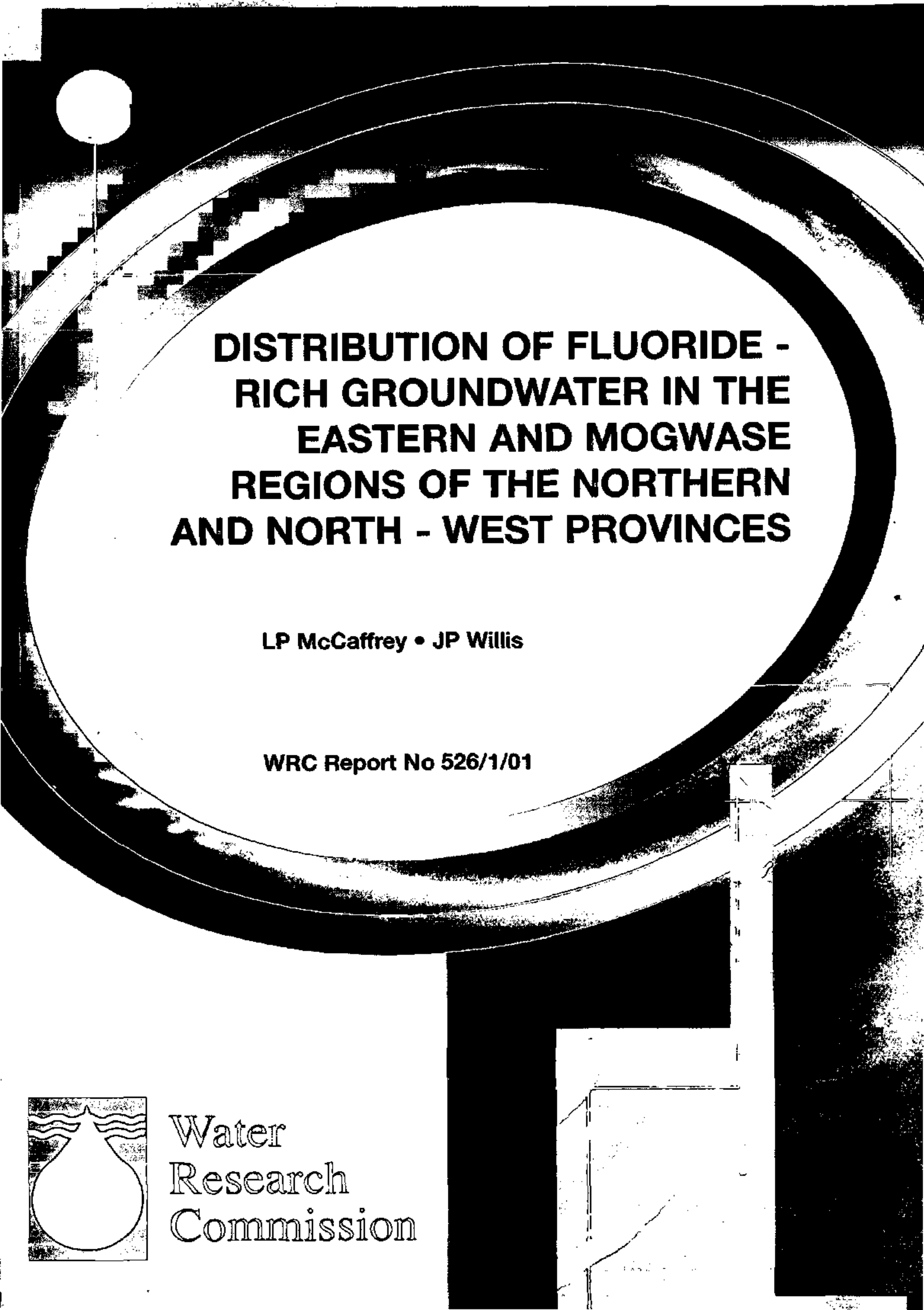


DISTRIBUTION OF FLUORIDE - RICH GROUNDWATER IN THE EASTERN AND MOGWASE REGIONS OF THE NORTHERN AND NORTH - WEST PROVINCES

LP McCaffrey • JP Willis

WRC Report No 526/1/01

Water
Research
Commission

DISTRIBUTION OF FLUORIDE-RICH GROUNDWATER IN THE EASTERN AND MOGWASE REGIONS OF THE NORTHERN AND NORTH-WEST PROVINCES

by

L P McCAFFREY and J P WILLIS

Department of Geological Sciences
University of Cape Town
Rondebosch 7700, South Africa

Report to the Water Research Commission on the Project
"Distribution of fluoride-rich groundwater in the eastern and Mogwase regions of the Northern and North-western Provinces: influence of bedrock and soils and constraints on utilisable drinking water supplies"

Head of Department:	Professor A P le Roex
Project Leader:	Professor J P Willis

WRC Report No. 526/1/01
ISBN 1 86845 694 3

TABLE OF CONTENTS

EXECUTIVE SUMMARY

DISTRIBUTION OF FLUORIDE-RICH GROUNDWATER IN THE EASTERN AND MOGWASE REGIONS OF THE NORTHERN AND NORTH-WEST PROVINCES

by

L P McCAFFREY and J P WILLIS

Department of Geological Sciences
University of Cape Town
Rondebosch 7700, South Africa

Supplementary to the full report to the Water Research Commission on the Project

"Distribution of fluoride-rich groundwater in the eastern and Mogwase regions of the Northern and North-western Provinces: influence of bedrock and soils and constraints on utilisable drinking water supplies"

Head of Department: **Professor A P le Roex**
Project Leader: **Professor J P Willis**

1 Background and motivation to the study

Fluorine is one of few potentially toxic trace elements whose primary path into the human body is via drinking water. Areas of southern Africa are amongst those notable in the world as experiencing endemic fluorosis on a regional scale. Fluorite-bearing granitic rocks provide sources of dissolved fluoride in groundwaters, and elevated fluoride levels are reported from most areas of the western Bushveld surrounding the Pilanesberg Igneous Complex, and from those underlain by granitic rocks of the Bushveld Igneous Complex. Fluorite mineralised veins within the igneous bedrocks, a number of which have been mined, provide particular potential sources of dissolved fluoride.

Prior to the commencement of this study approximately 95% of villages in the area were dependent upon groundwater for their drinking water supply. Ad hoc sampling had shown that fluoride concentrations in some parts of the area exceeded Department of Water Affairs and Forestry (DWAF) guidelines by 800%. Fluorosis, a severely debilitating illness resulting from excessive consumption of fluoride, is clearly manifested in the villages of Ruighoek, Ledig and Tlhatlhaganyane, where both children and adults showed the tell-tale mottling of the teeth produced by fluoride imbalance. A few cases of severe skeletal fluorosis in adults had been identified in the area. Clinical studies had been undertaken by the Department of Community Dentistry, University of the Witwatersrand, although these had been directed primarily at gauging the extent to which groundwater composition induces poor <u>dental</u> health amongst villagers. Additional research at MEDUNSA and UNISA was directed at both dental and skeletal effects.

The potential usefulness of this project would be in the identification of the most critical areas requiring an upgrading of the water supply, and the delineation of other areas in which the risk of fluorosis is less severe or does not exist, and where no additional water supply is required. This should allow for the most efficient utilisation of available water supplies, and of the available funds for water development, by effective programming of improvements to rural water supply within the area. Large savings in future expenditure on water provision measures can be envisaged, if the installation of unnecessary defluoridation plants and superfluous pipelines to localities having satisfactory local water quality can be avoided.

1.1 Distribution and causes of high F^- groundwater

High fluoride groundwater has been attributed to several separate causes: high fluorine content of aquifers; low groundwater flow rates; arid and semi-arid climate increasing potential evaporation; and water with high pH.

Several researchers have noted the high fluoride content of groundwater in South Africa, especially in the Pilanesberg and Bushveld Granite. It was suggested that fluoride in groundwater of the Springbok Flats came from the Ecca formation, and that detrital fluorapatite was the source. The current known distribution of F^- in South African groundwaters is presented in Figures 1 and 2. These figures are based on unpublished distribution maps calculated from the SA National Groundwater Database. It can be seen that large areas of the country are subject to fluoride concentrations in groundwater greater than 1.5 mg/ℓ, especially in the north-eastern parts and in the arid western parts.

