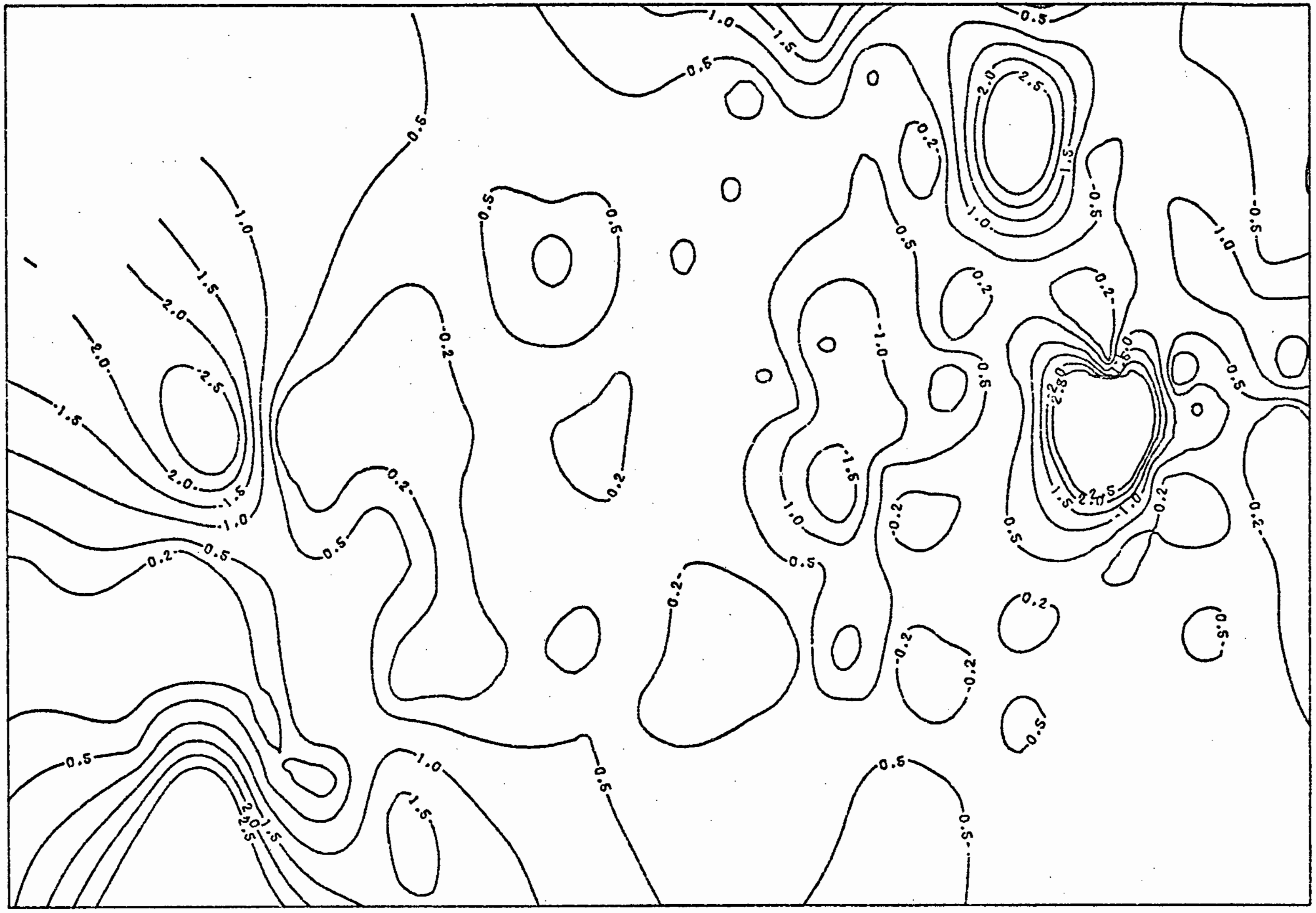

FIG.6TC S04/CL

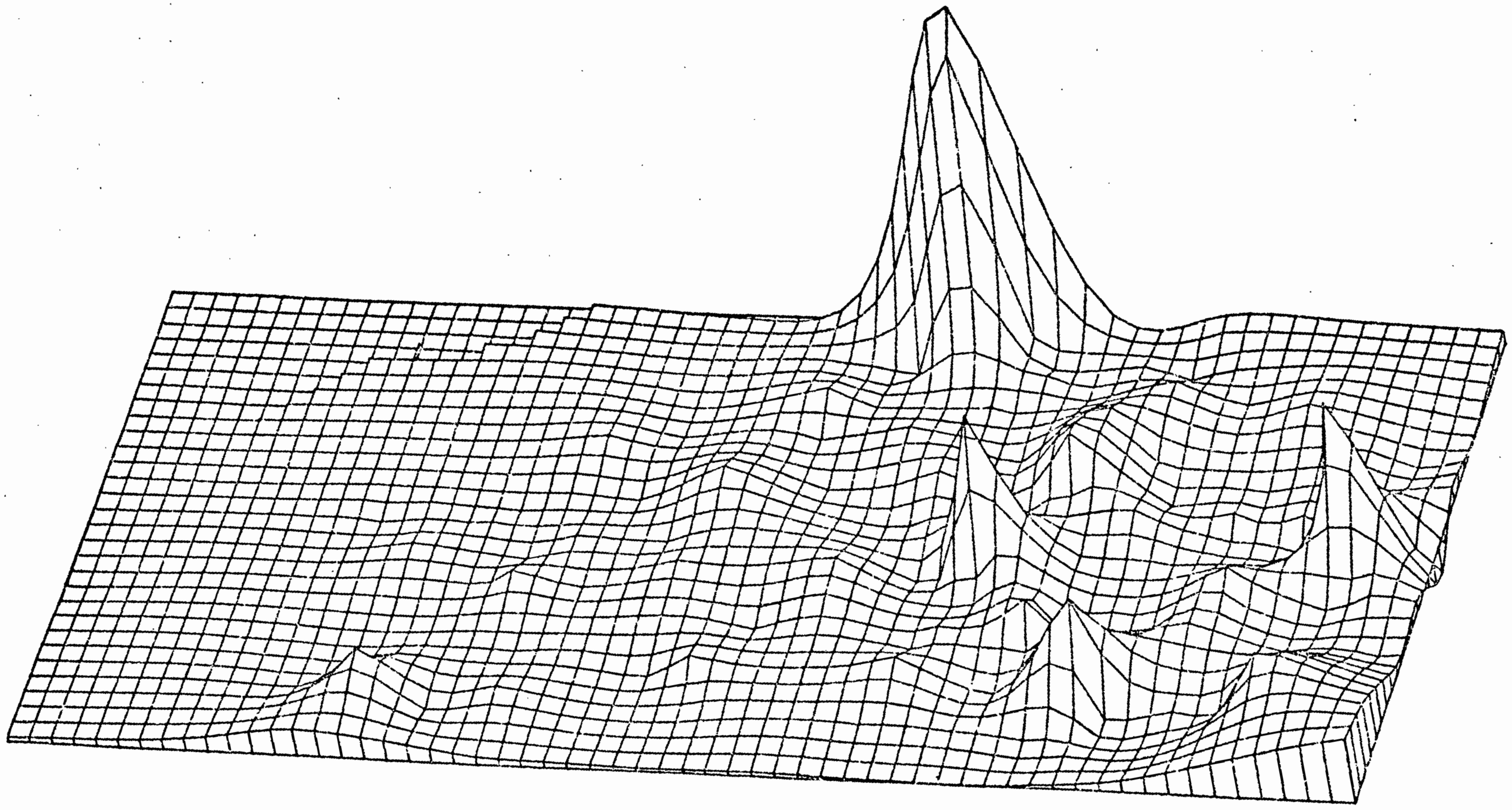

FIG.6U CU+PB

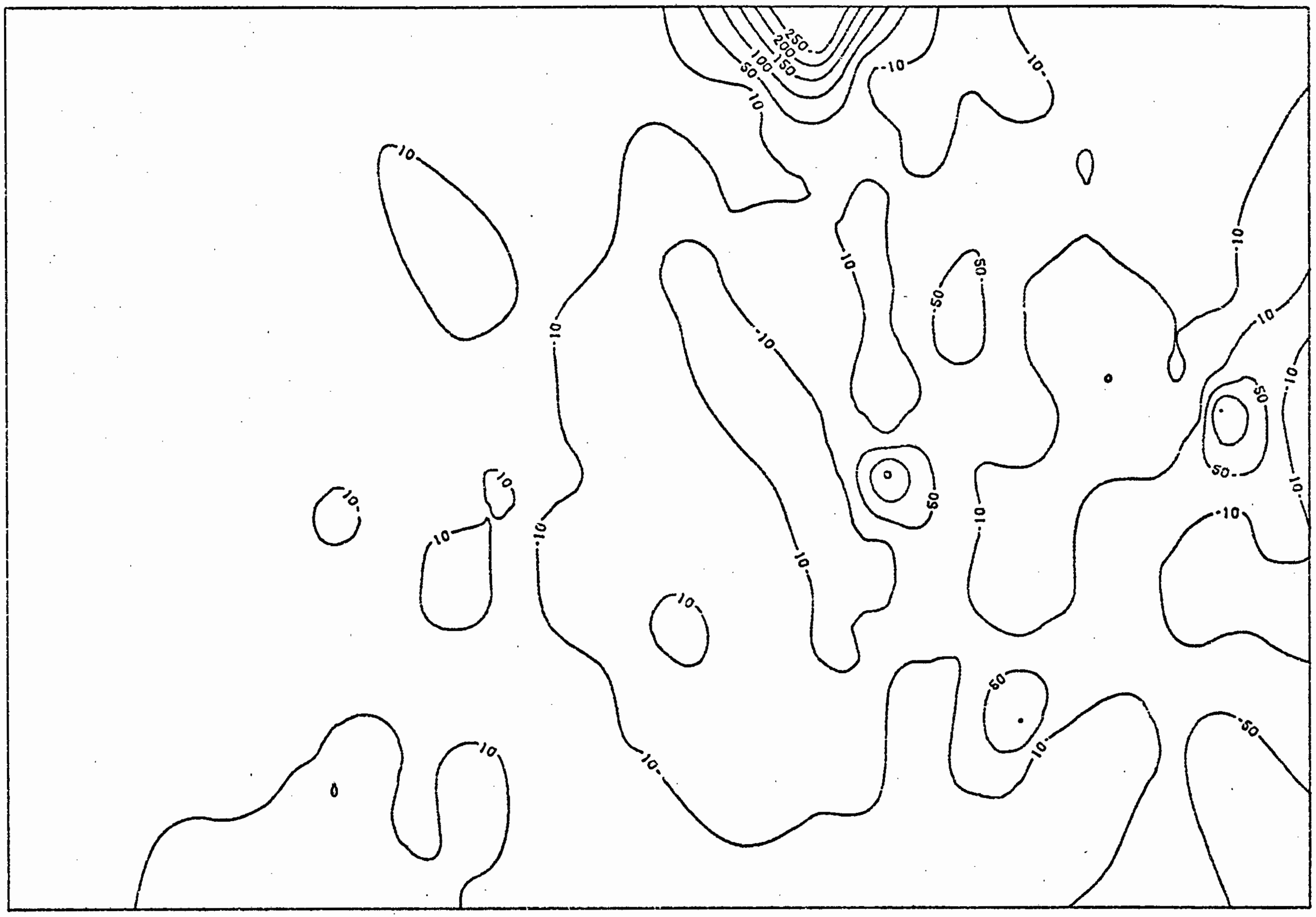

FIG.6UC CU+PB

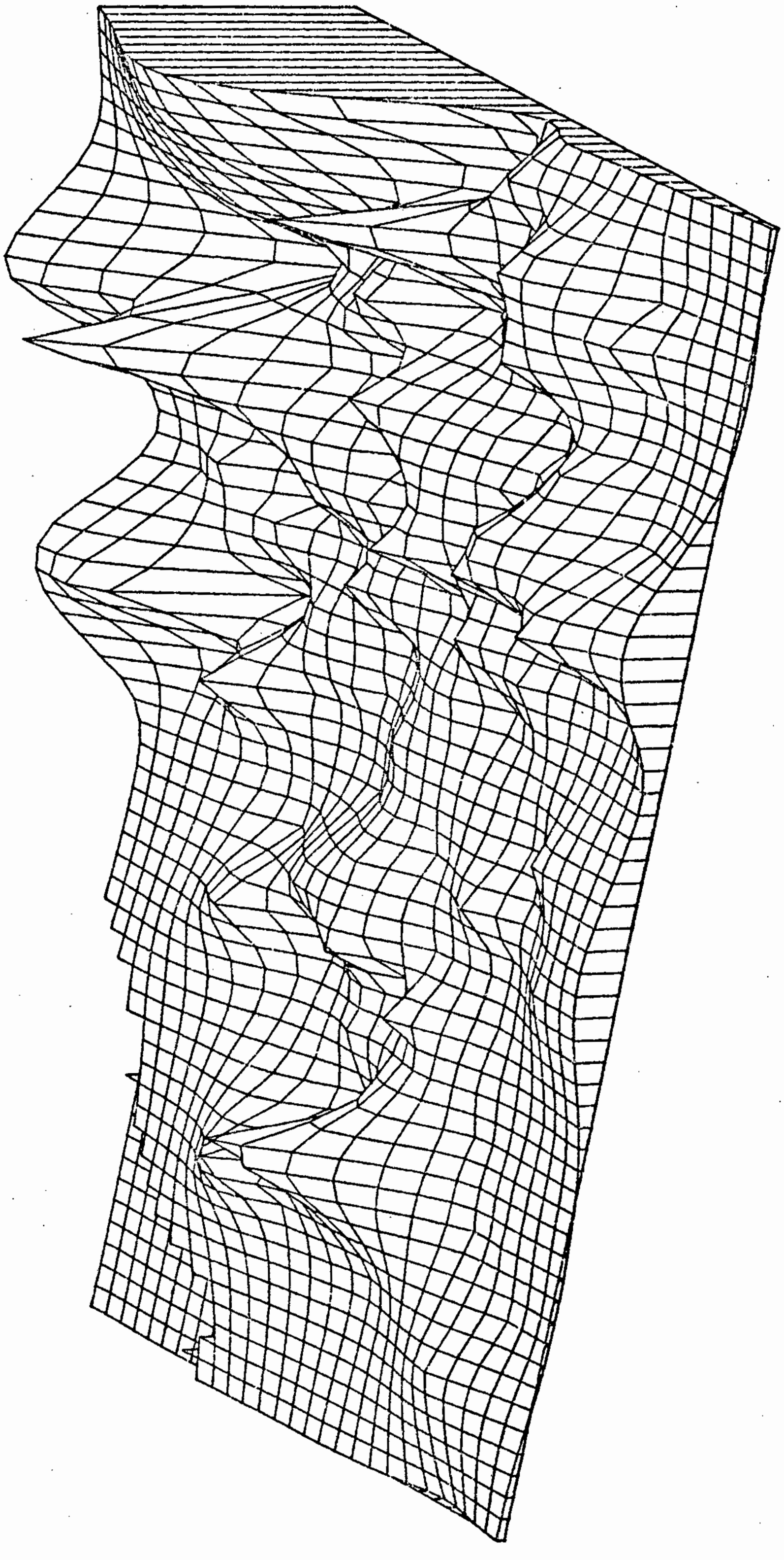

FIG.6V NA/TDS

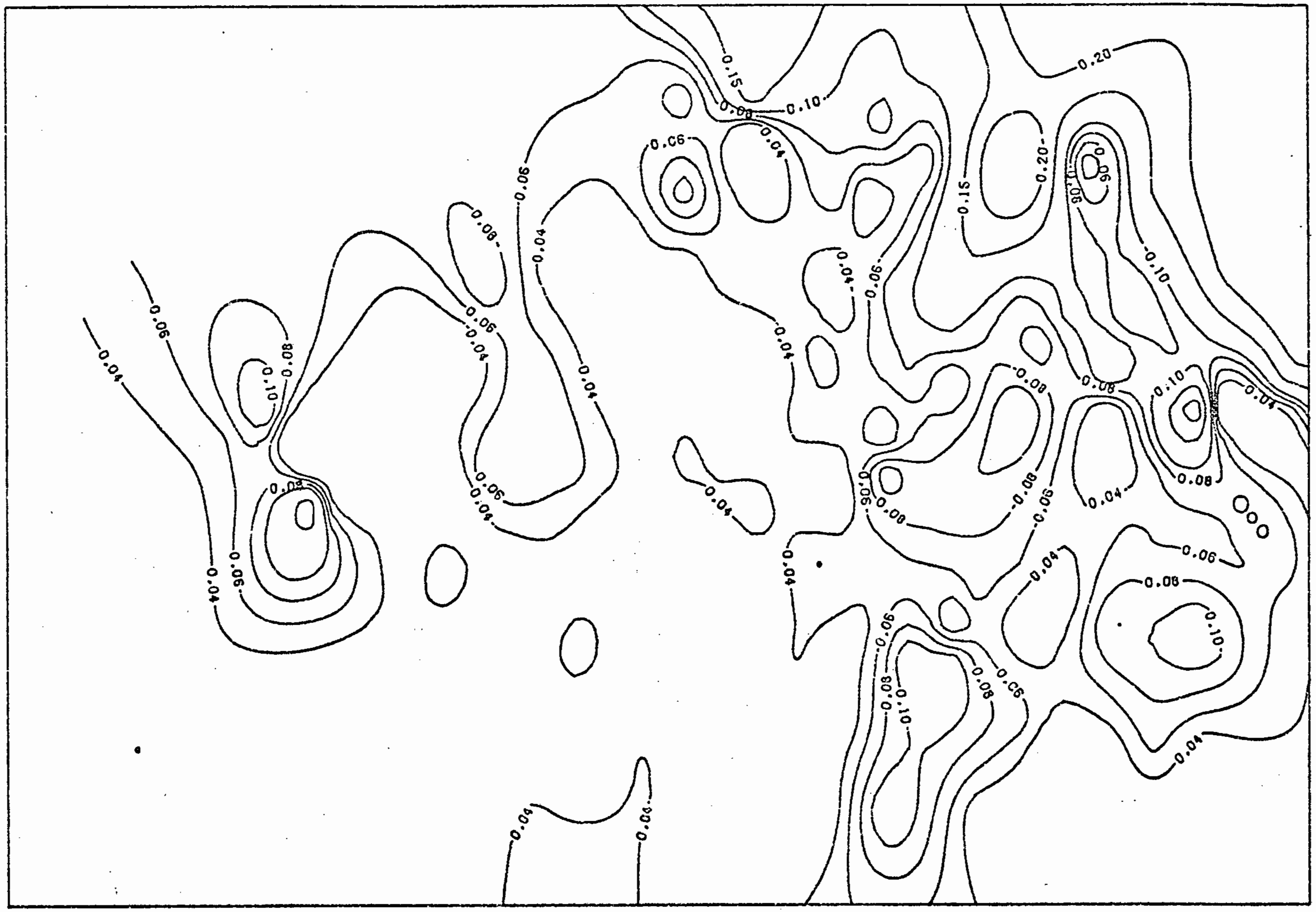

FIG. 6VC NA/TDS

virtual position bearing S 20^0 E at an elevation of 40^0 above the horizontal. (iii) The SACLANT program performs some interpolation and extrapolation with the raw data before plotting. Therefore (a) the boundaries of the contour map and the perspective "block" correspond only approximately to the boundaries of the Withdrawal Area shown in Fig. 6.1 (p. 153). (b) the virtual 3D surface created for either diagram is a smoothed version of the true surface defined by X and Y (geographical location of the sampling point) and Z (concentration of dissolved component in that sample).

Although the data were examined with the aid of fairly sophisticated, computer-executed statistical procedures /281/, the analysis did not reveal any important information that was not apparent from "eyeballing" the hydrogeochemical maps. There