



Geochemistry of some deep gold mine waters from the western portion of the Witwatersrand Basin, South Africa

M. J. DUANE,^{1,2} G. PIGOZZI² and C. HARRIS³

¹Geology and Applied Geology, University of Natal, South Africa

²Environment Institute, Joint Research Centre, Ispra 1-21020, Varese, Italy

³Department of Geological Science, University of Cape Town,
Rondebosch 7700, South Africa

Abstract—A suite of 12 mine water samples within the Witwatersrand Basin (South Africa) were analysed for trace element concentrations, strontium isotopic composition and stable isotopes (O and H). Chemical profiles for four Au mines (Western Deep Levels, Vaal Reefs, Freddie's and President Steyn) are used to infer origin, chemical and isotopic evolution of the brines and for comparison with basement brines from other Precambrian areas. Systematic relationships are observed between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$: two major mixing trends are required to explain the range of very radiogenic end-members. Possible end-members for the two components could be: (1) $^{87}\text{Sr}/^{86}\text{Sr} = 0.7251$, Sr concentration = 0.12 mg l^{-1} from a Vaal Reefs compartment and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7694$, Sr = 39.3 mg l^{-1} from a Freddie's compartment. (2) $^{87}\text{Sr}/^{86}\text{Sr} = 0.7251$, Sr = 0.12 mg l^{-1} (as above) with a $^{87}\text{Sr}/^{86}\text{Sr} = 0.7404$, Sr = 745 mg l^{-1} from Western Deep Levels. Strontium isotope ratios range above those expected for present-day seawater and are even higher than some locally-derived low Rb minerals from the Precambrian basement.

The brines acquired radiogenic ^{87}Sr through interaction with granitic basement (Kaapvaal Craton), shales of the Central Rand Group (in particular Ventersdorp Contact Reef), siliclastics within the West Rand Group and particularly with dolomites from the overlying Transvaal Supergroup. In order to obtain their multielement and radiogenic isotope signatures the meteoric waters descended through fractured rocks between the main dykes and faults (example: Oberholzer and Bank Dyke at Western Deep Levels). They slowly interacted with Au bearing conglomerates and quartzites of the West Rand Group. The inverse relationship between Sr isotope composition and precious/heavy metal concentration suggests fluid/rock interaction within the shales and volcanics of the Ventersdorp Contact Reef (high in Au and total organic carbon [TOC], less radiogenic strontium composition by comparison with other waters). Oxygen and hydrogen isotopes reveal a pattern that classifies the samples as meteoric but with modifications. The samples show extreme values especially for Western Deep Levels and President Steyn. © 1997 Published by Elsevier Science Limited.

Résumé—Les teneurs en éléments en trace, en isotopes de Sr et en isotopes stables (O et H) ont été analysées dans une série de 12 échantillons d'eau de mines provenant du bassin du Witwatersrand. Des diagrammes chimiques de quatre mines d'Au (Western Deep Levels, Vaal Reefs, Freddie's et President Steyn) sont utilisés pour déduire l'origine et les évolutions chimique et isotopique des saumures ainsi que pour les comparer à des saumures de socle précambrien provenant d'autres régions. Une relation systématique s'observe entre $^{87}\text{Sr}/^{86}\text{Sr}$ et $1/\text{Sr}$: deux tendances majeures de mélange sont nécessaires pour expliquer l'éventail de termes très radiogéniques. Pour les deux composés, ceux-ci pourraient être: (1) $^{87}\text{Sr}/^{86}\text{Sr} = 0.7251$, teneur en Sr = 0.12 mg l^{-1} pour un terme de Vaal Reefs et $^{87}\text{Sr}/^{86}\text{Sr} = 0.7694$, Sr = 39.3 mg l^{-1} pour celui de Freddie's. (2) $^{87}\text{Sr}/^{86}\text{Sr} = 0.7251$, Sr = 0.12 mg l^{-1} (comme ci-dessus)

avec un $^{87}\text{Sr}/^{86}\text{Sr} = 0.7404$, $\text{Sr} = 745 \text{ mg l}^{-1}$ pour Western Deep Levels. Les rapports isotopiques du Sr dépassent ceux escomptés pour l'eau de mer actuelle et sont même supérieurs à ceux de minéraux pauvres en Rb, dérivés du socle précambrien avoisinant.

Le ^{87}Sr radiogénique des saumures a été acquis par interaction avec le socle granitique (Craton du Kaapvaal), les schistes du Groupe du Central Rand (en particulier ceux du Ventersdorp Contact Reef), les roches silicoclastiques du Groupe du West Rand et, en particulier, les dolomies du Supergroupe sus-jacente du Transvaal. Pour acquérir leur signature particulière en multi-éléments et en isotopes radiogéniques, les eaux météoriques ont percolé à travers les roches fracturées à la faveur des dykes et failles principales (p. ex. le Dyke de Oberholzer et Bank à Western Deep Levels). Lentement elles ont réagi avec les conglomérats et quartzites aurifères du Groupe du West Rand. La relation inverse entre la composition isotopique du Sr et les teneurs en métaux précieux/lourds suggère une interaction fluide/roche au sein des schistes et des roches volcaniques du Ventersdorp Contact Reef (teneurs élevées en Au et en carbone organique total [TOC], appauvrissement en Sr radiogénique par comparaison avec d'autres eaux). Les isotopes d'O et d'H montrent des allures permettant de classer les échantillons dans le groupe des eaux météoriques modifiées. Les échantillons montrent des valeurs extrêmes, en particulier pour Western Deep Levels et pour President Steyn. © 1997 Published by Elsevier Science Limited.

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INTRODUCTION

In Africa retention of "fossil" water occurs in the basement rocks (Howard and Kurundu, 1992) and the deep Au mines where the storage of water, albeit contaminated by 100 years of mining activity, is ongoing and apparently permanent. The number of studies on the effects of mining on groundwater in Africa is small (Bamford *et al.*, 1990) compared with the US and Europe. Compared to most industrialized regions, and with the exception of some contaminated sites (Ajayi and Mombeshora, 1989), the concentration of heavy metals in African groundwaters are low and close to natural background levels (Biney *et al.*, 1994). The few completed studies in Africa have mostly focussed on stable isotope compositions (Mazor *et al.*, 1977; Sklash and Mwangi, 1991), groundwater recharge studies (Edmunds *et al.*, 1992), hydrogeology (Kafri and Foster, 1989) and geotechnical aspects (Venter, 1986; von Wagoner and Day, 1986) with little emphasis on trace element monitoring.

South Africa has traditionally relied for potable water on certain Tertiary and Quaternary deposits and karstic Precambrian dolomitic strata, particularly in the southern and western Transvaal. Gold mining began on the Witwatersrand in 1886 and, up to 1920s, Johannesburg was solely dependant on dolomitic groundwater. Then, up to the present day, the Vaal River was exploited for mining supplies, urban and industrial uses. Up to the 1950s groundwater research consisted mostly of drilling

to test reserves without significant geochemical signaturing. During this period considerable knowledge was obtained about the occurrence of groundwater in a variety of geological formations and attention was only later focussed on assesment of groundwater for urban supplies. In 1956, problems associated with the disposal of large inflows of groundwater from the overlying dolomitic strata into Au mines of the Far West Rand led to an intensive program of hydrogeological and geophysical investigations which continues today (Vegter, 1987). Little is published on the geochemistry of these waters and the extent of their leakage into mines.

Most of the water encountered in the larger Witwatersrand Au mines (Fig. 1a) is derived from precipitation at an average rate of 750 mm yr^{-1} (Wolmarans, 1986). Also the existence of fossil water within the Witwatersrand Basin and especially below the Ventersdorp Supergroup has been known for some time (Bekker, 1986). Water is apparently primarily fed into underground excavations through the arenaceous Witwatersrand beds (see Fig. 1a for a plan of the Witwatersrand Basin) from the overlying dolomites by *en echelon* faults within and between intrusive syenite aquicludes (Wolmarans, 1986; Gay and Jager, 1986). Water issuing from boreholes through the Ventersdorp Group lavas was found to have an average temperature of 28.4°C , and contains an average of 4150 ppm total dissolved solids (NaCl being