Dental fluorosis, manifesting as mottled tooth enamel, is a common sight in many rural parts of the world. The condition can be classified according to the severity of the manifestation: limited white patches covering the tooth surface is termed *mild* dental fluorosis, larger opaque areas with unsightly brown staining is termed *moderate*, whilst widespread brown and black staining in conjunction with noticeable pitting is termed *severe* dental fluorosis. Human beings throughout history have suffered from dental fluorosis, but until this century the aetiology of the condition was unknown.

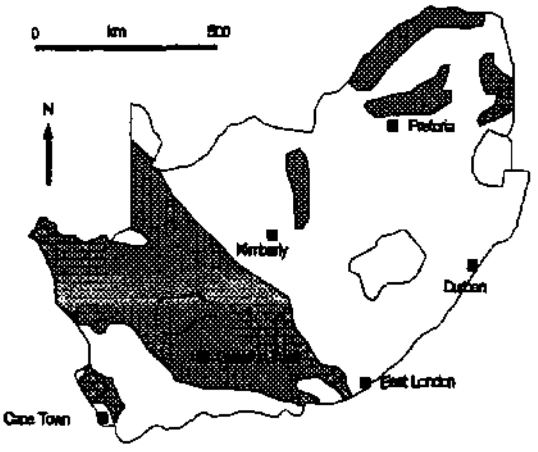


Figure 1. South African groundwater with F^- concentration greater than 1.5 mg/ℓ.

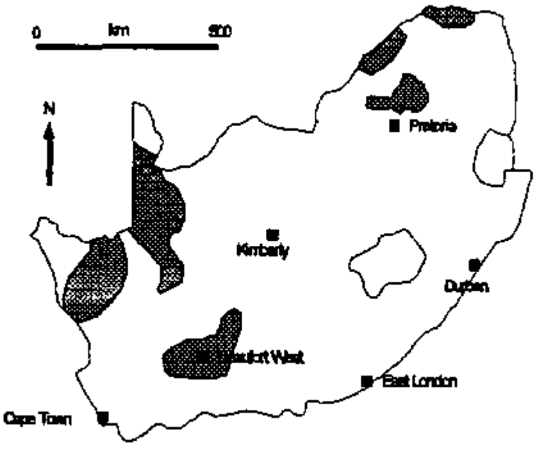


Figure 2. South African groundwater with F^- concentration greater than 3.0 mg/ℓ.

The causative agent of mottled enamel is the high fluoride concentrations in the drinking water supplies of the affected communities. It has been widely shown that high concentrations of fluoride in drinking water can cause deleterious physical effects in human dentition, goitre and bone defects. Fluoride has also been implicated in higher rates of cancer. In osteosclerosis, thickening of the joints and mineralisation of the tendons occur. In extreme cases the vertebrae of the back become rigid, giving rise to a condition known as 'poker back'. The rib-cage becomes rigid and all breathing is performed abdominally, whilst bony outgrowths form at the end of ribs and along the long bones. Unfortunately, the precise levels of fluoride dietary intake at which each level of fluorosis becomes apparent are not well established.

2 Aims of the study

The original aims of this study were:

(i) To produce a comprehensive database of the concentrations of fluoride and other common anions (F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and selected cations, and other physico-chemical parameters, in wells and surface water bodies in the study area.

(ii) To investigate the source and mobility of fluoride in the hydro-geochemical environment of the study area, and hence the spatial relations between fluoride-enriched groundwaters and fluoride sources in rocks, mineralised areas, and soils.

(iii) To investigate the thresholds above which clinical human health problems - osteoporosis, fluorosis - are exhibited in a population reliant upon fluoride-bearing well water.

(iv) To utilise results of (i) - (iii) to provide a map of the risk areas of fluorosis from fluoridised drinking water, which, with the groundwater composition data, will be of use to water supply planners.

The study also aimed to investigate and prove the following hypotheses: that groundwater fluoride concentration is correlated to aquifer composition, especially the content of fluorine-bearing minerals, and is controlled by the solubility of such minerals; that fluoride concentration is also correlated to the residence time of groundwater; and that very high levels of fluoride in groundwater are caused by processes additional to the simple dissolution of fluorine-bearing minerals from rocks.

At an early stage it was discovered that a considerable amount of epidemiological research on the health effects of fluoride uptake had already been carried out at MEDUNSA and the University of the Witwatersrand, and the steering committee agreed that work on aim (iii) would not be researched as part of the programme, but that the aim would be satisfied by summarising the findings of MEDUNSA and the University of the Witwatersrand. It was agreed further that detailed studies would concentrate only on groundwater, and not surface water as well.

3 Field area

The field area, with an areal extent of approximately 45 000 km^2, was defined initially in relation to the now defunct homeland of Bophuthatswana (Figure 3). The field area was redefined in terms of district boundaries after 27th April 1994 (the date when Bophuthatswana officially ceased to exist). Subsequently the steering committee requested that the field area be extended even further to include the Springbok Flats area (Figure 3), which increased the areal extent to approximately 150,000 km^2. The field area includes parts of the western lobe and much of the central area of the Bushveld Igneous Complex, the Pilanesberg Alkaline Igneous Complex, sedimentary rocks of the Pretoria

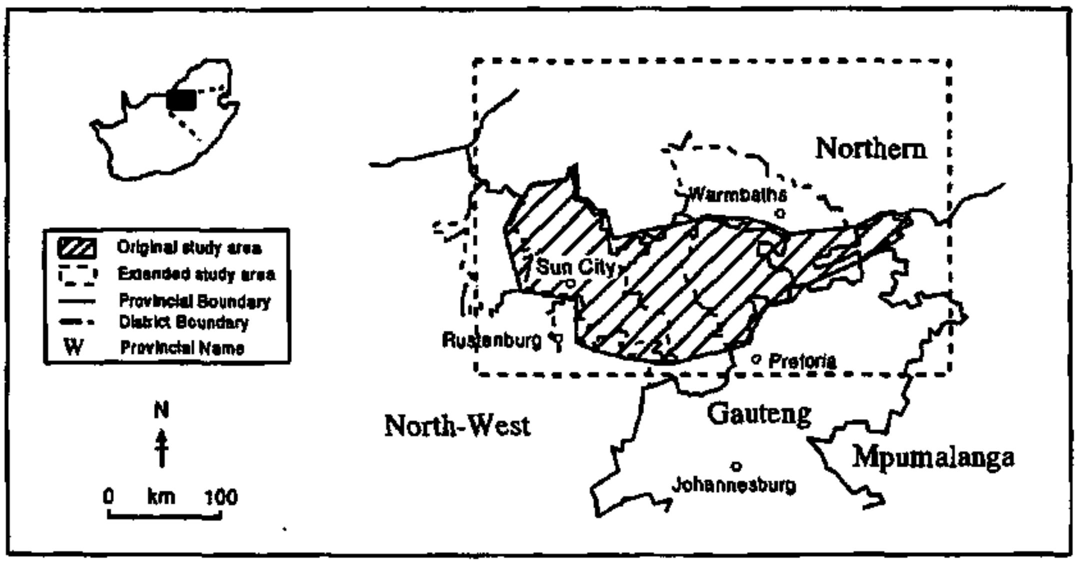


Figure 3. Location and extent of the original and extended field areas.

Group, the western part of a Karoo Group sedimentary basin and some small outcrops of carbonatites.

The main geological features of the original field area are shown in Figure 4. Rocks of the Transvaal Sequence and Bushveld Complex comprise much of the field area. Archaean Granite occurs in the northwest and south of the area, overlain by dolomites of the Chuniespoort Group and clastic sediments of the Pretoria Group, both of the Transvaal Sequence. Much of the area is underlain by rocks of the Bushveld Igneous Complex (BIC), which in this area was emplaced into the Pretoria Group, most prominently the Magaliesberg Quartzite Formation. The BIC is divided into the mafic rocks of the Rustenburg Layered Suite (RLS), comprising pyroxenites, anorthosites, norites and gabbros; the Rashoop Granophyre Suite; and the Lebowa Granite Suite (LGS). The LGS has two principal components in the field area - the Nebo Granite and the Lebowa Granite, the latter being more mineralogically variable and mineralised.