appeared to be no meaningful, objective basis for grouping the samples for discriminant function analysis. Principal component analysis failed to produce any clear separation of the data into natural groupings. Cluster analysis confirmed the highly individualistic nature of the compositions of most samples. The analysis failed to produce clean, readily identifiable groupings of samples. The only clear implication of the analysis was that the waters in the southern portion of the Withdrawal Area (WA) tend to be different from those in the northern part - a fact that is quite evident from even a cursory examination of the hydrogeochemical maps.

(B) *AN INITIAL EXAMINATION OF THE INDIVIDUAL HYDROGEOCHEMICAL MAPS*

(1) *Total dissolved solids (Map 4C; Figs. 6a,6ac)*

The distribution of the positive and negative anomalies in TDS follows a complex pattern. There are two principal groupings of dilute samples, one in the southwest where the WA abuts on the dolomites and another in the north-central part of the area.The most saline waters occur in a number of separate patches. An important one lies just north of the dilute waters in the southwest, while most of the others are located just within the northern, eastern or southwestern borders of the WA. This distribution is illustrated very clearly in the 3D diagram, in which the saline waters appear as "hills" in the west and "mountains" in the east and northeast. The reasons for the existence of these patterns is generally unclear. The southwestern grouping of low-TDS samples obviously represents a slight extension of the dilute dolomitic waters of the Mountainland into the Kalahari terrane. The western zone of high-TDS waters lies mainly on the projected extension of the Mulden beds that are exposed somewhat to the south, but there is no evidence from the orientation survey that these quartzites are associated with formational waters more saline than those of the dolomites. There is a vague association between the eastern high-TDS anomalies and the sheet of subcropping Kaoko basalt thought to exist in that area (/30/; Map 4b), but none of the other anomalies, whether positive or negative, appears to be related to anything in particular.