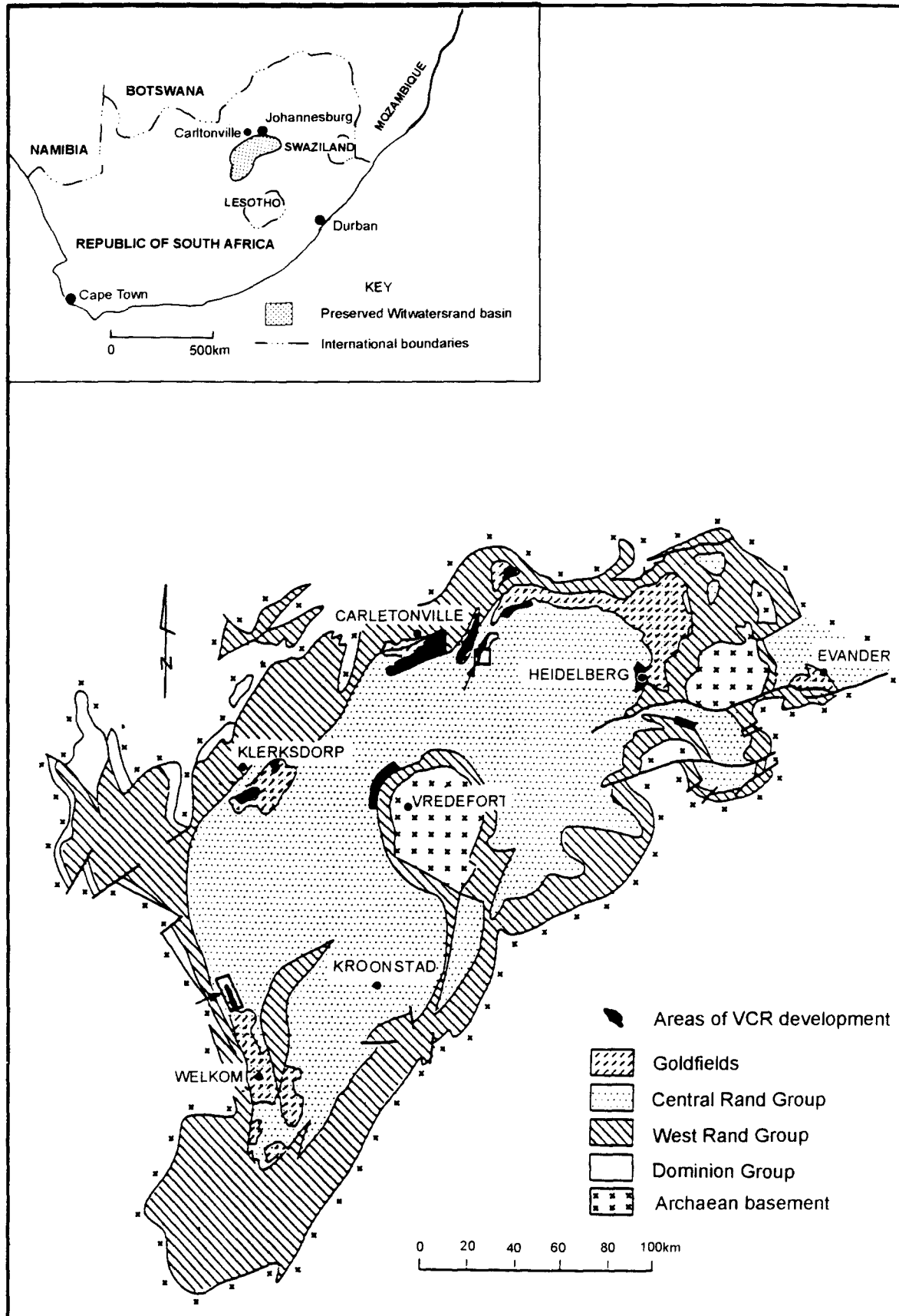


Figure 1a. Locality map for Witwatersrand Basin, major Au mines and main stratigraphic units. Adapted from McCarthy (1994).

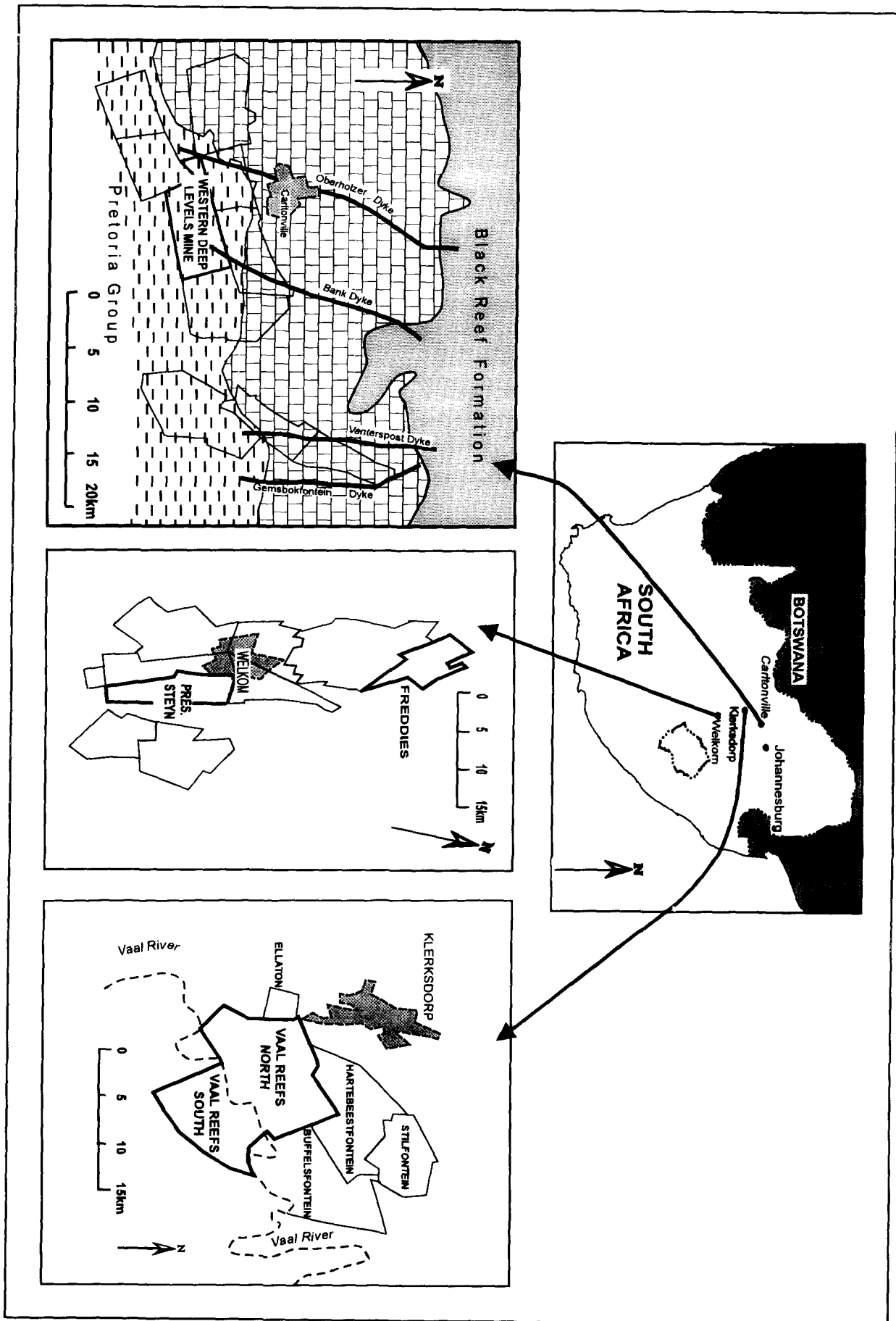


Figure 1b. Locality map for sampling points in the western Au fields of South Africa. Western Deep Levels Mine forms part of the West Wits Line of mines (including Vaal Reefs) while the Freddies and President Steyn mines are part of the Orange Free State field. Modified after Wolmarans (1986).

the commonest component of these waters) and dissolved gas 0.1% CO₂, 0.1% CO, 0.1% H₂, 6% He, 20% N and 73% CH₄ (Bekker, 1986). Groundwater on the other hand, flows mainly from east to west in the mines of the West Wits Line. Although transmissivity is low in quartzites the sediments are highly faulted (Wolmarans, 1986) which allows focussing of waters at depth and creates severe ingress problems for the miners. For example, an unprecedented volume of 1.6x10⁷ l hr⁻¹ poured into West Driefontein Mine at 874 m in October 1968. The accident was caused by failure of a hanging wall stope within a horst block below fractured and fissured dolomites of the Ventersdorp Supergroup (Wolmarans, 1986).

With the prospect of deeper Au mining to 5 km becoming a necessity in the Witwatersrand Basin, there is a growing need to define the extent and pervasiveness of fluids in mining areas, their role in rock-burst events and the mechanical properties of the rock, and for solution mining development. Currently, models that predict the fate of fluid flow in rocks cannot be addressed without first establishing the basic chemistry of the waters. Furthermore, one of the major questions addressed by economic geologists and geochemists over the last two decades has been the nature of the metal sulphide, dissolved organic matter and brine interaction in the production of stratiform Cu, Zn and Pb deposits. The controversy continues over the need to invoke one or two solutions for the migration of the trace elements and reduced S. Therefore, the measurement of trace elements in sulphidic brines may provide some insight into the role of brines in the behavior of metals under saline conditions. The complex mineralogy of the sediments within Witwatersrand Au mines (Au-U + Pb, Cu, Zn, Cr, Fe and other trace elements) together with interacting old brines and meteoric waters make the study pertinent to metal transport discussions.

GEOLOGICAL SETTING OF THE WITWATERSRAND BASIN AND STRATIGRAPHICAL COMPARTMENTS

The Witwatersrand Basin is an arcuate structural basin lying within the Kaapvaal Craton (Fig. 1a). The Witwatersrand Supergroup is divided into the Lower West Rand Group (WRG; 42,000 km², 7500 m in thickness) and Upper Central Rand Group (CRG; 10,000 km²; 2880 m in thickness), the former conformably overlies volcanics of the Dominion Group and non-conformably overlaps Archaean basement rocks of the Kaapvaal

Craton. The most prolific Au and U bearing placers in the Witwatersrand Supergroup lie within conglomerates located in the CRG. Pelites comprise up to 30% of the entire supergroup and even a greater proportion of the WRG (Wronkiewicz and Condie, 1987). The WRG represents shallow marine or intertidal environments while the CRG represents braided stream deposits that formed coalescing alluvial fans. Shales within the sequence can be useful indicators of provenance for the detrital components of the basin (Wronkiewicz and Condie, 1987, 1990) and likewise for the waters that traverse these lithologies.

The major element geochemistry of the shales (Wronkiewicz and Condie, 1987) is more variable than Phanerozoic shales compared with the NASC (North American Shale Composite). They are enriched in Fe and Al (especially the WRG) and are depleted in CaO, Na₂O, K₂O, TiO₂, K, Rb, Ba, Sr, U and Pb. Also, Nb and Hf are lower than NASC and most Phanerozoic shales. However, the Witwatersrand shales exhibit much higher Ni/Co ratios than most Phanerozoic shales. Shales in particular from the upper three groups are enriched in all transition metals compared to shales of the lower two subgroups. Cr, Ni and Co reach maximum values in the mid-CRG reflecting a greater contribution of mafic-ultramafic components from sources around the basin (Wronkiewicz and Condie, 1987). The large volume of quartzites and conglomerates in the succession demands plutonic sources be prevalent especially during deposition of the CRG. The occurrence of detrital uraninite, cassiterite, monazite, zircon and K feldspar in underlying Dominion Reef quartzites (Viljoen *et al.*, 1970) indicates that the granite sources must have been exposed to erosion prior to Witwatersrand deposition. Overlying the clastic sediments of the Witwatersrand Basin is the Ventersdorp Supergroup separated by the former Ventersdorp Contact Reef.