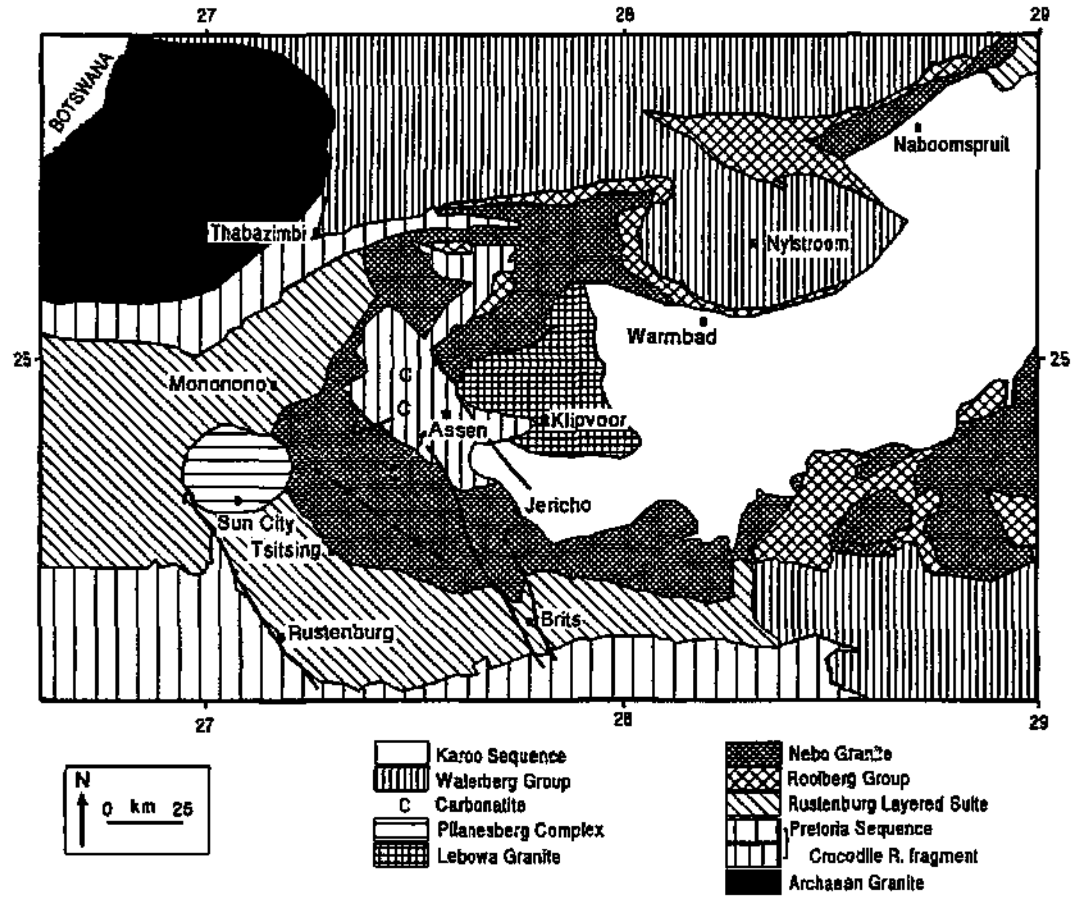


Figure 4. Sketch map of the geology of the extended field area.

Sedimentary rocks of the Crocodile River Fragment (CRF), dominantly carbonates, shales and ironstones, occur centrally. The Rooiberg Group make up the roof rocks of the BIC. The Rooiberg is a succession of predominantly volcanic rocks with occasional sedimentary lenses. They are often highly mineralised. The blanket term "felsite" is often applied to the Rooiberg Group rocks, but in reality basalt, andesite, dacite and rhyolite all occur in the group. Clastic and carbonate sediments of Karoo age overlie the eastern parts of the BIC in the field area. Several alkaline intrusions occur, including the Pilanesberg Complex nepheline syenite, the associated Pilanesberg Dyke Swarm and several carbonatite complexes, such as Kruidfontein, Bulhoek and Tweerivier.

A map of the principal physical features in the field area is given in Figure 5. Much of the area is above 1 000 m in elevation, with several notable mountain ranges and blocks.

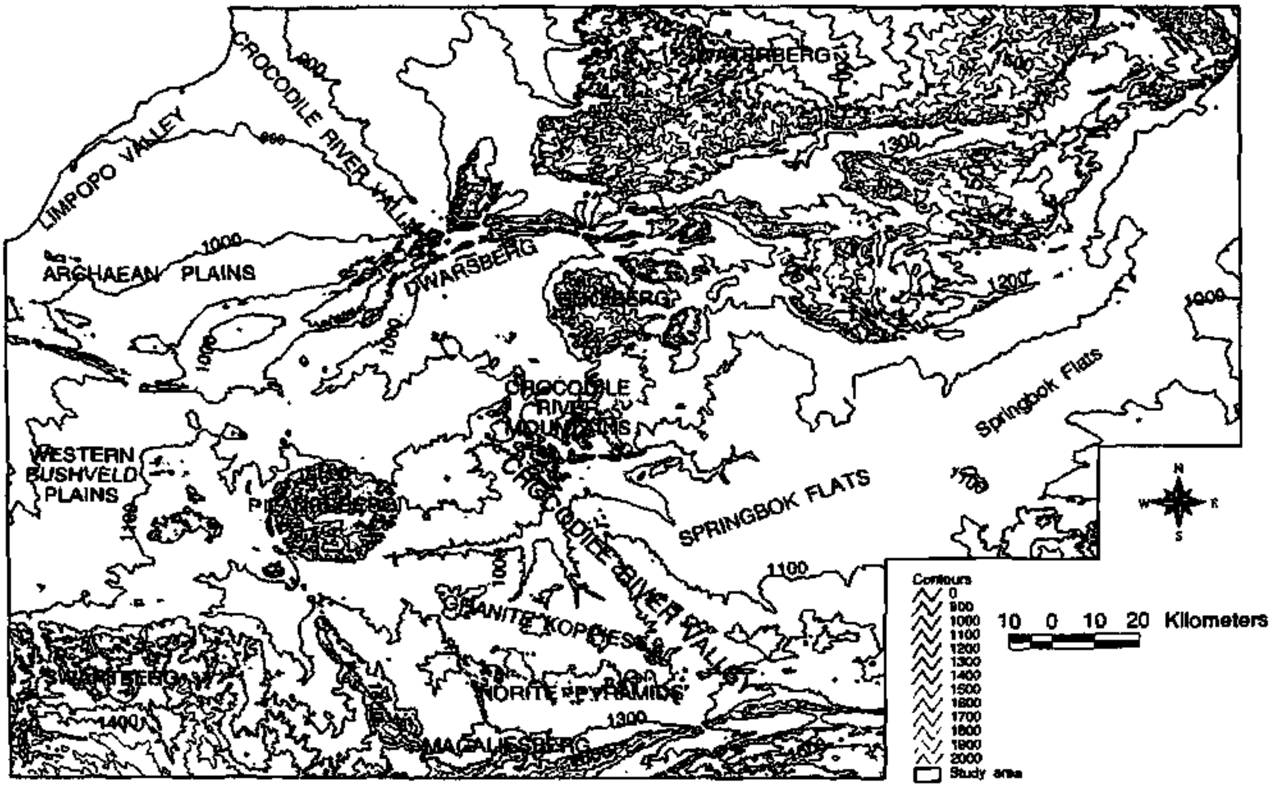


Figure 5. Physical features of the field area.

The area is semi-arid, with the mean annual potential evaporation (2135 mm) far exceeding the actual mean annual precipitation (MAP) of 620 mm for the field area as a whole. MAP increases from approximately 500 mm/yr in the west to almost 900 mm/yr in the east. MAP also increases near the southeastern corner (in the vicinity of Pretoria and the Magaliesberg Mountains) and in the northeast (in the Waterberg Mountains). Mean maximum temperature (MMT) is of importance in the epidemiology of fluorosis. MMT is strongly negatively correlated with elevation ($r = -0.98$). The correlation of MMT with latitude ($r = 0.63$), although significant at the 95% confidence level, is not as strong as that with elevation, and thus in the field area MMT is dominated by the effect of elevation.

Only two *major* rivers cross the study area. The river system is shown in Figure 6. Many non-perennial streams occur.