The waters of the WA are generally much more saline than those of the Mountainland. The mean concentration of TDS is the orientation samples ($\bar{x}$TDSm) is 577 mg/l, whereas the corresponding value for the application data ($\bar{x}$TDSd) is 1020 mg/l and the ratio of the two means is 1,77. Grade -I values in the Mountainland are typically less than 300 mg/l but in the WA they are typically more than 400 mg/l. The corresponding values for the Grade I anomalies are <1000 and >2000 mg/l. Only one Mountainland sample has more than a thousand milligrams of solids per litre but about 25% of the samples from the WA are more saline than this. It must be apprehended that the complex distribution of TDS in the WA and the generally high values thereof will complicate the interpretation of the trace element data collected during the application study.

(2) *pH (Map 4F; Figs. 6d,dc)*

Anomalous acidic waters are practically confined to the southern edge of the WA and are associated principally with areas apparently underlain by the dolomites or the Abbabis granite. It is likely that this reflects the influence of the relatively acidic Mountainland waters to the south. As expected, many of the acidic waters of the southwest are also low-TDS waters but generally speaking the pH and TDS anomalies are not closely related; the correlation coefficient (cc) for pH and TDS is 0,09. (All cc's quoted in this subsection are calculated for all the application data together). There are in the WA only eight pH values below 6,85 and none lower than 6,70 and it therefore seems improbable that depression of the pH could serve as a useful index for prospecting in this area.

The anomalously alkaline waters of the WA occur mainly in the central parts and appear to have no significant lithological associations.

(3) *Bicarbonate (Maps 4I, 4AM; Figs. 6g,6gc,6n,6nc)*

Bicarbonate-poor waters occur in two anomalies: a small one on the southwestern border of the WA and a larger, linear one running right across the WA from north to south a few kilometres from its eastern boundary. The most extensive positive anomaly occupies the west-central part of the area and two others occur just a little to the west of the eastern negative anomaly. Most of these features are rather muted on the 3D diagram owing to the occurrence of a pronounced peak in the northeast. There is very little apparent geological control over the concentration of the bicarbonate ion. Furthermore, there appears to be very little association between bicarbonate anomalies and either TDS (cc = 0,25) or pH (cc = 0,01) anomalies. This is not surprising, since the concentration of bicarbonate is contolled mainly by the carbonic system (Appendix I). This fact also explains why the waters of the WA are not much richer in bicarbonate ion than those of the Mountainland ($\bar{x}HCO_3^-m$ = 587 mg/l; $\bar{x}HCO_3^-d$ = 632 mg/l; ratio of the means = 1,08; cf. TDS/TDS ratio = 1,77).

There is no obvious relationship between the ratio HCO_3^-/TDS and the known lithology. Positive anomalies occur exclusively in the west and central parts of the WA and negative anomalies in the east. This simply reflects the effect of closure related to the build-up of other salts in the east; i.e. where sodium, chloride and sulphate form a bigger proportion of the total mass of dissolved salts. Thus there is a good correspondence between negative HCO_3^-/TDS anomalies and sodium anomalies (cc = -0,60). Several similar relationships can inevitably be demonstrated amongst the ion/TDS ratios for the major components and they do not appear to have any particular significance from the point of view of exploration.

The bicarbonate/TDS ratio is not governed by pH (cc = -0,19).

(4) *Calcium (Maps 4H and 4AL; Figs. 6f,6fc,6m,6mc)*

The distribution of calcium appears to be independent of the known geological factors. Most of the calcium-rich waters occur in a band running diagonally across the western third of the WA, while most of the negative values are crowded along the northern and northeastern borders. The concentration of calcium, like that of bicarbonate, is heavily modulated by the carbonic system and we therefore find that calcium, too, is scarcely more abundant in the Kalahari waters than in the more dilute dolomitic waters ($\bar{x}$ Cam = 99 mg/l; $\bar{x}$Cad = 115 mg/l; ratio = 1,16; cf. bicarbonate/bicarbonate ratio = 1,08 and TDS/TDS = 1,77). Thus one finds also that there is very little association between the locations of calcium anomalies and those of TDS anomalies. The cc for Ca:TDS is 0,45, but calcium and the other major components of the dissolved salts must inevitably correlate well with TDS. Neither do calcium anomalies show much tendency to correlate directly with those of pH (cc = -0,37) or bicarbonate (cc = -0,14), which reaffirms that the relationship between these three parameters, although mathematically definite (Appendix I), is rather subtle.

Calcium/TDS anomalies, like bicarbonate/TDS anomalies, tend to be positive in the western and central areas and negative in the northeast but the match between the anomalies produced by these two ratios is, at best, only moderately good.

(5) *Magnesium (Maps 4G and 4AK; Figs. 6e,6ec,6l,6lc)*

The distribution of magnesium anomalies is very patchy, but with most of the negative anomalies south or west of the positive ones. One negative anomaly seems to correlate well with the postulated northeasterly extension of the Abbabis granite but there is no obvious lithological control over any of the others.

The abundance of dissolved magnesium, unlike those of calcium and bicarbonate, is not tightly controlled by the carbonic system and the former ion can therefore be expected to show features in its distribution dissimilar to those exhibited by the latter two. Thus one finds that magnesium is appreciably more abundant in the Kalahari terrane than in the orientation area; compare the following figures: $\bar{x}$Mgm = 56 mg/l; $\bar{x}$Mgd = 102 mg/l; ratio = 1,82; cf. TDS/TDS = 1,77, Ca/Ca = 1,16 and bicarbonate/bicarbonate = 1,08. Furthermore, the magnesium and TDS anomalies coincide rather more closely than the anomalies of any pair of parameters thus far examined (cc = 0,83). Nevertheless the fit between the areas of Mg and TDS anomalies is not outstanding.

The correspondence between the magnesium anomalies and those of either pH (cc = 0,01), bicarbonate (cc = 0,04) or calcium (cc = 0,38) is poor. The Mg/TDS anomalies follow the patterns established for the Ca/TDS and bicarbonate/TDS ratios, in that most of the positive anomalies lie west of the negative ones. The anomalous Mg/TDS ratios correspond only weakly or moderately with those of Ca/TDS (cc = 0,20) and bicarbonate/TDS (cc = 0,56).