In southern Africa the mainly volcanic Ventersdorp (8 km in thickness) and siliclastic-carbonate Transvaal (12 km in thickness) Supergroups cover >200,000 km² and 500,000 km², respectively. The Transvaal pelites are characterised by >K than the Witwatersrand and appear to have more Zr, Hf and Nb in pelites relative to the Ventersdorp rocks, but about the same concentrations as the Witwatersrand shales. The Ni and Cr contents of the Ventersdorp pelites are similar to most Palaeoarchean southern African pelites such as the those in CRG; both granitic and komatiitic

Table 1. Mine sites in the Witwatersrand Basin, South Africa. Localities underground and abbreviations used in text.

Name of Au mine in Witwatersrand Basin	Sample No.	Locations underground	Depth (m)
Western Deep Levels	1	#2 Shaft, Level 120H	3400
	2	#2 Shaft, Level 81, return airway	2400
	3	#2 Shaft, Level 61	1800
	4	#1 Shaft, 87-49 roof-drive east	2000
Vaal Reefs Goldmine	5	#8 Shaft VR61, FE 52 cross-cut	1910
	6	10 Shaft 10/50	1050
Freddies Goldmine	7	#5 Shaft, 55w2 82 cross-cut east	2152
	8	#5 Shaft, 55w2 haulage north	2152
	9	#5 Shaft, 55 65 cross-cut east	2156
	10	#9 Shaft, 7-59-31-3-x/c, peg D4415	2308.3
	11	#9 Shaft, 7-59-2-1b x/c	2308
President Steyn Goldmine	12	No. 4 Shaft, 4 82x/c 98, x/c east peg 972	2980

sources appear to be present in the Ventersdorp rocks (Wronkiewicz and Condie, 1987, 1990).

Liebenberg (1955) presented the first detailed mineralogy of the Dominion Reef, the reefs of the Witwatersrand Supergroup, the VCR and the overlying Black Reef in detail. Recently more detailed studies have been made (Smits, 1994 and references therein) and a range of sulphides, sulpharsenides, kerogen, and other minerals have been identified. Unusual altered, Ti bearing, Zn bearing and unaltered chromites have been identified, which suggests some volcanic contribution to the reefs.

EXPERIMENTAL PROCEEDURES

Sampling sites

The purpose of the research was to characterize mine waters geochemically and integrate the concentrations of a range of inorganic elements, radiogenic isotopes and geology to construct a first order model for the origin of the fluids and compare them with other ancient cratonic areas. Four Au mines on the West Rand and Orange Free State Au mining areas (Western Deep Levels, Vaal Reefs, Freddies and President Steyn) were recognised to have localised "hot" water ingress at depth and were considered to be candidates for identification of palaeo-aquifers (Table 1, Fig. 1b). The mine staff helped in locating the largest and most dramatic water ingress sites prior to the sampling program. Miners had occasionally witnessed explosive release of hot water (up to 40°C) at depth when

the drilling bits penetrated compartments during normal development procedures, suggesting the existence of old geopressed water compartments which could now be identified by using ultra-trace element signatures and isotopic compositions.

Four samples are from Western Deep Levels (#2 Shaft and #1 Shaft) covering a sampling length from 1800-3400 m. Two samples of water are from Vaal Reefs Mine both sampled below 1000 m. Five samples from Freddies mine were collected, three water samples from #5 Shaft and two samples from #9 Shaft, below 2100 m. One sample is from President Steyn Mine (#4 Shaft) sampled at 2980 m (Table 1). The samples were collected underground with a large plastic syringe coupled to a Millepore fine (<0.45 micron) ashless filter paper. The samples were obtained from flowing roof boreholes, mining face boreholes and fractures associated with sub-vertical dykes. The water emanating from the fissure was allowed to pass through a 0.5 m tube prior to filtering to prevent bubbles in the water stream. Five hundred millilitres was filtered and acidified for major cations and 500 ml was filtered and acidified for major anions and ultratrace elemental analysis. The samples were acidified to 1% at site using ultrapure nitric acid (65%), sealed and refrigerated on return to the lab for future analyses.

Trace element analysis

A modified FISIONS P Qe (Plasmaquad "eclipse" mass spectrometer) was used for the trace element analyses. The analytical range for this

Table 2. Tabulated data for major, minor elements, trace elements and isotopic composition in mine waters

Element	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10	# 11	# 12
Be	13.1	20.1	17.7	9.6	7.1	0.2	0.2	8.7	6.9	4.1	5.9	5.8
Cr	63.4	36.2	24.7	17.3	67.9	0.5	0.5	4.5	11.7	6.7	14.9	173
Co	107.8	175.8	102	4.5	1	0.45	<0.08	<0.08	24.9	7.5	6.2	3032
Ni	2945	27	2.8	175	238	<0.08	0.22	4.3	417	189	157	6570
Cu	90.3	15.6	6.8	3.6	51	2.5	0.5	0.5	3.1	9.1	16.2	1041
Zn	45.6	19.5	9.3	3.2	149	14.4	0.5	0.5	0.5	11.1	<0.5	1511
As	413	41	18.5	34	90	0.5	0.5	9	531	0.5	33.4	29
Se	2638	77.6	11.5	250	1395	12.1	30	160	493	624	429	171
Cd	1.8	26.7	3.4	5.5	7.7	0.5	1.2	0.5	0.5	1.2	3.2	7.6
Pb	79.1	15	6	3.4	102	<0.06	3.74	0.88	<0.06	<0.06	<0.06	126.3
U	5	2.5	1.6	10.6	6.5	0.6	0.4	1.1	27.2	1.1	0.8	1160
Au	28	11.6	7.4	<0.06	30	43	22	8.9	8.9	4.8	<0.05	5.1
Ir	10.3	3.4	1.2	<0.05	7.6	9.9	3	4.6	15	3.1	<0.05	9.6
Fe	268	1680	247	358	469	1414	335	1425	9200	1470	548	3435
Nb	2.7	1.5	1.6	<0.05	18	1	<0.05	<0.05	12.4	<0.05	2.1	2.2
Hf	19	8.7	<0.05	<0.05	17.9	29.5	14.3	13	12.5	6	<0.05	0.6
Ti	290	107	60.5	59	111.5	46	30.4	40	188	84	120	533
Mn	1855	200	89	18	388	83	24	178	258	321	272	3759
Ge	<0.05	3.4	<0.05	17.5	35	5.1	<0.05	<0.05	28.3	34.1	27.2	276
B	520	420	480	1200	650	980	2170	2110	360	1850	2010	450
Al	335	116	89	262	186	176	138	103	82	280	268	182
Ca	16805	11.6	10	951	1235	0.87	16.7	18.1	724	989	753	658
Na	12490	501	367	1401	12175	242	664	688	3165	2643	2072	966
K	51	1	308	11.5	82	2.5	3.8	4	23	25	20	30
Mg	2.1	0.1	0.2	0.1	310	0.2	0.3	0.3	21	12	8.8	59.5
Ba	44882	180.4	57	3330	51392	31	57.3	51.1	435	8022	6359	58
Sr	745	0.5	0.4	22.7	96.2	0.1	0.5	0.5	26.2	52.5	39.3	5.4
Rb	0.006	0.002	0.007	0.042	0.125	0.0002	<0.01	0.0003	0.003	<0.06	<0.05	0.075
⁸⁷ Sr/ ⁸⁶ Sr	0.740348	0.740856	0.747479	0.753334	0.741625	0.725055	0.735347	0.735071	0.734761	0.767247	0.769359	0.733371
TOC	24.5	21.5	24.3	11.9	15.8	43	17.7	18.8	16	11	12	14
Cl ⁻	1420	140	135	3980	560	260	1000	1030	145	6800	5180	60
SO ₄ ²⁻	200	900	760	270	20	20	20	20	20	20	20	540

Data produced by ICP-MS, ICP-AES/GFAAS, Micromass MM30 MS and VG 354 MS. Elements in $\mu\text{g l}^{-1}$ concentrations except the following which are in mg l^{-1} : SO₄, Cl, TOC, Rb, Sr, Mg, K, Na, Ca, Al.

mass spectrometer being 0.001–1 mg l⁻¹. Higher concentrations may be determined through sample dilution. The precision was tested measuring the mass calibration elements in standard solutions made in deionised water and also with reference water standard NIST 1643c prepared by the US Geological Survey. Detection limits for a test solution of Be-Al-Co-In-Pb-Bi-U are >0.05 µg l⁻¹. Results indicate that the precision expressed as coefficient of variation is in the range of 2–10%. A peristaltic pump was used for sample delivery (Gilson Minipuls 3) and the flow rate was optimised to plasma stability. Certified nitric acid was used for blanks and samples. The samples collected in this study were analysed in the EU's Joint Research Ispra site, Italy in 1995.

A Perkin-Elmer 5500 ICP-AES was used for determining Mn, Ca, Mg, B, Na and K concentrations in the waters (Al and Fe were determined by GFAAS). The carrier gas for the ICP-AES was Ar (99% pure). A Dionex DX 100 ion chromatograph was used for determining the Cl⁻ and SO₄²⁻ concentrations. Samples were diluted X10 prior to analysis. Both instruments are housed at the Joint Research Centre at Ispra (Italy). Table 2 contains the trace, Sr isotope, anion and cation data.

Total organic carbon analyses

Samples were analysed for total organic carbon (TOC) as follows. A Maihak (Hamburg) TOC thermal oxidation analyser was used for the analyses. Potassium hydrogenphthalate standard solution was used to complete a calibration curve for 5, 10 and 20 mg l⁻¹ prior to water analysis. The sample was continuously drawn by the instrument stripping firstly the inorganically bound C. After sparging, the sample is then passed into the thermal reaction furnace controlled at approximately 850°C. Carbon dioxide resulting from the combustion of the organic pollutants in the sample is delivered in a carrier gas stream to an infrared gas analyser.