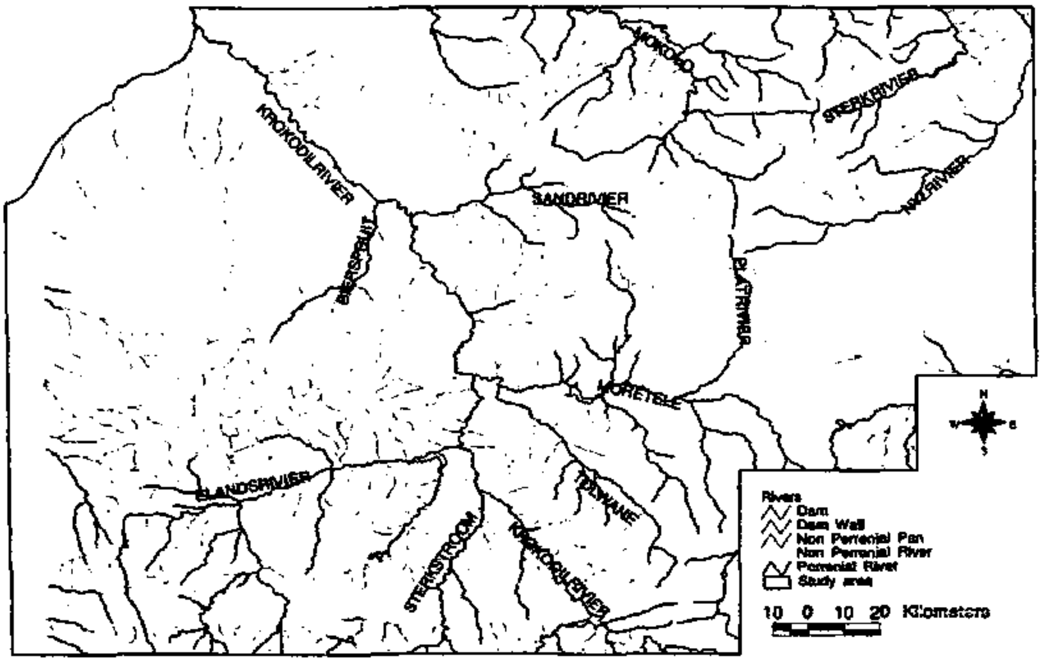


Figure 6. River system of the extended field area.

4 Geochemistry of Fluorine

Elements of the halogen group are readily soluble in water. The Eh and pH conditions of halide speciation are shown in Figure 7. Under the conditions in which water is stable (between the solid lines in Figure 7), the halides exist only as monovalent anions, the exception being iodine which can exist in oxidising aqueous solutions as iodate, IO_3^-. The halogens, therefore, generally exist in aqueous solutions in the form of F^- (fluoride), Cl^- (chloride), Br^- (bromide) and I^- (iodide). Fluorine

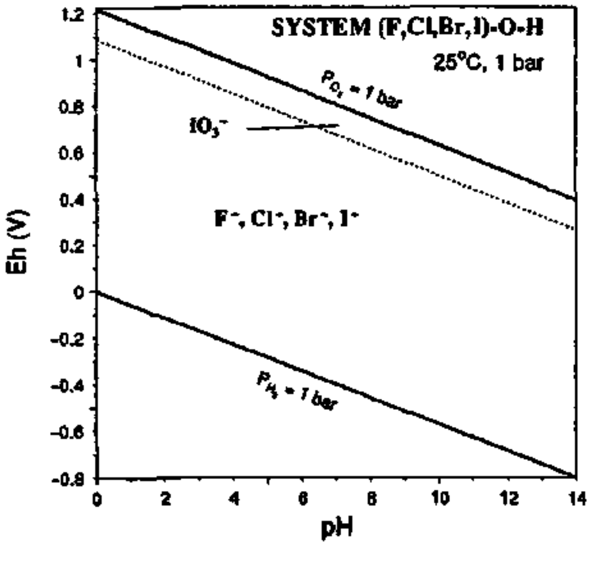


Figure 7. Speciation of halides under varying conditions of Eh and pH.

can also occur as a complex, such as $(AlF_6)^{3-}$ or AlF^{2+} or MgF_2. At a pH below 3.5, fluorine in solution may occur in the HF° form.

Only two rock-forming fluorine-bearing minerals exist, topaz [$Al_2(SiO_4)(OH,F)_2$] and fluorite (CaF_2). Just under 150 fluorine-bearing accessory minerals are known, and many others contain small amounts of F^- replacing OH^- and O^{2-}.

Fluorine concentration within similar rock types is subject to large variations, but in general the concentration trend follows ultramafic < intermediate < granitic < alkaline. The mean F concentrations are approximately 100, 400, 800 and 1000 ppm, respectively.

Fluorine is generally depleted in soils relative to the fresh parent rock as a result of dissolution, but the behaviour of fluorine during weathering is complex. In general, fluoride can be adsorbed onto mineral surfaces in place of hydroxide, but is displaced by the hydroxide ion with increasing pH.

5 Materials and Methods

The aims of the project were addressed by:

- (i) collecting and analysing ~320 groundwater samples from boreholes;
- (ii) collecting and analysing fresh rock and associated soil samples;
- (iii) extracting chemical and physical data on ~3000 groundwater samples from the DWAF database;
- (iv) evaluating the data set as a whole.

5.1 Groundwater

Groundwater sample locations were selected primarily to give an even spread over the field area and secondly to fill in spatial gaps in the existing (Bophuthatswana) groundwater database. This meant that sampling took place in agricultural areas rather than villages. Several factors affect the spatial distribution of the data. In rural areas there is often a clustering of the data, since boreholes are most common in villages. In game parks, such as Pilanesberg and Borakalalo, data is more evenly distributed because of the need for game to have evenly distributed watering points. Groundwater availability (and conversely, the availability of river water) has also modified the sample distribution. Some parts of the study area have a low data density because of the absence of boreholes, such as the granite areas to the northeast of the Pilanesberg and north of Brits. Boreholes in these areas have low success rates and low yields, and hence are either abandoned after drilling or rapidly fall into disrepair after being equipped, so that samples are unavailable from these areas. Few boreholes exist in the vicinity of the Apies River, since water is usually available from the river all year round. A third factor influencing data distribution is groundwater quality. Boreholes with good quality water are maintained and more boreholes are drilled in the area. However, boreholes with poor quality water tend to be abandoned after drilling, or are equipped but fall into disrepair, and naturally act as a disincentive for further drilling in the area.

Any data concerning groundwater chemistry collected from rural areas, anywhere in the world, might be affected in these ways. The current data set is therefore highly biased, in that it is "clustered" and biased towards boreholes with high yields and good water quality. The results from this study are, therefore, of the "best scenario" type; the unbiased reality may show a much worse picture of water quality.

Groundwater was analysed in the field for pH, electrical conductivity (EC) and dissolved oxygen (DO) using solid state probes and a voltmeter. Total alkalinity was determined on-site by titration with HCl. Fluoride was measured each evening at the field base using a fluoride ion selective electrode (FISE) with a total ionic strength adjustment buffer (TISAB). Fluoride was remeasured at the University of Cape Town (UCT) using TISAB with and without CDTA. The CDTA was used to dissociate any F^- complexes that may have been present, and thus give a total F^- analysis. It was established that the use of the very expensive CDTA was unnecessary in determining F^- in the groundwaters of the study area.

A Dionex high pressure ion chromatograph (HPIC) was used to determine the concentrations of the major ions (F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}) in groundwater. Analysis for iodide was conducted by the South African Institute for Medical Research using a Waters High Pressure Liquid Chromatograph, with a Ag electrode as a detector.

Stable isotopes (hydrogen and oxygen) were measured on a VG 602E gas-source mass spectrometer at UCT.

A gas-proportional counter was used to analyse for radiocarbon at the Schonland-CSIR Research Centre at the University of the Witwatersrand.

Strontium isotope analyses were carried out at UCT using a VG Sector solid-source mass spectrometer, run in dynamic multi-collector mode. The measured $^{87}Sr/^{86}Sr$ values were normalised to $^{88}Sr/^{86}Sr = 0.1194$, to correct for mass fractionation.

5.2 Rocks and soils

The objective was to collect at least three samples of each major rock type and associated soil in the area, to provide an indication of the composition of each rock and soil type. Rock and soil samples were taken in pairs, with the samples usually located not more than 10 m from each other. Forty two rock samples and 40 soil samples were collected. Difficulties were encountered in sampling Karoo rocks, since they produce a flat relief with few rock outcrops. Only two samples from the Karoo Sequence were collected.