(6) *Sodium and chloride (Maps 4K, 4E, 4Ap and 4AN; Figs. 6i,6ic,6c,6cc,6v, 6vc,6o,6oc)*

The distributions in the WA of these two ions are quite closely related (cc = 0,60) and the respective positive and negative anomalies match fairly well. Negative anomalies tend to occur near the dolomite in the southwest and positive values in the east and north, but there is no clear-cut correlation between the positive anomalies and the putative location of the subcropping basalts. Sodium and chloride appear to accumulate rapidly in formational waters moving outwards from the Mountainland. The NaCl content of the WA is, on average, more than double that of the orientation samples:

$\bar{x}\mathrm{Nam}$ = 35 mg/l; $\bar{x}\mathrm{Nad}$ = 86 mg/l; ratio = 2,46
$\bar{x}\mathrm{Cl}^{-}\mathrm{m}$ = 70 mg/l; $\bar{x}\mathrm{Cl}^{-}\mathrm{d}$ = 144 mg/l; ratio = 2,06
cf. TDS/TDS = 1,77; Ca/Ca = 1,16 and Mg/Mg = 1,82.

It is therefore logical to find that a fair correlation exists between sodium and chloride anomalies, on the one hand, and TDS anomalies on the other (respective cc's = 0,85 and 0,92). It is also logical to find that the Na/TDS and Cl^{-}/TDS maps "compliment" the Mg/TDS, Ca/TDS and bicarbonate/TDS maps (Table 6.3B). Whereas the latter three show ratios that decrease towards the northeast, the former two have values that increase towards the northeast. This is not highly significant; it is clearly impossible for them all to increase in the same direction.

(7) *Sulphate and sulphate/chloride ratio (Maps 4D, 4AO, 4BO; Figs. 6b, 6bc, 6p, 6pc, 6t, 6tc)*

Sulphate is a potential pathfinder in this operation and only positive anomalies are of any real interest. It is clear that the distribution and significance of sulphate in samples from the WA are not at all the same as they are in the waters of the Mountainland. In the orientation survey sulphate was encountered in appreciable amounts only in anomalous waters but in the Kalahari terrane the ion appears commonly to be a significant component of typical background waters. Compare the following figures: $\bar{x}\mathrm{SO}_4^{=}\mathrm{m}$ = 25 mg/l; $\bar{x}\mathrm{SO}_4^{=}\mathrm{d}$ = 65 mg/l; ratio = 2,6; cf. TDS/TDS = 1,77. Furthermore, the two major sulphate anomalies are packed quite neatly into the northern and northeastern parts of the WA. They are not really co--extensive with the supposed field of subcropping basalt but the association is close enough to raise suspicion, since those parts of the anomalies that are underlain by the basalt can certainly not be related to mineralization. Moreover, there is a moderate to good correspondence between these anomalies and the fields of high TDS (cc = 0,63) and this makes the significance of them even more dubious /1048-50/.

The general features of the sulphate/TDS map are the same as those of the sulphate map, reaffirming that the amount of sulphate, like those of sodium and chloride, rises proportionately faster than the concentration of TDS does as the groundwater moves towards the northeast.

The sulphate/chloride ratio does not appear to be very helpful. It did not perform well in the orientation survey and shows some discouraging characteristics in the WA. The anomalies in the southwest are in dilute waters and are associated with small absolute concentrations of sulphate ion, which are no greater that the background values in some of the orientation

TABLE 6.3B SELECTED CORRELATION COEFFICIENTS

	Mg/TDS	Ca/TDS	HCO_3^-/TDS
Na/TDS	-0,55	-0,68	-0,57
Cl^-/TDS	-0,27	-0,47	-0,79

	Zn	Na	Cl^-	$SO_4^=$
Cu	-0,01	0,10	0,04	0,10

samples from dolomitic formations. Some of the sulphate/chloride anomalies in the northeast lie partially or entirely on the supposed subcropping basalt, making most of the peak values here suspect. The significance of the sulphate/chloride anomaly in the centre of the WA is unknown. There is an interesting, isolated anomalous sample in the northwest, near the buried magnetic anomaly shown on Map 4B.

(8) *Zinc (Maps 4J and 4AX; Figs. 6m, 6mc, 6r, 6rc)*

On average, zinc is ten times more common in the dolomitic groundwaters of the Mountainland than in those of the WA ($\bar{x}Znm$ = 1924 µg/l; $\bar{x}Znd$= 192 µg/l). This is not unexpected, since dolomitic provinces are quite often permeated by zinc-rich formational waters /45,48/. Nevertheless, the average concentrations quoted above are actually not very meaningful, because the range of zinc values in both sets of data is extreme and the mean value for the orientation samples is heavily weighted by the massive 61 mg/l anomaly at Kranzberg East. (The coefficient of variation for zinc in the orientation data was 4,39 and for the application data 3,45. The corresponding values for TDS were only 0,82 and 0,88).

The zinc anomalies depicted in Map 4J can be grouped into four important categories:

(a) Southwestern: These are in dolomitic waters and with one outstanding exception - a sample from the farm Amoy 664 - they are not very zinc-rich when contrasted with even the Grade II anomalies of the orientation area.

(b) Southeastern: This is a weak, probably spurious anomaly almost certainly lying on subcropping granite.

(c) Northeastern: Most of the anomalous zinc samples lie in this area and half of them come from areas that are probably underlain by basalt. Seven of the ten Grade I samples found here are in waters with TDS values in excess of 1000 mg/l.

(d) Northwestern: This is a scattered anomaly, probably underlain in part by an appreciable thickness of Mulden quartzite. Several of the anomalous sampling points are also the sites of positive TDS anomalies.

Of the eleven Grade I zinc anomalies in the northwestern and northeastern groupings, eight are associated with sodium (cc = 0,04) and/or chloride (cc = 0,03) anomalies and eight with Grade I sulphate anomalies (cc = 0,01). It may well be that corrosion and contamination, accelerated by the high concentrations of these salts, is responsible for many of the apparent zinc anomalies.

The Zn/TDS anomalies are practically co-extensive with the absolute zinc anomalies.

(9) *Copper (Maps 4L and 4AW; Figs. 6j,6jc,6q,6qc)*

Copper is nearly as abundant in the waters of the WA as it is in those of the orientation area ($\bar{x}$Cum = 21 µg/l; $\bar{x}$Cud = 15 µg/l). The copper-rich samples are fairly scattered and many "single point" anomalies occur throughout most of the area. The 3D diagram is dominated by a single extreme value in the far north. The few coherent groups of anomalous samples that are present are confined to the central and southeastern parts. About one third of the anomalous samples - mainly in the south and east - lie on unfavourable lithologies, especially basalt. About one third are associated with TDS anomalies (cc = 0,09). The correspondence between copper and either zinc, sulphate, sodium or chloride anomalies is generally fairly poor to very poor (Table 6.3B). The distribution of Cu/TDS values is very similar to that of the absolute copper data.

(10) *Lead (Maps 4M and 4BA; Figs. 6k,6kc,6s,6sc)*

The mean concentration of lead in the orientation samples was 21 µg/l but in the application samples it was only 1,4 µg/l. There is thus a general suppression of lead values in the Kalahari terrane, with only about 3% of the observed values rising above 10 µg/l and none of them approaching anything like the extreme concentrations of lead seen at Kombat and Kranzberg East. It is therefore not surprising to find most of the lead anomalies crowded into the southwestern corner of the WA, where the northward-moving dolomitic waters still retain some of their Mountainland-like characteristics (compare their TDS values and pH). The other lead anomalies, which are mainly single points, are scattered in the central and north-central portions of the WA but are practically absent from the areas above or adjacent to the granite and the basalt. There is, of course, some association between lead-rich and salt-free waters in the southwest but elsewhere the lead anomalies appear to be located with indifference to the concentration of TDS (cc = -0,11).