⁸⁷Sr/⁸⁶Sr analyses

Ten millilitre aliquots of water were extracted from the bulk samples and spiked with ⁸⁴Sr in the geochronology laboratory of the Bernard Price Institute for Geophysical Research, (Johannesburg). Strontium was extracted from the water samples with standard cation resin ion-exchange techniques using 2.5 n HCl. Rubidium and strontium concentrations were performed on a Micromass 30 mass spectrometer. The Sr isotopic ratio was obtained

Table 3. δ¹⁸O and δD values for analysed waters.

Sample	Location	δ ¹⁸ O	δD
D1	WDL	-10.4	-22
D2	WDL	-3.1	-22
D3	WDL	-3.1	-23
D4	WDL	-5.8	-31
D5	Vaal Reef	-7.7	-41
D6	Vaal Reef	-4.4	-31
D7	Freddies	-5.2	-39
D8	Freddies	-6.5	-38
D9	Freddies	-5.0	-34
D10	Freddies	-5.7	-37
D11	Freddies	-6.2	-38
D12	Pres. Steyn	+4.5	+39

on a VG 354 thermal ionization mass spectrometer using a triple collector peak-hopping routine. Repeated runs on SRM 981 were well within the range with precision on runs from ±0.002% to 0.004%, 2σ mean.

Stable isotope procedures

Oxygen isotope ratios of the waters were determined by the standard method of equilibrating about 3 ml of water with CO₂ at 25°C, analysing an aliquot of the equilibrated CO₂, and calculating the O isotope ratio of the water assuming a value of 1.0412 for α_{CO₂-H₂O}. Hydrogen isotope ratios were determined by Professor Verhagen (University of Witwatersrand) using methods published elsewhere (Verhagen 1984). Both O and H isotope data are expressed in δ notation where δ = (R sample / R standard - 1) × 1000, and R is the ¹⁸O/¹⁶O or D/H ratio (Table 3). The data are expressed relative to the SMOW scale to which they were referenced using the SMOW and SLAP standards. The data were normalised such that SLAP gave -55.5‰ relative to SMOW as recommended by Coplen *et al.* (1983).

ISOTOPE HYDROLOGY

Samples from Western Deep Levels have ⁸⁷Sr/⁸⁶Sr ratios that are very radiogenic (see Table 2) showing a trend of less radiogenic compositions with depth in #2 Shaft (from 0.7475 to 0.7404). The sample from #1 Shaft is the most radiogenic of the Western Deep Levels group (0.7533). Freddies Mine ⁸⁷Sr/⁸⁶Sr ratios show a range from 0.7351 to 0.7694 (Table 2) with the samples from #9 Shaft being

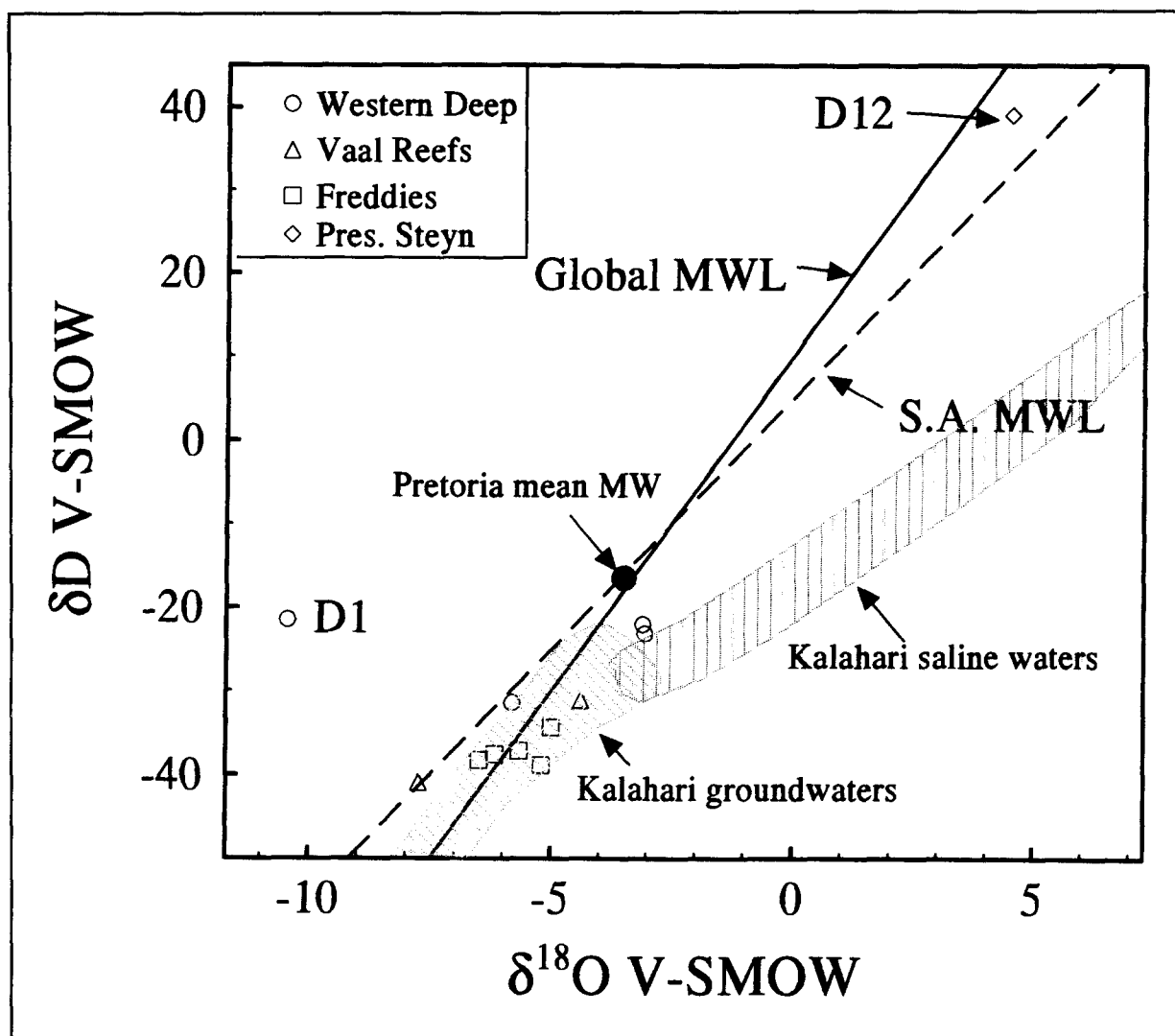


Figure 2. δD versus $\delta^{18}O$ for water samples. Global meteoric water line and local meteoric water line (Mazor and Verhagen, 1983) are also shown. The field for Kalahari saline waters is from Verhagen (1984) as is the value for Pretoria meteoric water

the most radiogenic samples from any mine (>0.7500). The Sr/Ca ratios follow the same trend increasing with depth in #5 Shaft and showing a sharp increase within #9 Shaft. The single sample from President Steyn has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7333 and is one of the lowest values obtained.

The stable isotopes (Table 3) reveal a similar linear relationship but with some anomalous samples evident. Figure 2 shows that with the exception of two samples, the analysed waters lie close to the meteoric water line. The exceptions are D1 (Western Deep Levels) which lies well to the left of the Meteoric water line, and D12 (President Steyn) which has very high (positive) δD and $\delta^{18}O$ values although it lies close to the extension of the meteoric water line. The main group of samples which lie close

to the meteoric water line are all depleted in ^{18}O and D relative to average Pretoria meteoric water (Fig. 2). It is therefore possible that the samples represent meteoric water falling at higher altitudes than in Pretoria, and therefore isotopically lighter. Alternatively, the samples could represent "old" water precipitated during colder climates. A combination of these two effects could easily produce waters which are isotopically lighter than typical Pretoria meteoric waters. Note that the spread of values corresponds quite closely to the field for groundwaters from the southern Kalahari (Gordonia) region (Verhagen, 1984).

There are no obvious systematic isotope differences between the waters collected at the different mines. The samples from Freddies form a tight cluster but it should be noted that these

were collected from a fairly narrow depth range (2152-2308 m depth). The two anomalous samples require further explanation. The isotopically heavy sample D12 can most easily be explained by evaporation of water vapour from an original water having an isotopic composition similar to the bulk of the analysed samples. Since evaporation is a complex process that may be controlled by a number of variables (e.g. Merlivat and Jouzel, 1979), it is necessary to consider both the kinetically controlled evaporative loss of water molecules and the equilibrium isotope exchange of water vapour and liquid surface (Welham, 1987). Figure 2 shows the trend for Kalahari saline waters which are interpreted as an evaporation trend (Verhagen, 1984). The Kalahari trend has a less steep gradient on Fig. 2 than the meteoric water line, and this type of array is characteristic of regions with low relative humidity and high daily temperatures (Welham, 1987, p141). That sample D12 is close to the meteoric water line is indicative that the evaporation must have taken place in conditions of very high humidity such as would be experienced at great depths in South African Au mines. Simple calculations assuming Equilibrium Rayleigh separation of water and vapour indicate that about 70% evaporation of water having $\delta^{18}\text{O}$ and δD values of -5% and -30%, respectively, could produce the isotope composition of sample D12.

The large deuterium excess of sample D1 (i.e. it lies above the meteoric water line) is most likely to have been caused by either isotope exchange with surrounding rock, or by hydration. Relatively low temperature exchange with carbonate or silicate rocks would shift the $\delta^{18}\text{O}$ value of the water to lower values without significantly affecting the δD values of the fluid (there being no H in the rock to exchange with). The relatively large shift in $\delta^{18}\text{O}$ value would imply low water-rock ratios. This mechanism seems unlikely because of the lack of susceptibility of the host quartzites to isotope exchange at temperatures less than 100°C. It is more likely that hydration of, for example, Ventersdorp lava produced the shift to lower $\delta^{18}\text{O}$ values. In this mechanism, ^{18}O is preferentially taken up by the lavas during hydration leading to a depletion in the remaining fluid. Again low water/rock ratios are necessary for such a large shift in water $\delta^{18}\text{O}$ to have occurred.