With a study area of ~150 000 km^2 and only ~40 rock and soil samples, data density is very low. However, an evaluation of the Regional Geochemical Survey maps of the study area (Council for Geoscience, 1995) showed that the stream sediments and soil samples derived from a particular lithological unit have similar geochemical characteristics over their full areal extent. It is inferred from this that in the study area a small number of samples from a particular lithological formation can be taken to be representative of the rock body as a whole. The main rock types were sampled at least three times, and the more important rock types (Pilanesberg foyaites and Lebowa granite) were sampled at least four times.

Major and trace element concentrations were measured using X-ray fluorescence spectrometry (XRFS) at UCT. Mineral phases were qualitatively determined using X-ray diffraction (XRD) analysis at UCT. The equivalent CO_2 contents of several samples were determined by reacting the specimen with HCl and measuring the volume of CO_2 gas given off. Stable isotope analyses were conducted using gas-source mass spectrometry at UCT. Sr isotope ratios were determined using a VG Sector 7-collector thermal-ionisation mass spectrometer at the Radiogenic Isotope Facility at UCT. Chemical analysis of mineral phases was undertaken using a Camebax Microbeam electron microprobe at UCT. The solubility of fluoride bearing phases in rock and soil samples was investigated using leaching experiments (96 hours) with weak carbonic acid.

Tight quality control of analyses was maintained at all times.

5.3 Computer manipulation of spatial data

Analysis of data with a spatial component was carried out using an ARC/INFO Geographical Information System (GIS). The data points used to produce a 'fluorosis risk map' are plotted in Figure 8. The F^- concentration of groundwater samples was classified into four groups: <0.7, 0.7-1.5, 1.5-3.0 and >3.0 mg/ℓ. These are designated **no risk**, **low risk**, **medium risk** and **high risk**, respectively. Theissen polygons were generated for each sample point, resulting in approximately 3 240 polygons. Where adjacent polygons had the same classification, they were merged. In this way 300 areas have been delineated where there is a medium or higher risk of fluorosis (Figure 9).

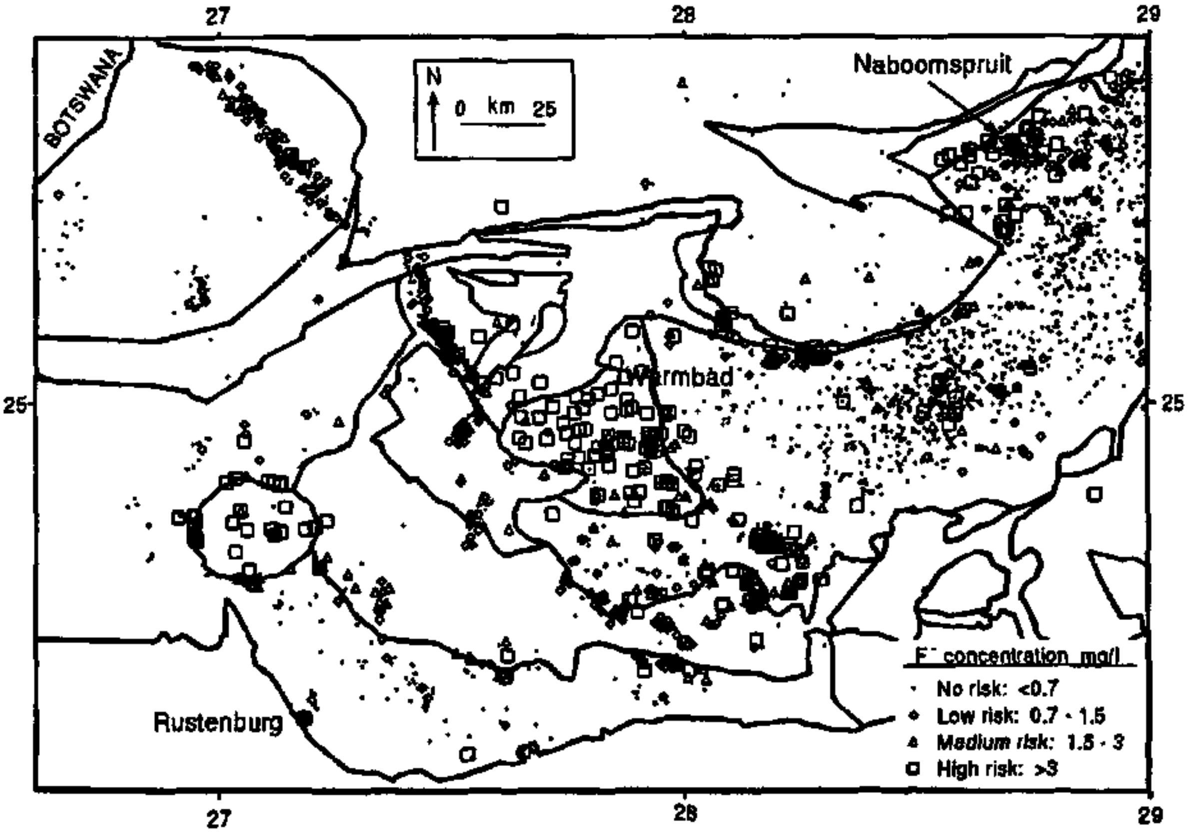


Figure 8. Plot of F^- concentrations in 3244 groundwater samples from the extended study area. Samples are divided into four risk levels. Lines are lithological boundaries (see Figure 4).

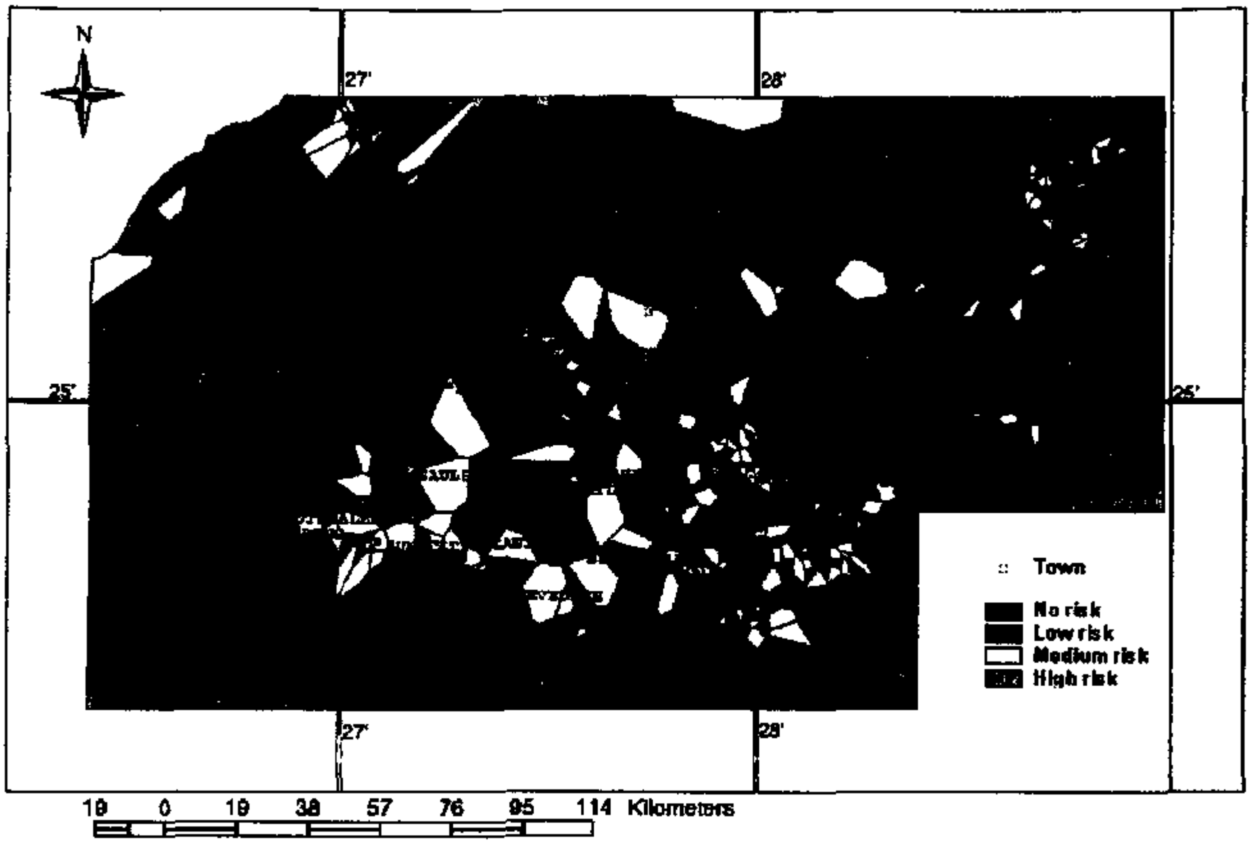


Figure 9. Fluorosis risk zones in the study area. <0.7, 0.7-1.5, 1.5-3.0 and >3.0 mg/ℓ F^- are designated **no risk, low risk, medium risk** and **high risk**, respectively.