There is a slight association between lead anomalies and zinc anomalies in the southwest, but elsewhere the relationship is poor (cc = 0,34). Copper anomalies are not associated with lead-rich waters anywhere (cc = 0,12). Lead is associated with sodium- and chloride-poor waters in the southwest but elsewhere no strong relationships are apparent (cc = -0,08 and -0,10 respectively).

Lead sulphate is very insoluble and it is therefore natural to find that almost no lead anomalies occur in the areas occupied by sulphate-rich waters (cc = -0,08). The lead/TDS and lead maps are very similar.

(11) *Sum of copper plus lead. Sum of copper plus lead plus zinc. (Maps 4BP and 4BQ; Figs. 6u,6uc)*

The (Cu + Pb) map did not prove to be very useful. Copper is, on average, eleven times more abundant in the waters of the WA than lead and swamps the summed index, so that the (Cu + Pb) map is practically a duplicate of the copper map. Similarly, the Cu + Pb + Zn index is swamped by zinc.

(C) *INTERIM SUMMARY, CONCLUSION AND RECOMMENDATIONS*

It was shown earlier in this work that the interpretation of the data from the WA would have to rely heavily on extrapolation of the exploration criteria established during the orientation study of the dolomitic groundwaters of the Otavi Mountainland. The foregoing examination of the application data was sufficient to cast grave doubts upon the reasonableness of this proposal. The reader may note, in particular, the following features of the appropriate variants of Map 4:

(1) The generally high values of TDS and the marked contrasts between the salinities of groundwaters in various parts of the WA.

(2) The relatively very high background values for sulphate and the correlation between high sulphate and high TDS, or between positive sulphate anomalies and areas thought to be underlain by basalt.

(3) The general suppression of the abundance of lead and the dubiousness of many of the copper and zinc anomalies for one or other of several reasons.

In view of this situation, the question that had to be asked - and it was a practical, *economic* and not merely an academic one - was : " Are you prepared, on the basis of the available information, to select target areas where the geophysicists and geologists can go confidently to spend a great deal of time and money in a detailed exploration effort?". To the writer, the answer was definitely negative. It was felt that it would be highly desirable to obtain additional geological, chemical and other data before returning to the question of committing the specialists to a detailed investigation of specific targets. The following recommendations were therefore offered:

(1) Visits should be made to the sites of various metal anomalies to examine the terrane and the pumping equipment and to question farmers about the history and other characteristics of the boreholes involved. (It transpired that almost nothing of significance was learned from this).

(2) Additional orientation work should be performed to the east of the WA in order to learn more about the nature of the waters associated with granites and, especially, with basalts. It was hoped that this might enable us to

recognize more clearly and thus exclude spurious trace metal anomalies caused by the migration of basaltic or granitic formational waters in the east or south of the WA.

(3) There ought to be a program of resampling and analysis of waters from boreholes that had yielded anomalous samples, in order to check that these anomalies were reproducible.

(4) Drilling should be undertaken at selected sites within the WA to obtain some real control between observed hydrochemical compositions and the lithology of the rocks from which they were drawn.

These recommendations were accepted by TCL and were implemented under the direction of the writer during the latter part of 1975. It was obviously necessary and desirable to work particularly closely with members of the TCL geological staff at this time and the writer is pleased to acknowledge gratefully the debt he owes to these gentlemen, and particularly to Doug Buerger, for material assistance and fruitful interchanges of ideas.

6.4 Advanced investigations and interpretation

(A) *CHARACTERIZATION OF FORMATIONAL WATERS FROM GRANITES AND BASALTS*

The object of this exercise was to collect and analyze waters from boreholes known to be drilled into either of these rock types in order to ascertain whether these waters have any singular characteristics. This idea is quite sound in theory. Brooks /1179/ has discussed the principles of "fingerprinting" formational waters lying in specific kinds of rocks. In particular, it is well known that Karoo lavas can have a profound and perhaps specific effect on the hydrogeochemical properties of groundwaters in the Kalahari areas (/33/ and Smit, Geological Survey, pers. comm.). Stormberg rocks are not present in the Mountainland *per se* and there appeared to be no way of predicting from the data of the second orientation study what influence subcrops of these rocks might have had on the concentrations and distribution of pathfinders originally identified in purely dolomitic groundwaters.

An area just to the east of the eastern boundary of the WA was selected for the experiment, because borehole logs supplied by the Department of Water Affairs /33/ indicated that a number of boreholes in this region had intersected either granite or basalt under a relatively thin superficial cover. The nearest to the WA of these known intersections is on the farm Abendruhe, less than 10 km from the boundary of the area.

It proved to be unexpectedly difficult to identify these boreholes in the field. After two full days of investigation only six holes that were still operational had been identified and it was decided to utilize these in a pilot study before investing a great deal of additional effort in locating additional boreholes that might never be required.

The methods used for sampling and analysis were identical to those previously described in this thesis. The analytical results are compiled in Table 6.4A. Although there are only six samples, the results are statistically meaningful in the sense that we wished to establish whether the variance of the data was small enough to allow us to "fingerprint" an igneous formational water with good confidence; if the absolute variance in a small population is large, then it can only become worse in a larger population.

The results of the pilot study suggested that it would not be possible to differentiate between "granitic" waters and "basaltic" waters or between "igneous" waters and "Kalahari" waters. The six samples represented in the table are not systematically different from the typical waters encountered in the eastern and central parts of the WA. (Sample BA is a remarkable exception but we will see later that it cannot be a "basaltic" water anyway). Moreover, in the case of each individual analyte or measurement the range of granitic values lies within, or spans most of, the range of basaltic values.

The only possible alternative at this stage was to collect many more samples and to examine the results with some sophisticated statistical technique such as cluster analysis or discriminant analysis. There were two convincing reasons for rejecting this alternative:

(a) it seemed improbable that we should be able to find enough samples.

(b) it seemed highly probable that the six pilot samples were in any case not drawn from the subcropping igneous rocks but from the overlying veneer of aquiferous Kalahari materials. Bond /228/ analyzed some three dozen groundwaters taken from basaltic formations in other parts of southern Africa but he never encountered a water anything like the unique sodium carbonate water from Welverdiend. (The origin of this water remains a mystery).

The "fingerprinting" project was therefore considered to be unfeasible under the prevailing circumstances and was abandoned.