HYDROCHEMISTRY RESULTS

Western Deep Levels TOC values have a wide range (11.8-24.5 mg l⁻¹) with the lowest value

occurring in #1 Shaft. Ca-Mg-Na with Ba increase with depth from 1800 m to 3400 m in #2 Shaft. In Vaal Reefs mine the TOC values are 15 and 43 mg l⁻¹ (#10 Shaft), the highest for all the waters sampled. Selenium correlates with K and Ni/Co. In Freddie's Mine, TOC values decrease with depth in #5 Shaft and are lower still in samples from #9 Shaft (from 17.7 mg l⁻¹ to 10.9 mg l⁻¹). Ca-Mg-Na-Ba concentrations increase with depth within #5 Shaft and a sharp increase in concentration is apparent within #9 Shaft. B-Al pairing shows a decreasing trend within #5 Shaft and a sharp but parallel increase again in #9 Shaft. Uranium increases with depth in #5 Shaft and tapers off again to lower values in #9 Shaft. Au-Hf go from higher values in #5 Shaft to lower values with depth and towards the fractures in #9 Shaft while Se shows an equal but opposite trend. Copper also correlates positively with Se. Uranium increases with depth in #5 Shaft and tapers off in #9 Shaft. Titanium follows the trend. Manganese increases with depth in #5 Shaft and towards the fractures in #9 shaft. Potassium increases also with depth in #5 Shaft and carries on increasing towards #9 Shaft. Chloride concentrations are variable with the highest values >6000 mg l⁻¹ in #9 Shaft at 2308 m depth and the SO_4^{2-} values are all <20 mg l⁻¹ (Table 2).

President Steyn TOC values (14 mg l⁻¹) are approximately average for the mines but the concentration of Cr, Co, Ni, Cu, Mn, Pb, Cd, Ti, U and Ge are an order of magnitude greater than the other mine waters sampled. Ca-Mg-Na-K concentrations are similar to Freddie's #9 Shaft. Aluminium is again high similar to Freddie's #9 Shaft. The Ba concentration is similar to #5 Shaft. The Cl⁻ concentration (600 mg l⁻¹) is amongst the lowest of the waters analysed while the SO_4^{2-} value (540 mg l⁻¹) is the second highest concentration of the group.

PRINCIPAL COMPONENT ANALYSIS

Principal component analysis (PCA) was used to identify possible links in the aquifer chemistry and to identify the variability in the data. An advantage of this type of statistical treatment is that only a small number of principal components (PCs) are usually required to represent most of the information in the data. The other uses of PCA on the water data are to identify common categories of elements and to highlight connections to each of the aquifers. Since minor PCs contain most of the random error in the data, eliminating them from further discussion tends to remove extraneous variability in the data.

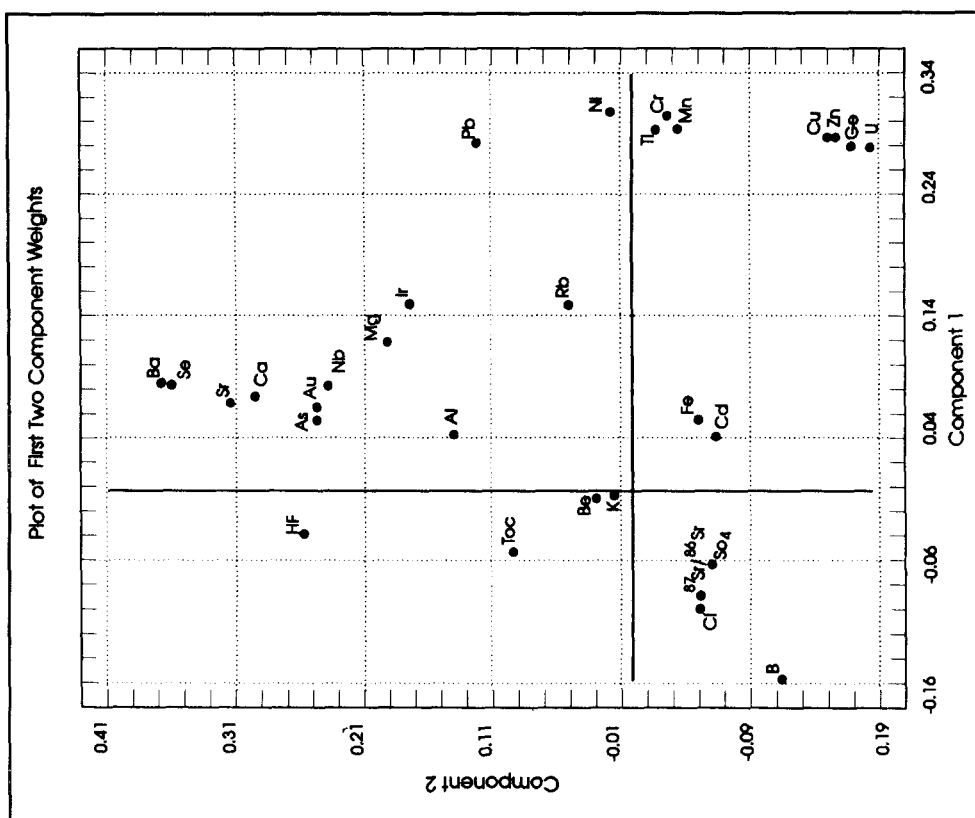


Figure 4. Plot of first two Principal Components for data set in table 3.

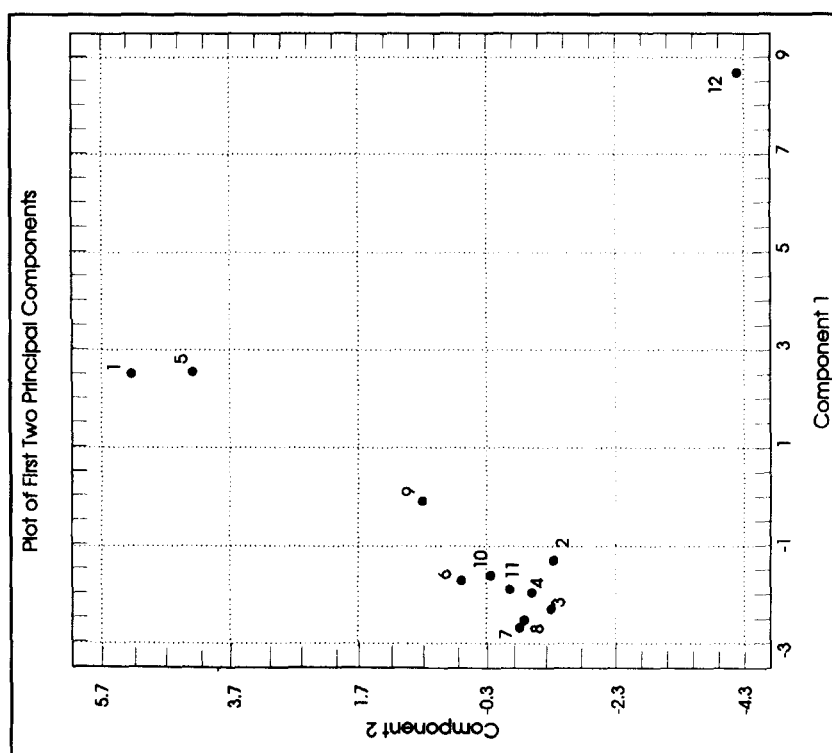


Figure 3. Plot of Principal Component Analysis for the 12 sites samples. Site numbers are explained in Table 1.

Pearson Correlation regression analysis was applied firstly and established the presence of 3 major element groups. The group showing the highest correlation are Cr-Co-Ni-Cu-Zn-Pb-U-Ti-Mn-Ge ($r > 0.8$). The second group is Ir-Fe-As-Nb-Au with a negative correlation ($r > -0.5$) between Ir-Cl-B- $^{87}\text{Sr}/^{86}\text{Sr}$ and a third group ($r < 0.8 > 0.6$) being Se-Al-Ca-Na-Ba-Sr-Pb-Au. Using PCA (Fig. 3) it is noted that the President Steyn water sample accounts for most of the variability on Component 1 while sample #1 from Western Deep Levels and Vaal Reefs #5 account for most of the variability in the second component. Samples #2, #3 and #4 (Western Deeps) and samples #6 (Vaal Reefs), and #8, #10 and #11 (Freddies) account for less than 10% variability in the data.

PCA on the 12 sets of 32 variables reveals that the first 3 principal components account for more than 60% of the variability of the data (Fig. 4). This group U-Ge-Zn-Cu-Mn-Cr-Ti-Ni-Pb weighs heavily on Component 1 while Ba-Se-Sr-Ca-Au-As-Nb-Mg-Ir weighs heavily on Component 2. From Fig. 4 it is apparent that B-Cl-SO₄- $^{87}\text{Sr}/^{86}\text{Sr}$ -Cd-Fe account for little if any variability in the data and are negatively correlated with those elements in group 1.

Discussion

The waters sampled in deep mines in the Witwatersrand basin can be considered $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$ low salinity brines. Thus processes responsible for enriching waters in some trace elements and depletion in others with respect to seawater occurring in rocks deeper than 1900 m in the Witwatersrand Basin appear to be common to Precambrian cratons (Green and Canfield, 1984).

The B concentration of the waters is lower than reported for the Canadian Shield waters (Bottomley *et al.*, 1994) but the shield waters have a lower concentration (maximum of 2170 $\mu\text{g l}^{-1}$) relative to seawater (4.5 $\mu\text{g l}^{-1}$). The B concentrations of the waters range from 360–2170 $\mu\text{g l}^{-1}$. The WDL samples have a mean value of 655 $\mu\text{g l}^{-1}$, Vaal Reefs 815 $\mu\text{g l}^{-1}$, Freddies 1700 $\mu\text{g l}^{-1}$ and President Steyn 450 $\mu\text{g l}^{-1}$. Low B concentrations have been invoked to suggest B-stripping from waters through adsorption on clays (Stueber *et al.*, 1993; Spivack *et al.*, 1987) which can be found on surfaces in highly fractured host rock where B is readily leachable. In permeable zones (e.g. Western Deep Levels is bounded east and west by the Oberholzer and Bank dykes; Fig. 1b) fractures containing clay gouge will not readily promote leaching and

flushing of B and descending waters will tend to be depleted.