6 Main results

6.1 Fluorine in rocks and soils

Many of the soil F concentrations are up to an order of magnitude less than that for the corresponding rock. The leaching of F from rock during the soil forming process is a well known and global phenomenon. F concentration would be expected to be at a minimum at the soil surface, increasing downwards towards the fresh rock boundary.

Figure 10 shows the spatial distribution of F in the soil and rock samples. F in soil has a similar relative distribution to F in rock, but the absolute concentrations are lower. The Pilanesberg and Lebowa Granites have high rock and high soil F contents, whilst the Nebo granite has scattered high values and the RLS values are uniformly low. The distribution of high F in rock and soil is very similar to the distribution of high F concentrations in groundwater.

Leaching experiments were conducted on all soil and rock samples. The highest concentrations of fluoride in the leachate came from rocks and soils with the highest fluorine concentrations. Figure 11 shows the relationship of total F to leachable F in rock and soil samples. In the rocks several of the

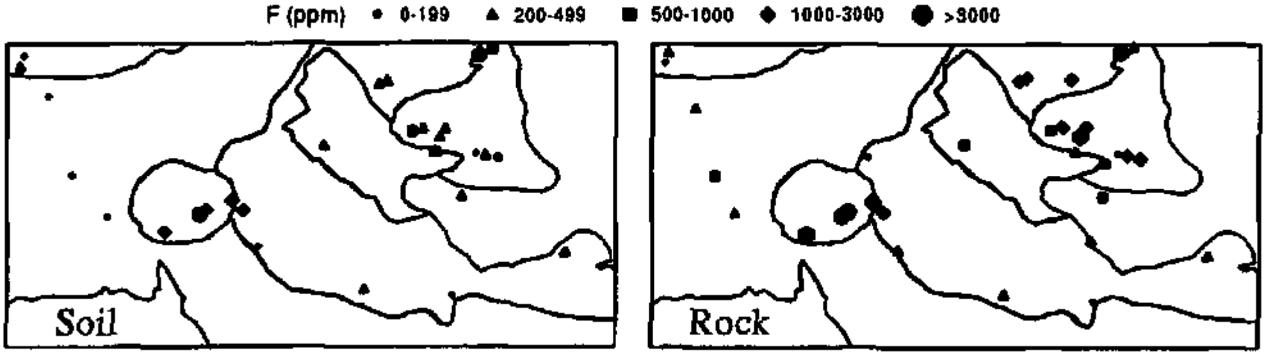


Figure 10. Distribution of F in soil and rock samples in the western Bushveld. Lines represent lithological boundaries (see Figure 4).

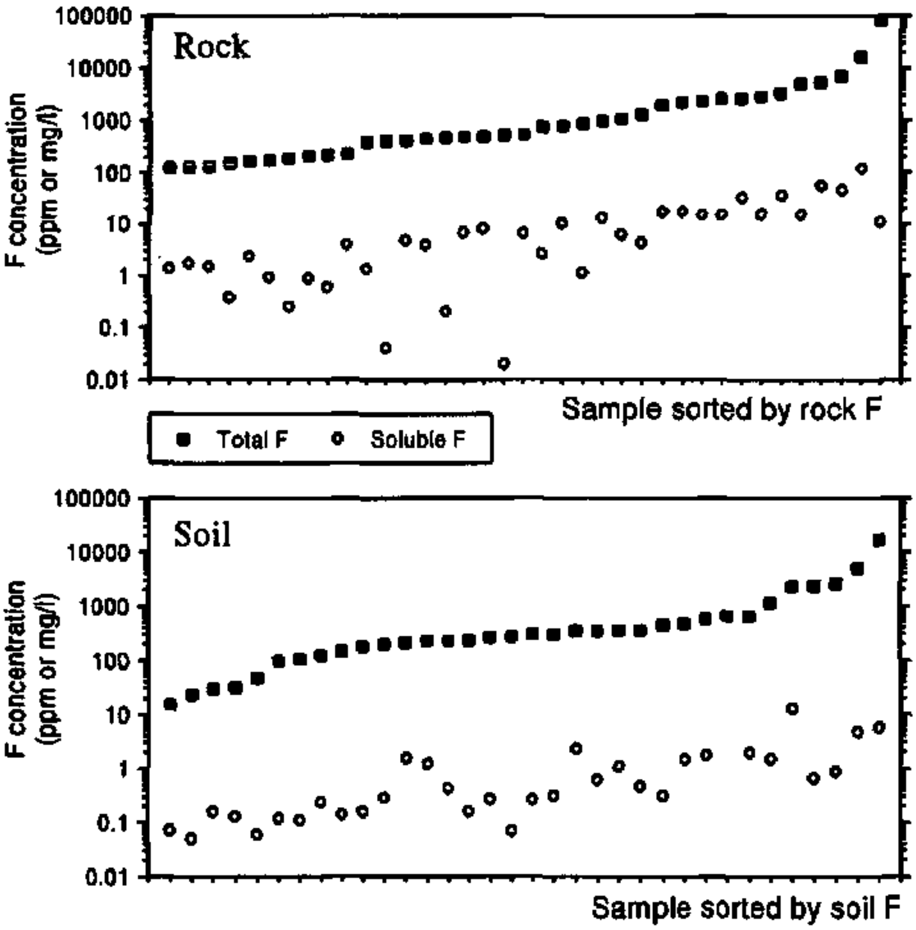


Figure 11. Results of leaching experiments on rock and soil samples. F concentrations in leachates are 2 or 3 orders of magnitude less than those in fresh rocks and soils, respectively.

samples had leachate with very high fluoride concentrations, and in general the leachate had a concentration approximately 2 orders of magnitude less than the whole rock concentration. In the soil leachates very low absolute concentrations of F were obtained, and leachable F is generally three orders of magnitude less than total F in the soils. Most of the fluoride concentrations in the leachate derived from soil samples were below ~4 mg/ℓ.

6.2 Groundwater chemistry

Figure 12 shows F^- concentration in groundwater in the study area as a whole, plotted as a histogram. The human dose response curve is superimposed on the histogram. The median concentration is 0.3 mg/ℓ and the mean is 1.4 mg/ℓ F^-; the population is strongly skewed towards high fluoride concentrations. Although the tail of the histogram is irregular, there is an increased frequency of fluoride values at ~3 mg/ℓ.