(B) *RESAMPLING AT SELECTED SITES TO CONFIRM THE PRESENCE OF TRACE ELEMENT ANOMALIES*

Some of the boreholes that had produced the best trace element anomalies were resampled and the waters analyzed in the manner previously described. This exercise merely underscored what any experienced hydrogeochemist knows to be almost a foregone conclusion - that a proportion of the "anomalous" values

TABLE 6.4A ANALYSES OF WATERS FROM BOREHOLES IN AREAS UNDERLAIN BY SUBCROPPING KAOKO BASALT OR ABBABIS GRANITES

Sample	Farm	Lithology	pH	HCO_3^-	Ca	Mg	$SO_4^=$	Cl^-	TDS	TSS	Cu	Pb	Zn	Na
BA	Welverdiend	Granite	7,0	400	50	528	9	9	985	2	<1	1	112	73
BB	Welverdiend	Granite	7,3	812	10	115	57	42	768	4	14	<1	134	900
BC	Welverdiend	Basalt	8,9	1521*	1	0	77	145	1732	14	6	<1	105	1100
BD	Voorpos	Basalt	7,0	346	49	553	7	3	329	5	5	<1	215	44
BE**	(Check sample)		6,9	341	56	500	7	3	317	-	6	<1	155	29
BF	Dismyne	Basalt	6,8	390	48	432	10	3	373	0,3	<1	3	72	100
BG	Arbeidskroon	Basalt	7,0	424	41	485	19	27	450	0,2	<1	<1	406	99

* This is a theoretical value. At pH 8,9 about half of this total is actually present as the carbonate ion.

** Sample BE is a duplicate of sample BD.

Values for copper, lead and zinc are in micrograms per litre. Values for the other components are in mg/l.

TABLE 6.4B RESAMPLING TO CONFIRM THE PRESENCE OF METAL ANOMALIES

Sample*		Farm	Cu new	Cu old	Pb new	Pb old	Zn new	Zn old	Na new	Na old
R1α	β53	Emmanual	5	3	1	14	41	27	42	20
R2^{1}	54	Emmanual	5	10	<1	12	7	17	68	60
R3^{1}		(Check)	5		<1		4		140	
R4	55	Emmanual	4	4	1	4	41	90	55	20
R5	39	Elandsvlak	4	4	1	<1	71	291	41	280
R6	38	Elandsvlak	<1	<1	2	<1	68	71	11	11
R7	151	Silverstroom	9	28	<1	<1	216	77	12	7
R8^{2}	150	Silverstroom	3	31	<1	<1	36	48	23	20
R9^{2}		(Check)	6		<1		43		21	
R11^{3}	11	Cork	1	<1	3	16	850	2600**	26	18
R12^{3}		(Check)	<1		7		1230		24	
R13	12	Deal	<1	<1	1	6	70	43	22	13
R14	5	Notweide	<1	3	<1	1	1536	62	3,7	2
RECOVERY TEST			19		80		157			
RECOVERY TEST CHECK			41		80		183			

* There are two sample numbers: α is the laboratory sample number, β is the borehole sampling site number shown on Map 4A.

** A sample collected from this borehole during the orientation survey (Chapter 5) contained 10 200 μg Zn per litre.

Samples marked with corresponding superscript numbers are pairs of check samples.

Values for sodium in milligrams per litre. Other values in micrograms per litre.

in any project will be spurious. (Everyone likes to believe the analytical numbers that they produce. One must nevertheless not lose sight of the fact that a typical Grade I copper anomaly in the WA has 30 *millionths* of a gram of copper per litre of acidified sample. The minutest fragment from a brass bush will enhance the natural background value in the sample a hundredfold).

Table 6.4B contains selected data from the resampling survey. Note that many apparently important copper and lead results, in the range 10-30 µg/l, are shown to be really only background samples. No examples were seen where the new copper or lead values were significantly higher than those previously reported. Zinc, on the other hand, behaved erratically, with some new values being relatively depressed and others being relatively enhanced. This tended to add to the growing suspicion that many of the borehole waters in the WA were contaminated with zinc and that the degree of contamination varied from time to time, probably depending on variations in the amount that the borehole was used during a given period of days or weeks prior to sampling.

The question of a complete re-examination of all the interesting trace metal anomalies in the WA was deferred until the results of the drilling program (*vide infra*) had become available.

(C) *DRILLING TO OBTAIN LITHOLOGICAL CONTROL*

The reader will recall that the chief difficulty preventing the selection of target areas within the WA resulted from (a) the strong indications that the empirically-derived orientation criteria were not valid in the application study and (b) the almost total inability to "tie" the observed hydrochemical data from the WA to any definite subcropping lithology. What was needed at this stage was (to corrupt a term originated by the remote-sensing fraternity) some "underground truth". Thus it must be clearly understood that at this juncture the principal object of drilling was *not* to investigate individual anomalies *per se*, but was to see what underlay areas occupied by formational waters of specific kinds.

Tsumeb Corporation very kindly undertook to drill four boreholes at selected points within the WA. Diamond drilling is extremely expensive and there was no question of being able to drill more core at this stage. The sites for the holes were therefore selected rather carefully. The siting of the second and subsequent holes was obviously influenced by the information obtained from the drilling already completed. The drill cores from these exploratory holes were subjected to exhaustive petrological, mineralogical and geochemical examinations, which resulted in a great volume of data and written reports /32,52,1198/. It would be pointless to reproduce this bulky detail here in its entirety and instead the findings of principal interest will be summarized in the following discussions of each of the four exploratory boreholes. These holes were always sited near to a farm borehole sampled during the application study. The number of the corresponding application sample is given in parenthesis after the name of the exploratory borehole:

(1) *Borehole 1. Klingenberg (64)*

The object of this hole was to investigate the subsurface lithology and stratigraphy in the central-northeastern part of the WA. It would obviously have been pointless to drill deliberately into the basalt, because there is no possibility at this time of using hydrogeochemical techniques to locate sulphide mineralization buried under a sheet of lava that is in turn buried by overburden. The hole was therefore sited comfortably west of - but not too far beyond - what was supposed to be the edge of the buried extrusives /30/. This edge is shown on the magnetic data map 4B. The "magnetic edge" cannot be exactly related to the edge of the basalt and so the borehole was placed so as to avoid high-TDS waters and any other waters that could conceivably have been a reflection of extrusives lying somewhat west of the apparent magnetic boundary. Thus the borehole at Klingenberg is positioned just far enough west and south to avoid the patches of waters rich in TDS, sulphate, sodium and chloride that occur in the northeastern portion of the WA. Sampling site number 64 was chosen as the exact position of the exploratory borehole because the application sample from that point had been anomalous in zinc, copper and lead.

The Klingenberg exploratory borehole disappointed us by revealing that the bedrock was much more deeply buried than we had supposed. After drilling 56,5 m the bit was still in the Kalahari Formation and we could not, in conscience, justify any deepening of the hole. The borehole core consisted principally of light-coloured, poorly-sorted, poorly-bedded, massive, highly calcareous arenites and gravels; sometimes rudaceous, with rounded and angular fragments of quartz, shale, feldspar, granite, sandstone and chert. The profile above 22 m below collar is greatly altered and mottled by replacement and cementation. The replacement is partly siliceous but mainly calcareous and is of at least two generations. Towards the top of the profile this replacement becomes so intense that the original detrital nature of the rock is practically obliterated.