The origin of high water salinity in basement aquifers is presently explained by subsurface dissolution of evaporites, infiltration of subaerially evaporated seawater, leaching of fluid inclusions, or any form of rock sulphate or saline fluids trapped in crystalline basement (see Fontes *et al.*, 1989). The Witwatersrand stratigraphy consisting of intercalated sediments and volcanics capped by Precambrian dolomites containing evaporites could have provided the salinity via fractures extending to the basin-basement contact e.g. in Western Deep Levels gold mine. Alternatively, the fluid inclusions of the basement granites may have been leached by circulating groundwaters as suggested for other Precambrian areas (see Fontes *et al.*, 1989) but alternative sources are worthy of discussion.

The Sr isotope ratio is strictly controlled by rock-water interaction and is not complicated by atmospheric sources or meteoric input into the mines. Waters in contact with the basement rocks should be higher than waters in contact with mafic igneous rocks such as those that occur in the Bushveld Igneous Complex. The extremely radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ nature of the waters in this study suggests a complex mixing behavior. The marked enrichment in Ca and Sr relative to evaporated seawater ($\text{Ca} \sim 410 \text{ mg l}^{-1}$ and $\text{Sr} \sim 8 \text{ mg l}^{-1}$) is typical of saline fluids from many sedimentary basins (Land and Macpherson, 1992) and requires significant fluid-rock interaction. The relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 5a) indicate that this interaction predominantly involved K-feldspar or silicate clay minerals in the rocks of a granitic detritus. In any case this would be expected from the long-term residence of these fluids in the Witwatersrand Basin.

On the other hand a proportion of the highly radiogenic nature of the waters could have been inherited from minerals within the Ventersdorp and Transvaal Supergroup supracrustals as highly radiogenic Sr signatures in carbonate minerals have been reported over a wide area of the Kaapvaal Craton (Duane *et al.*, 1991). Figure 5b presents the data in a $^{87}\text{Sr}/^{86}\text{Sr}$ - $1/\text{Sr}$ diagram in order to show possible mixing relationships. Possible end-members for the two components could be:

(i) $^{87}\text{Sr}/^{86}\text{Sr} = 0.7251$, Sr concentration = 0.12 mg l^{-1} from a Vaal Reefs compartment and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7694$, $\text{Sr} = 39.3 \text{ mg l}^{-1}$ from a Freddies compartment; and

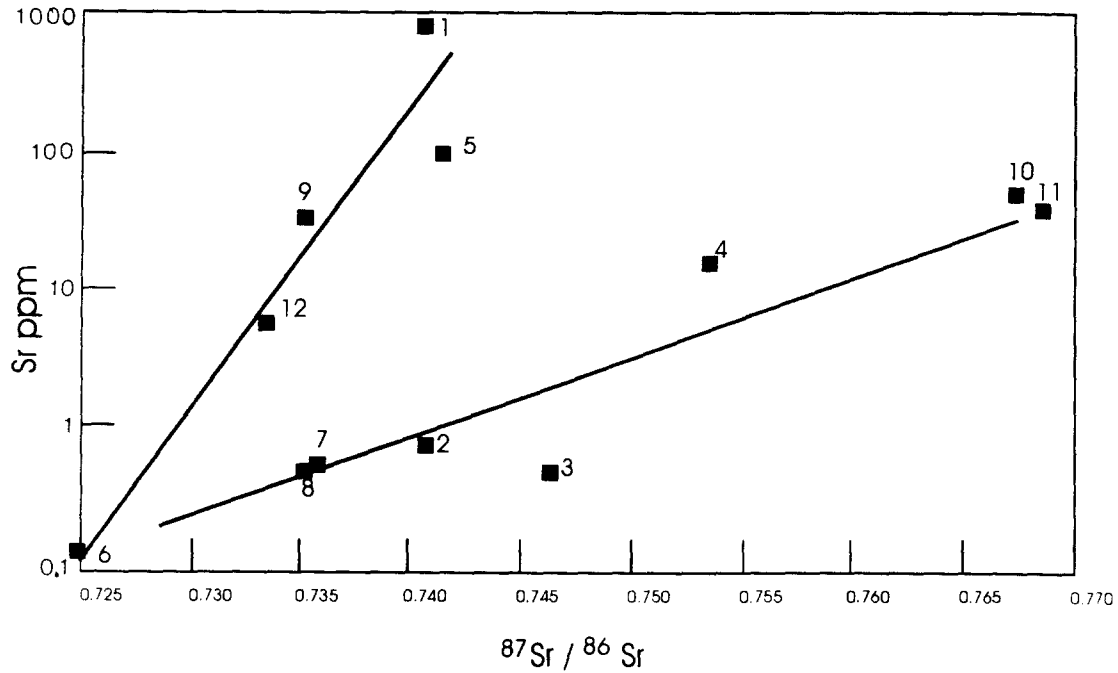


Figure 5(a). $\text{Sr-}^{87}\text{Sr}/^{86}\text{Sr}$ plot for 12 mine waters. Two "mixing" lines are apparent but disturbed by mining excavations. See text for discussion 1, 2, 3 and 4 = Western Deep Levels mine; 5, 6 = Vaal Reefs, 7, 8, 9, 10 and 11 = Freddies mine and 12 = President Steyn mine.

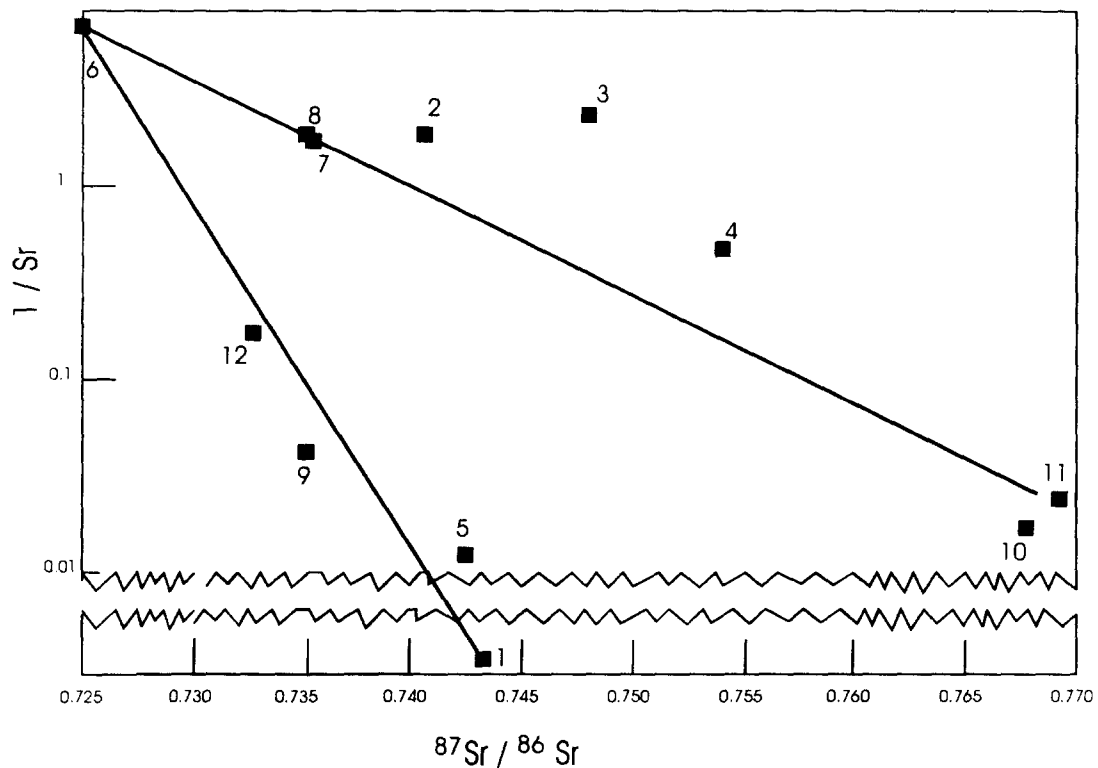


Figure 5(b). $1/\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ plot for 12 mine waters. Two mixing lines are shown suggesting 2 sources for the ^{87}Sr in mine waters but the common low end-member reflecting the regional significance of the Transvaal Dolomites. 1, 2, 3 and 4 = Western Deep Levels; 5, 6 = Vaal Reefs, 7, 8, 9, 10 and 11 = Freddies mine and 12 = President Steyn mine.

(iii) $^{87}\text{Sr}/^{86}\text{Sr}=0.7251$, $\text{Sr}=0.12\text{ mg l}^{-1}$ with a $^{87}\text{Sr}/^{86}\text{Sr}=0.7404$, $\text{Sr}=745\text{ mg l}^{-1}$ from Western Deep Levels. The Rb contents of the brines are very low ($\ll 1\text{ mg l}^{-1}$), implying that it is quickly incorporated into secondary minerals (clay or micas) and does not migrate far in the system.

There is an overall tendency of the isotope ratios to increase with increased Sr content and more significantly, the large variability within the Sr concentrations at WDL does not appear to have affected the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Since both mixing trends have a common end-member with low Sr (0.12 mg l^{-1}) and the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio this common end-member assumes an important regional role for the mines. The only surface "reservoir" of low Sr (and high unsupported radiogenic Sr compositions) is the Transvaal dolomite (Duane *et al.*, 1991).

The radiogenic Sr compositions agree with other studies in Archean and Proterozoic terranes (Frape *et al.*, 1984). Also the mineralogy of typical Archean terranes has some influence on the availability of Sr and Rb to migrating brines. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of any Rb bearing mineral will increase with time while that of Rb free mineral will not. Therefore, it is important to evaluate the role different minerals might have played in the formation of the Sr isotope composition of the mine waters.