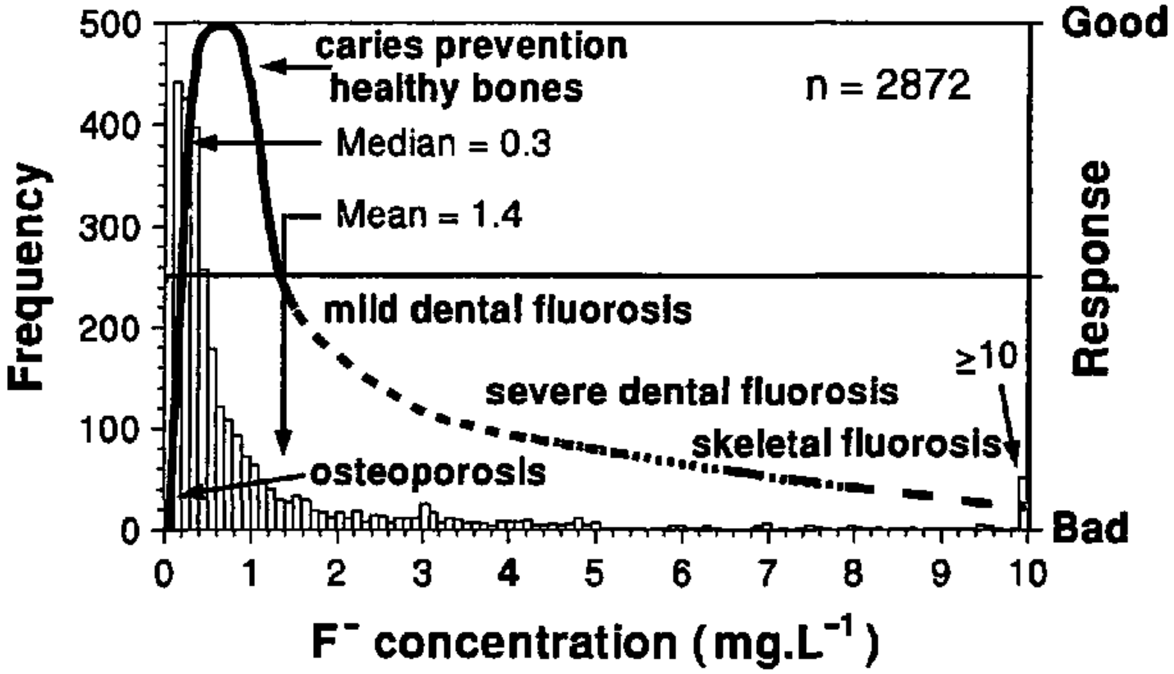


Figure 12. Groundwater fluoride histogram for the study area as a whole.

Sixteen host rocks were identified for initial groundwater classification purposes, namely, in age order: Archaean Granite (AG); Chuniespoort (Ch) and Pretoria Group (Pr) sediments; Rustenburg Layered Suite basic rocks (RL); Rashoop Granophyre (Gr); Nebo Granite (Nb); Lebowa Granite (Lb); Rooiberg felsites (Rb); Pilanesberg Complex nepheline syenite (Pl); Carbonatite (Ca); Letaba basalt (Lt); Ecca (Ec), Irrigasie (Ir) and Clarens (Cl) formations of Karoo age; Waterberg sandstone (Wt) and Quaternary deposits (Qu). The abbreviations are used in Figure 13.

Figure 13 shows summary statistics of fluoride concentration in the 16 major lithologies of the study area.

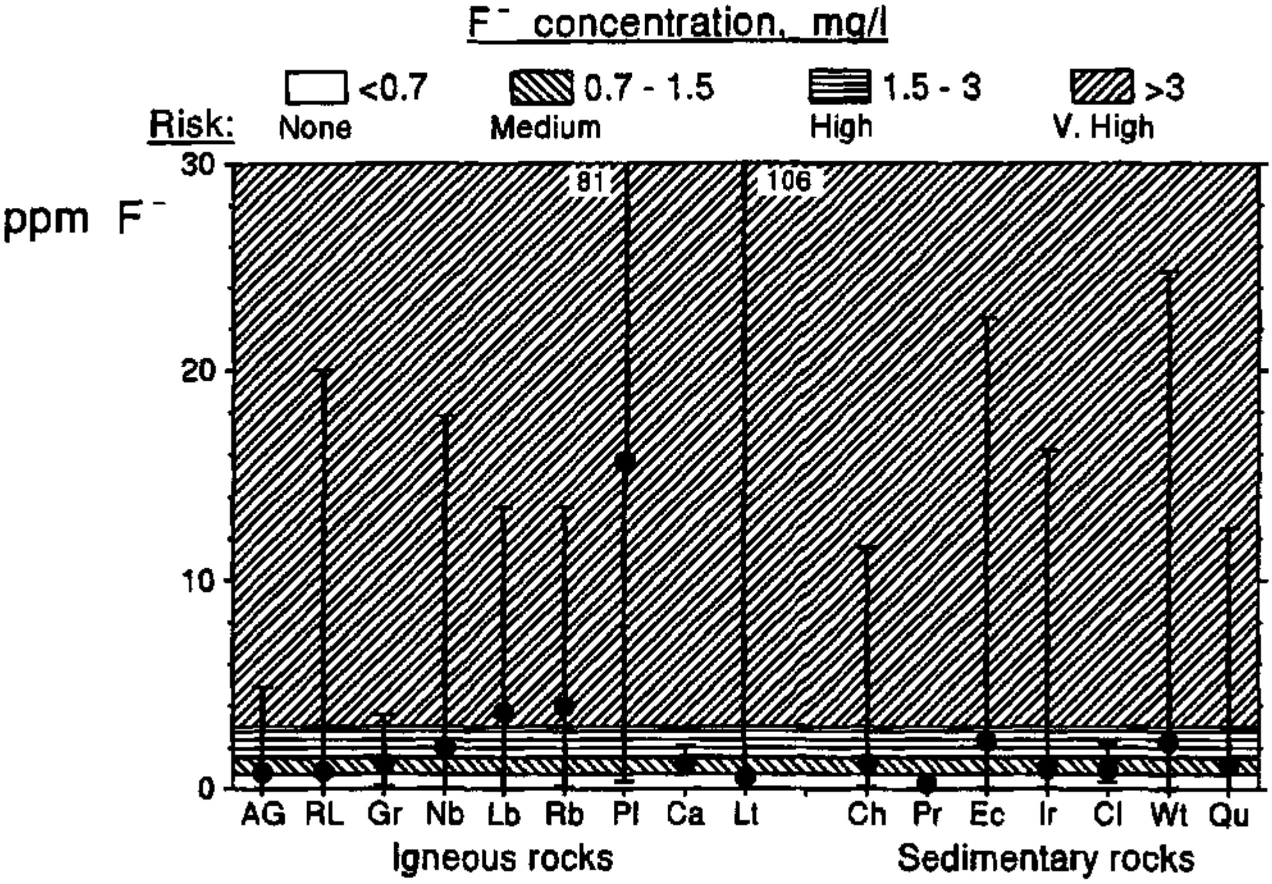


Figure 13. Summary statistics of F⁻ in 16 lithologies from the western Bushveld. ● = mean. Ticks = minimum, maximum. See text for key to lithology abbreviations.

Fluoride is found at low concentrations in most samples from the Rustenburg Layered Suite, with a mean of 0.4 mg/ℓ fluoride. High values occur in isolation and these may be due to Pilanesberg dykes. Fluoride concentrations are high in the acid parts of the BIC, with the two granites showing very different levels of groundwater fluoride. Nebo Granite groundwater has a mean concentration of 2.0 mg/ℓ F⁻ (Figure 13). The data plotted in Figure 13 reflect the much higher mean concentrations for the Lebowa Granite and the Pilanesberg, and the very high values (> 10 mg/ℓ F⁻) for the Pilanesberg perimeter groundwaters. Samples from the Lebowa Granite have a mode at over 10 mg/ℓ and a mean value of 5.0 mg/ℓ F⁻. Groundwater around the Pretoria Salt Pan, which is hosted in Nebo granite, had fluoride concentrations up to 20 mg/ℓ, and the brine in the pan 195 mg/ℓ F⁻. The Rooiberg Group has a number of elevated fluoride concentrations as well as a group of low concentrations. The two populations may reflect the heterogenous nature of the Rooiberg Group.

Groundwater from boreholes in the outcrop area of the Ecca shales have a mean value of 2.3 mg/ℓ F⁻. The majority of samples have less than 3 mg/ℓ F⁻, but outliers occur at much higher values. The groundwater from boreholes in the outcrop areas of the Irrigasie and Clarens Formations, in the central part of the basin, have lower mean fluoride concentrations, at 1.0 and 0.9 mg/ℓ F⁻ respectively, and there are fewer high fluoride outliers than from the Ecca.

6.2.1 Anions

Only NO_3^- concentrations gave cause for concern. Mean values for groundwaters in the RLS, Nebo granite, Pilanesberg Complex, carbonatites and Letaba basalt rocks were all above the high risk limit for drinking water. This is most likely due to anthropogenic pollution by livestock and/or pit latrines.

6.2.2 Trace elements

Groundwater samples from eight lithologies were analysed for trace elements. Only zinc and molybdenum were enriched in the groundwaters sampled. Zinc occurs in appreciable quantities, especially in the Pilanesberg, where one sample was above the maximum safe drinking water limit (10 mg/ℓ). Mo concentrations were generally at very low levels, close to the detection limit. However, Lebowa Granite groundwater had a mean concentration above the maximum safe drinking water limit of 0.2 mg/ℓ Mo.