Four carefully selected samples of the core were analyzed for sulphate, which was found to constitute no more than an insignificant fraction of the the rock (0,19 ± 0,2%). There was no petrological evidence that gypsum had been present in the sequence. The drill core was found to contain very low concentrations of the principal metallic pathfinders. Twenty eight samples were analyzed and the observed ranges of concentrations were as follows (µg/g): Cu: 3-10 Pb: 3-16 Zn: 3-7 . There was thus no indication in any part of the profile of a secondary accumulation of base metals that might possibly have been related to dispersion from an underlying orebody.

These results were considered to be most discouraging. No one associated with this hydrogeochemical project - least of all the writer - believed that there was any realistic possibility of locating meaningful regional anomalies in a highly calcareous overburden as thick as the one revealed by the drilling. It was therefore decided to abandon the north--eastern end of the WA forthwith and to focus attention on the region further to the southwest of the zone of saline waters.

(2) *Borehole 2. Swerwestroom (150)*

It was decided to site the second hole near the middle of the WA but somewhat south of centre, in the hope of encountering thinner overburden. The borehole was sited comfortable north of the projected contact between the dolomites and the Abbabis granite (or perhaps the Nosib Formation - see Map 4B) that outcrops on the farms Dundee and Durban, some 30 km northeast of Grootfontein. The exploratory hole was well clear of the saline eastern waters but also clear of the patch of dilute waters further south that may have represented "migrating" Mountainland water.

The diamond bit revealed a redoubtable 103 metres of calcrete and ill--sorted arenites and gravels and was stopped without encountering solid bedrock. The materials logged were rather similar to those from the first borehole and showed the same intense recementation or "capping" in the upper section (0-40 m). This profile, like the first one, was also very poor in base metals; twenty nine sections of core were analyzed and the ranges of concentrations (µg/g) were: Cu: 3-5 Pb: 10-17 Zn: 3-7 .

We had hoped against encountering such thick cover in the southern area and this finding greatly reduced the prospects for further work in the central and eastern parts of the Withdrawal. Few farm boreholes in this region draw water from so great a depth. The water table stands well above the Kalahari/bedrock interface and the chances are therefore very poor that regional anomalies would be detectable at shallower depths. It was decided to retreat further to the west.

(3) *Borehole 3. Elandsvlak (39)*

The third borehole was accordingly sited on the farm Elandsvlak at the western end of the WA. This is the site of an isolated and interesting sulphate/TDS anomaly that lies more or less along the line of projection of the string of sulphate/TDS anomalies that describe a southwest-northeast trend on either side of the Tsumeb mine (Map 4D). Furthermore, this exploratory hole had the important attribute of being right on top of a magnetic anomaly that had interested TCL geophysicists for some time /30/ (Map 4B).

The drill revealed the existence of 59 metres of Kalahari beds similar to those seen in the first two holes, and then passed into a consolidated, weathered sandstone that almost certainly belongs to the Karoo Formation. This surprise was equally as unpleasant as the one provided by the second borehole. No one had suspected that the Karoo Formation might be interposed between the Kalahari beds and the Outjo Facies so far to the west within the WA (although, with hindsight, we can see that we ought to have done so). Under these circumstances hydrogeochemical exploration is quite out of the question.

There was no secondary concentration of metals in any of the 35 samples of core that were analyzed. The ranges of concentrations (µg/g) were: Cu: 3-7 Pb: 3-24 Zn: 3-7 .

(4) *Borehole 4. Cork (297)*

It was decided to move the investigation further south, near to the edge of the exposed rocks of the Mountainland block, in the hope that much thinner layers of overburden would be encountered. A site was selected on the farm Cork, next to the borehole that had yielded sample number 297 in the application phase of the project. This sample was highly (if variably) anomalous in zinc and consituted an important anomaly in the non-saline waters of the southern part of the WA. The geological map (Map 4) suggested that this area was underlain by Mulden quartzite and not dolomite. It therefore appeared that the Cork anomaly was a false one and drilling here gave us the opportunity to confirm or refute this postulate while at the same time establishing the thickness of the Kalahari beds along the south-western edge of the Mountainland.

It transpired that the bedrock here *is* Mulden quartzite and there was nothing in the core to indicate the presence of secondary dispersion of base metals that might conceivably have taken place along a fault zone etc. Furthermore, the typical, gravelly, partly-recemented, calcareous Kalahari beds here are already 46 metres thick, despite the fact that the border of the "solid geology" is but 4 km distant. This left little hope that any major portion of the WA might be covered with relatively shallow overburden.

(D) *SUMMARY, CONCLUSIONS AND RECOMMENDATIONS*

An analysis of the data from the original application study had shown that formidable problems stood in the way of making an objective and confident selection of small exploration targets within the WA. The additional work described in this subsection (6.4) had reaffirmed that this goal could very probably not be achieved with known hydrogeochemical techniques. The chief obstacles encountered were as follows:

(i) the characteristics of the waters of the WA were, by and large, so different from those of the dolomitic waters of the orientation area that there arose serious doubts about the feasibility of applying in one area the exploration criteria established in the other.

(ii) the overburden throughout the WA is much thicker than had been anticipated. Even were we able to identify a regional anomaly with some confidence, the geologists responsible for investigating it would be extremely hard pressed to find some way of following up this discovery through 60 to 100 metres of overburden. Wildcat drilling to these depths is an exceptionally unattractive alternative. The depth of the Kalahari overburden increases rapidly to the north of the Otavi Mountainland block, so that hydrogeochemical techniques could be applied to no more than a narrow belt along the southern edge of the WA.

(iii) the solid geology below the sands of the WA is more complex than had been supposed. There is strong evidence for the existence of sheets of basalt in the east; Karoo sedimentary rocks occur in the west; Mulden sandstones occupy areas to the southwest. There is no way of confidently telling from analysis of groundwaters what the subcropping solid lithology is.

(iv) Drilling has practically condemned some of the trace element anomalies within the WA. Whatever their origin, these anomalies are not related to secondary dispersion from ores in buried dolomite. There is no justification for claiming that any of the other anomalies in the WA is a better candidate for investigation than those already examined. Each additional anomaly would have to be tested by drilling to at least 40 metres and this is too expensive to be seriously contemplated.

Shortly after the last of the data became available from the exploratory diamond drilling it became necessary to consider whether or not the Withdrawal Order, which was about to expire, should be renewed. The writer did not believe that additional, expensive exploration work in the WA could be justified at that time. Buerger concurred, and as a result of our recommendations to management the Withdrawal Order was allowed to lapse.

The abandonment of the exploration effort in the WA brought the field work for this thesis study to an abrupt ending. The writer, and those at TCL who had been closely involved in the hydrogeochemical project, recommended that a second Application study be undertaken in other areas of exposed dolomite, where the experience gained in the second orientation survey and within the WA could be more meaningfully utilized. This recommendation was accepted by TCL and a second hydrogeochemical exploration project, in the lightly-covered dolomitic terrane southwest of Tsumeb, was begun in 1976 under the able direction of A. D. Buerger. It was never intended that any additional application studies undertaken outside of the WA would constitute part of the writer's doctoral research and so the results of Buerger's recent work cannot yet be made public (cf. recommendation 14, subsection 5.4C). Nevertheless, the writer is pleased to conclude this treatise with the news that those who have taken over from were he left off have reported what practising exploration geochemists like to refer to as "encouraging results".