Muscovite, biotite, plagioclase, K feldspar, albite, diopside and anorthite are common rock-forming minerals that contain significant amounts of Rb and/or Sr. The relative Rb/Sr ratios and typical present-day $^{87}\text{Sr}/^{86}\text{Sr}$ values of the minerals for a 2.7 Ga Archean rock have been calculated by McNutt *et al.* (1990) and can vary over a wide range. K-feldspar would have the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of between 0.730-0.800 and albite 0.710-0.725. The waters in contact with basement rocks which are the footwall to the metasediments at Western Deep Levels and Freddie's Au mines would therefore be expected to have high values since these granites are typically 2-feldspar, mica and quartz. Both muscovite and biotite have high Rb/Sr ratios and therefore would lead in time to high $^{87}\text{Sr}/^{86}\text{Sr}$ values, but these are not major components of typical basement rocks but rather the shales in the basin.

McNutt *et al.* (1984) and Fritz *et al.* (1987) proposed that the Sr signature in brines reflects water-rock interactions followed by mixing of waters of diverse origin. The strong correlation between Sr and Ca in the Witwatersrand samples ($r=0.9971$) suggests that Sr is a tracer for Ca in these "older" waters. The brines however vary in Sr concentration but since meteoric waters

have very low Sr contents in general (McNutt *et al.*, 1990), the influence of shallow aquifers is not immediately apparent from the isotope chemistry. If the host rock is mafic in composition e.g. diabase dykes etc., then the mineral phases that control the Sr are plagioclase and clinopyroxene, both with low Rb/Sr ratios. Therefore, since the waters are often focussed in faults on the West Wits Line within and adjacent to basic dykes the influence of the low Rb/Sr expected in these rocks appears not to have influenced the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ of the waters. This implies further that the residence times in the faults is rather short and their role would only be as temporary pathways for the fluids.

The literature gives limited information on the concentrations and speciation of Be in waters. Beryllium concentrations have been measured in mine waters and can be $10\text{ }\mu\text{Molar}$ in some mineral and mine waters with high fluoride contents (see Vesely *et al.*, 1989). Samples from one locality in Vaal Reefs and Freddie's Mines have the lowest concentration ($< 1\text{ }\mu\text{g l}^{-1}$) while the highest values occur in President Steyn gold mine. The solubility of Cr in water is low and the high correlation between Cr and Ti ($r=0.9$) and Cr with Ge ($r=0.88$) at least suggests a common source in heavy minerals with the conglomerates. As yet there appears to be no transport mechanism for such elevated concentrations of Cr in low temperature brines.

Germanium concentrations within the Witwatersrand samples have a wide range from below detection limit to $> 270\text{ }\mu\text{g l}^{-1}$. In geothermal waters the range is expected to be $2\text{--}30\text{ }\mu\text{g l}^{-1}$ (Arnorsson, 1984) which is an order of magnitude lower than the brines in the Kaapvaal Craton. Minerals that contain Ge are rare in nature but it is most concentrated in the least linked silicate structures. According to Harris (1954), olivine phenocrysts in acid glasses contain $1.5\text{--}3.4\text{ mg g}^{-1}$ Ge, whereas feldspar phenocrysts contain less than 1 mg g^{-1} . In hydrothermal deposits Ge is concentrated in sulphides (up to 10 mg g^{-1} in pyrite) and concentrations run in tens to hundreds of mg g^{-1} in several other sulfide minerals (see references in Arnorsson, 1984). The average concentration of Ge in fresh basalt and gabbro in Iceland was found to be 1.3 mg g^{-1} (Arnorsson, 1984) but the ratio of Ge to silica is 5-50 times higher in geothermal waters than in the associated rocks. Boiling of water as it ascends through the volcanic pile appears to favour dissolution. In the Witwatersrand samples the extreme range in concentration cannot be accounted for by such mechanisms but in the absence of

speciation experiments one cannot say for sure what the mechanisms of extraction under acid mine conditions were operative for minerals such as pyrite (Sullivan and Yelton, 1988). Certainly the ubiquitous presence of quartz in the conglomerates must imply some association of Ge with the arenites.

Gold on the other hand has been more widely studied in waters especially in relation to Au-organic matter associations. The Vaal Reefs sample (10/50; #10 shaft) has the highest concentration of Au ($43.1 \mu\text{g l}^{-1}$), which correlates positively with Ir, Hf and TOC. Humic substances have been shown to aid in the distribution of Au in weathering situations (Bowell *et al.*, 1993) and the suggestion may have application to Ir and Hf as well. Benedetti and Boulegue (1991) have studied the transport of Au in the supergene environment and have noted strong enrichments with Au for Zn, Cd and Sb as water percolated through the sulphide oxidation zone. Gold solubility may be controlled by $\text{Au}(\text{HS})$ and $\text{Au}(\text{HS})_2^-$ in reducing environments because the dissolved reduced sulphur species are high promoting the growth of organic ligands. Benedetti and Boulegue (1991) argue that in underground aquifers leaching Au-rich sulphides, the dispersion of Au could be efficient as long as excess oxygen is not available to destabilize the organic Au complexes.

The source of the Ir in the Witwatersrand samples is a mystery except to restate the findings of Byerly and Lowe (1994) that Ir contents of some of the Barberton Greenstone Belt rocks have up to 200 ppb Ir. The occurrence of mafic greenstone remnants in the Witwatersrand Basin could well be responsible for the high Ir concentrations of the brines in this study.

Typical mean concentrations of the soluble form of Mn found in natural waters is $5 \mu\text{g l}^{-1}$ (Balikungeri *et al.*, 1985). In this study the highest values are found in President Steyn gold mine and at 3400 m in Western Deep Levels gold mine. Values increase exponentially with depth in WDL with a low value of $18 \mu\text{g l}^{-1}$ disrupting the trend.

Calcium, Na, Ba and Sr are positively correlated which can be related to chemistry in the Precambrian dolomites present in the stratigraphy. Niobium is widely distributed in nature and has been detected in clays, soils, rocks and freshwater in concentrations ranging from $2\text{--}150 \text{ mg g}^{-1}$ in igneous rocks, and $0.02\text{--}6.3 \text{ mg g}^{-1}$ in meteorites (see references in Abbasi, 1988). The values in the Witwatersrand samples are generally low (less than $3 \mu\text{g l}^{-1}$

except in Vaals Reefs at 1910 m ($18 \mu\text{g l}^{-1}$) and in Freddie's at 2165m ($12.4 \mu\text{g l}^{-1}$). Nb-Au ($r=0.79$), Nb-Mg ($r=0.8$) suggests a common origin and mobility behaviour in saline waters but little is published on the matter as yet.

Boulegue (1978) has argued that a high percentage of the dissolved Cu present in anoxic waters, including brines, should be Cu^+ . This is important since Cu^+ forms strong chlorocomplexes as well as very strong polysulfide and organosulphur complexes. Jacobs and Emerson (1982) and Boulegue *et al.* (1982) have suggested that Cu^+ , Zn^{2+} , Au^+ and Pb^{2+} should form strong complexes with sulphur ligands. Therefore, high concentrations of the sulphur species could enhance the solution of Cu^+ , Zn^{2+} and Pb^{2+} in sulphidic brines. There does not appear to be strong correlations between metals and the TOC values in the mine waters suggesting that these metals are associated with sulphides rather than organic matter. The exceptions are Au-Ir-Hf where a peak value of 46 mg l^{-1} . TOC correlates with high Au ($43 \mu\text{g l}^{-1}$), Ir ($9.9 \mu\text{g l}^{-1}$) and Hf ($29.5 \mu\text{g l}^{-1}$) in Vaal Reefs water samples. The source for all metals and TOC may be the Ventersdorp Contact Reef which is particularly endowed with organic matter and base metal sulphides (pyrite, pyrrhotite, galena, sphalerite and chalcopyrite; Zhao *et al.*, 1994). On closer statistical treatment of the data of Henckel and Schweitzer (1994), who studied the geochemistry of the VCR, it becomes apparent that like the water chemistry presented here certain element groups are highly correlated. Cu-Ni-Co-U-Au, B-Rb-MgO and Mn-Zn-Ca define strong chemical groupings which can be related back to the mineralogy of the reefs.

There is no apparent relationship established between Cl^- and SO_4^{2-} (Table 2), but there are positive correlations between SO_4^{2-} and Cd ($r=0.7$) in samples from WDL and President Steyn gold mine. Beryllium, Co, Cu, Zn, Cd, Pb, Ti and Mn increase sympathetically with depth in three samples from WDL. The trend is continued in President Steyn gold mine and suggests the presence of sulphidic brines, probably products of pyrite weathering in the Au-bearing reefs. Ni/Co ratios and Se correlate again suggesting a common source in sediments of the basin. Sulphides are common in the reefs (>5%) and the passage of warm saline waters could strip the sulphides of the inorganic fractions during long residence times. The source of the metals and the S is different for Vaal Reefs and Freddie's mines, where the organic-

rich Ventersdorp Contact Reef probably provides the metals, organic C and Au to the waters.

The Cl concentrations of the mine waters range from 140 to 6800 mg l⁻¹. The brines show a strong positive correlation between Cl⁻ and ⁸⁷Sr/⁸⁶Sr ($r=0.8857$) and a weak negative correlation ($r=-0.5$) with TOC, again reinforcing the idea that the Transvaal carbonates are important sources of radiogenic Sr. Within WDL there is a gradient towards higher values with depth which agrees with most of the trace element trends and suggests that they were added during the mining process when fluids interacted with carbonates on descent.

Significant microcracking of granitic rocks begins above 70–75°C (Kranz, 1983) and temperatures such as these are not unknown in deep mines. The positive correlation trend between Al and Cl ($r=0.67$) suggests again contact with feldspar rocks and a possible mixing trend of a more saline water with dilute meteoric water. All of these constituents that plot in a well-behaved positive trend with chloride imply that a process has the same chemical signature regardless of the total dissolved solids or location above the granitic basement. Magnesium and K on the other hand are independent of Cl⁻ and this relationship appears typical of fluids that have gained salinity through long residence times within or close to Archean basement (McNutt *et al.*, 1990). Ground waters from the Canadian Shield and the Witwatersrand Basin lying within the Kaapvaal Craton of southern Africa have chemistries common to Precambrian basement aquifers. In Fig. 6a, b the Na/Ca-Mg/Ca and Ca-Mg-Na-K characteristics of the Canadian Shield, Witwatersrand samples and mid-continental US waters are compared. The Witwatersrand mean Na/Ca ratio is similar to the Ontario region of Canada and the Mg/Ca is similar to the Yellowknife region reflecting the Archean and Proterozoic signatures of the rocks. It is interesting to note the inverse relationship between Na/Ca and Mg/Ca values reflecting the regional nature of the equilibration processes and

supporting the major role of plagioclase feldspar in the generation of the brines. For Sudbury, Keeweenaw and Witwatersrand (mean) the ratios are antithetic. Potassium is approximately 50 mg l⁻¹ and the Witwatersrand average closely agrees with Thompson (Manitoba), Keeweenaw. Potassium closely follows the Na concentrations in all cases (Fig. 6c). The lower B values in the Witwatersrand mine waters are in contrast with the Canadian Shield waters (Bottomley *et al.*, 1994), suggesting differences in basement structure and petrology between the cratons (i.e. metamorphic versus granitic provenances).

CONCLUSIONS

It is now common knowledge that major horizontal fracture zones are present at depths of several kilometres in crystalline rocks which are capable of producing large volumes of saline waters (Emmermann *et al.*, 1991). Chemical modification of originally meteoric water by both surface infiltration and deep mining conditions (humidity) occurs in the Witwatersrand Basin. Infiltration through the cover and basement rocks of the Witwatersrand Basin occurred along dykes and faults that changed the original waters to a brine composition. The processes responsible for producing relatively high ⁸⁷Sr/⁸⁶Sr values may have integrated Sr that was incorporated during a long migration history, predominantly from reactions with clays and feldspars in the Precambrian basement, and subordinately from carbonates. The slow migration of a brine across a thick (8 km) succession of quartzites, conglomerates, shales and carbonates may have provided a setting for ionic exchange between the brine and minerals in the rocks, thereby enriching the brine in Ca, Sr, ⁸⁷Sr and various heavy metals. The evolved brine may then have mixed with dilute meteoric waters in the sediments during mining operations occurring over 100 years duration, which may account for the disturbed mixing trends noted in the isotopic Sr plots. The release of brines stored in

Figure 6(a). Na/Ca and Mg/Ca plots for Canadian Shield and Witwatersrand mines. Extreme values are evident for Vaal Reefs and Western Deep Levels samples while the remainder are similar to the Canadian brines (data for Canadian Shield taken from Fritz and Frapé (1982), White, *et al.* (1963). (1 = Yellowknife, 2 = Thompson, 3 = N.W. Ontario, 4 = Sudbury, 5 = Keeweenaw, 6 = saline waters from Missouri, 8 = Kansas oilfield brine). Remaining 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 and 21 = 12 waters from Witwatersrand basin (and 9 = mean of waters), 22 = seawater (source: see references in Banner, *et al.*, 1989; Chaudhuri *et al.*, 1987).

Figure 6(b). Ca-Mg plot for water samples from Canadian Shield, Witwatersrand (mean), saline water in mid-continental USA, oilfield water and seawater (source: Banner *et al.*, 1989). Na-K plot for saline systems from Canadian Shield (1 = Yellowknife, 2 = Thompson, 3 = N.W. Ontario, 4 = Sudbury, 5 = Keeweenaw, 6 = saline waters from Missouri, 8 = Kansas oilfield brine). Remaining 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 and 21 = 12 waters from Witwatersrand basin (and 9 = mean of waters), 22 = seawater (source: see references in Banner *et al.*, 1989; Chaudhuri *et al.*, 1987).

Figure 6(c). Similar plot as 6a, b but with Na and K concentrations only.

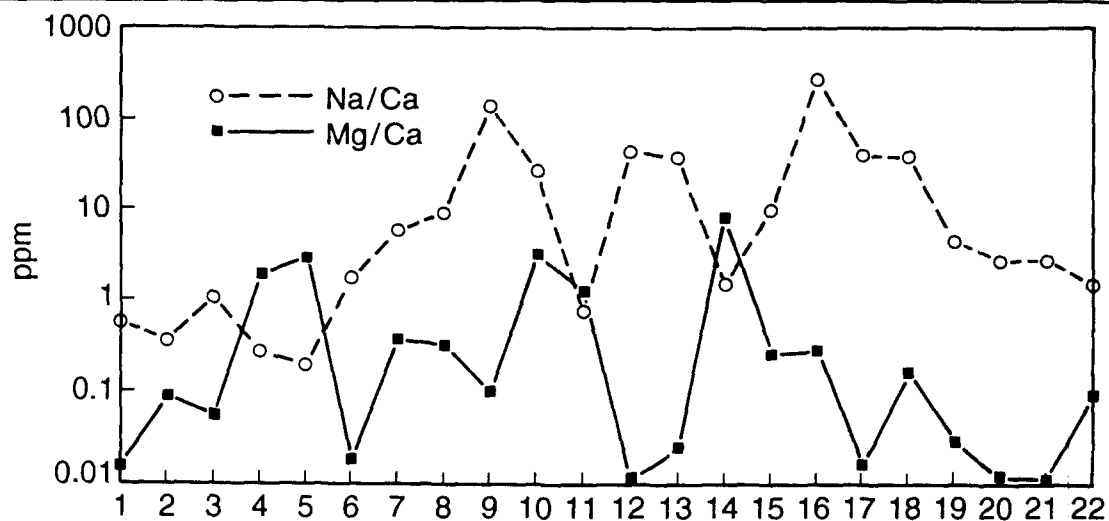


Figure 6(a). See caption opposite.

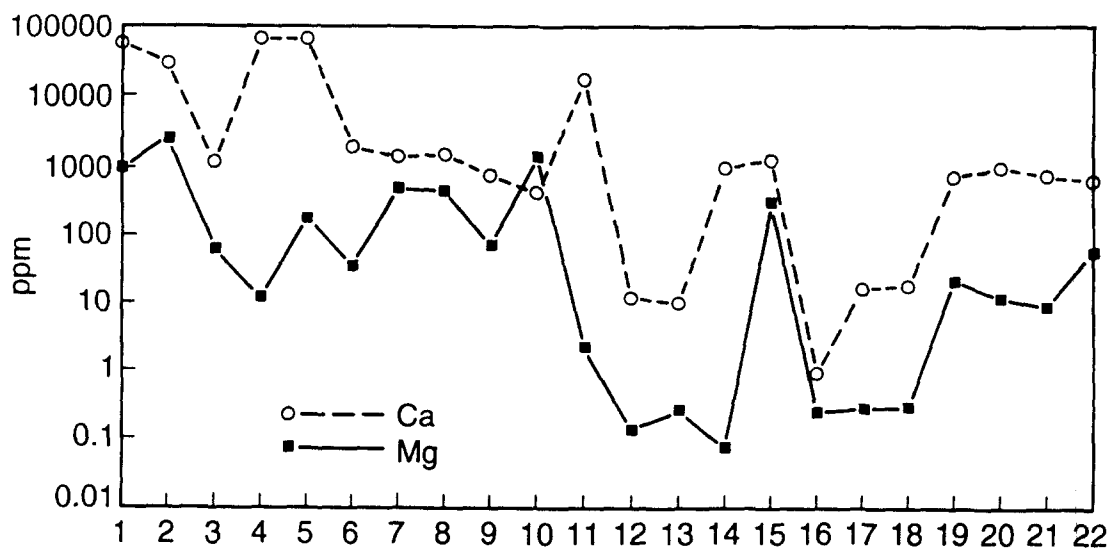


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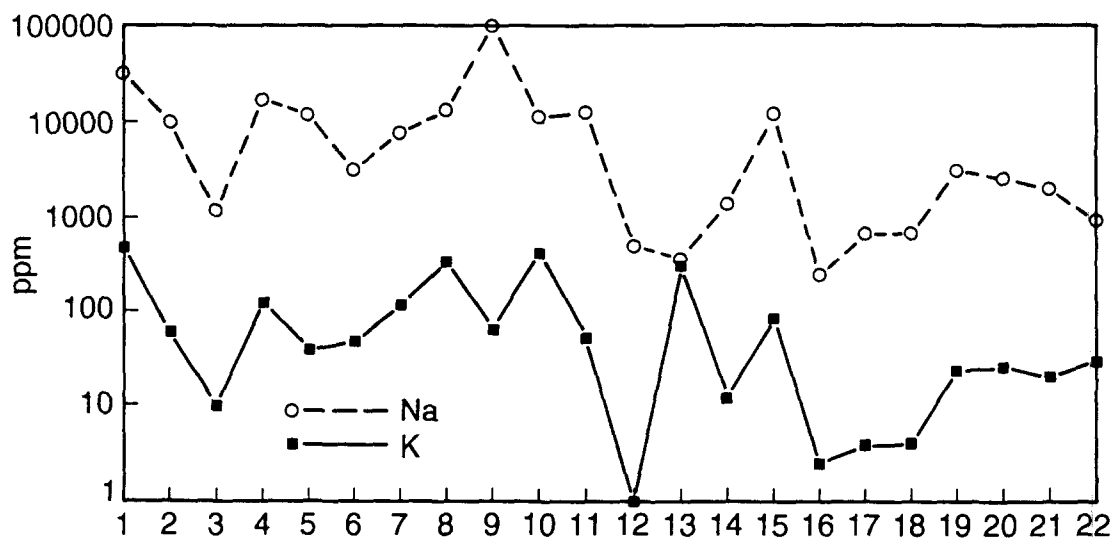


Figure 6(c). See caption opposite.

the basement rocks by mining activities is not new (Nordstrom *et al.*, 1989) but the pathways and source of the components within the waters are not well understood and more tracer research is required.

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