6.2.3 Temporal variation

A number of boreholes were resampled to determine possible temporal variation in chemical composition. The major anions and cations vary considerably, but F^- showed very little variation over two years.

6.2.4 General

The results summarised above showed that much of the study area is underlain by groundwater having a F^- concentration above the optimum (~0.7 mg/ℓ) and also above recommended maximum drinking water concentrations (1.5 mg/ℓ). Approximately 17 000 km^2 of the western Bushveld have groundwaters with a F^- concentration >0.7 mg/ℓ. Just over 540 of the 3 000 groundwater samples have a F^- concentration >1.5 mg/ℓ, and 82 000 to 109 000 people are drinking groundwater which may induce fluorosis in the long term. 145 500 to 194 000 people are drinking water with F^- concentrations higher than optimal.

For the purpose of effective planning of water supplies for the area it is essential to have a map of areas in the western Bushveld where F^- concentrations in groundwater are above optimum levels. Figure 8 gave a detailed plot of borehole/risk value locations and Figure 9 showed a plot of Theissen polygons classified into **no risk** (<0.7 mg/ℓ), **low risk** (0.7-1.5 mg/ℓ), **medium risk** (>1.5-3.0 mg/ℓ) and **high risk** (>3.0 mg/ℓ).

Although many fluorite prospects occur in the Lebowa Granite Suite and Rooiberg felsite, few large working fluorite mines still exist in the study area. Major fluorite mines are still active in the Malmani Dolomite of the Chuniespoort Group, on the edge of the study area. The impact of dust generated by blasting and processing the ore is likely to be restricted to areas close to the mines, and no gaseous emissions are generated. Two other large fluorine-handling industries exist in the study area, namely the Atomic Energy Corporation's uranium enrichment plant at Pelindaba in the south (now closed), and a major ore smelter in the centre of the area. Industrial emissions of fluorine are unlikely to be a serious source of groundwater pollution, except perhaps on a very localised basis.

7 Conclusions

All the aims of the project have been successfully addressed, namely:

- (i) a comprehensive database of the concentrations of F^- and other common anions and cations, together with data on pH, temperature, EC and alkalinity, has been produced for a further 323 groundwater sites over the study area. In addition F^- concentrations over the extended area have been collated and evaluated.
- (ii) The source and mobility of F^- in the hydro-geochemical environment of the study area was established, and also the spatial relations between F^--enriched groundwaters and fluoride sources in rocks, mineralised areas and soils.
- (iii) Existing epidemiological information on the health related F^- effects have been reviewed and compiled in a F^- concentration *vs.* effect plot.
- (iv) The results have been successfully utilised to provide maps of areas of no risk, low risk, medium risk and high risk of fluorosis. These should be of use to engineers and planners concerned with the supply of drinking water to the rural population in the study area, and hopefully will result in considerable cost-savings in the future supply of water in the area. The results should bring about, over the next generation, a marked improvement in the dental and skeletal health of the local populace.

By implementing a very wide variety of analytical techniques to gain information on physical and geochemical characteristics of both groundwaters and their host rocks, by interpreting the results of chemical and isotopic analyses, and by the use of theoretical modelling calculations of element speciation, the project has both created and successfully integrated a huge database of knowledge of the study area. It is believed that the work has contributed significantly to the knowledge of fluoride in South African groundwaters, and that the results will be of use in studying groundwaters in other parts of the country.

8 Recommendations

Technology transfer

1. There is a very high probability of groundwaters from the Pilanesberg Complex and the Lebowa Granite having a F^- concentration above the maximum safe limit for human consumption (1.5 mg/ℓ F^-). It is recommended that any further installation of boreholes by the Department of Water Affairs and Forestry in these areas should be accompanied by suitable defluoridation procedures.

2. Since the start of this study the Pilanesberg area has been the subject of water quality remediation measures, in the form of the Saulspoort pipeline scheme. The population in this area now have access to good quality water supplied from the Vaalkop Dam. The population resident on the outcrop areas of the Lebowa Granite have had no such attention, and it is strongly recommended that a *district-wide alternative water supply scheme* be instituted for the Lebowa Granite area.

3. The Nebo Granite and parts of the Karoo sub-basin have scattered high fluoride concentrations. A district-wide alternative water supply scheme in these areas is not warranted, since good

quality boreholes do exist in the area. It is recommended that poor quality boreholes are either closed down or have borehole-scale defluoridation measures implemented on them. Good quality boreholes have been identified and it is recommended that these boreholes be <u>publicly identified</u>, *e.g.* by being painted green, and developed as a primary source of human drinking water. Poor quality boreholes also should be publicly identified, *e.g.* by being painted red.

4. Understanding and awareness of the risk of fluorosis from the ingestion of high fluoride groundwater is limited to a few specialists. The general population in the field area is almost entirely unaware of these problems, although the job-seeking population in the Pilanesberg area are rapidly coming to realise that a smile spoilt by dental fluorosis can severely limit a person's job opportunities.

   It is recommended that a 'technology transfer' programme be initiated. This should could take the form of health education comics, talks, community meetings, perhaps even a short video program. It is recommended that suitably qualified members of the local population be trained to do this in a manner acceptable to the local populace. At these meetings it should be explained exactly what the problem is, how it can be overcome, and what the local government is planning to do to solve the problem.

5. Where necessary and cost-effective, *e.g.* in areas of isolated boreholes, house-based defluoridation should be implemented, possibly through the utilisation of the 'clay pot' method, as developed in Scandinavia, or through more technologically advanced methods, as developed by the CSIR. House-based defluoridation should be encouraged, possibly through province-sponsored training sessions and the development of local clay resources. This would provide much-needed job opportunities in rural areas. More research into the occurrence and suitability of local clay resources is needed. Lest the supposed high cost of defluoridation be regarded as a limiting factor, it must be emphasised that it is <u>**only drinking water**</u> that requires treatment. Water for general household use and gardening does not require treatment. For an average household of 8 people only about 20ℓ of treated water are required daily.

6. Only small variations in groundwater F^- over time can be expected. However, it became clear from discussions with local village chiefs and headmen that the groundwater from many boreholes had never been analysed since the boreholes were first installed. Even then the results had never been communicated to the consumers. It would seem prudent to put in place a plan to monitor the F^- content of boreholes every five to ten years. It would be even better if a simple, rapid and cheap test, similar to a litmus paper test for pH, could be developed for the determination of F^- in groundwater. Suitable kits could be distributed to local authorities who could arrange for testing on a regular basis. In this way the consumers would develop confidence in the quality of their drinking water. If the water quality deteriorated, regular testing would provide an early warning system, allowing remedial steps to be taken timeously.

7. Finally, it is recommended that this report be brought to the attention of all governmental, provincial and local authorities, and also to all non-governmental organisations, operative in the area.

Research recommendations

1. Water quality in the Lebowa Granite area has been shown to be of poor quality and to have levels of molybdenum above the high risk limit for human consumption. It is recommended that further sampling and study of this area be undertaken.

ACKNOWLEDGMENTS

The research in this report emanated from a project funded by the Water Research Commission and entitled "Distribution of fluoride-rich groundwater in the eastern and Mogwase regions of the Northern and North-western Provinces: influence of bedrock and soils and constraints on utilisable drinking water supplies"

The Steering Committee responsible for this project consisted from time to time of the following persons:

Mr H M du Plessis	Water Research Commission (Chairman)
Mr D Huyser	Water Research Commission (Secretary)
Mr F P Marais	Water Research Commission (Secretary)
Mr A G Reynders	Water Research Commission
Mr Z M Dziembowski	Department of Water Affairs and Forestry
Mr M Fayazi	Department of Water Affairs and Forestry
Mr K U Pelpola	Department of Water Affairs and Forestry
Mr F C van Zyl	Department of Water Affairs and Forestry
Prof J B du Plessis	MEDUNSA
Mr B Mothusi	Department of Health, North West Province
Prof A P le Roex	University of Cape Town
Mr W van der Merwe	Department of National Health
Mr F S Viviers	Department of National Health
Dr J C Vogel	CSIR

The critical and constructive contributions of the Steering Committee are gratefully acknowledged.

The authors wish to thank all the people who helped us logistically in the field, including Paramount Chiefs Makapan and Mamogale, headmen, tribal policemen and officials, the interpreter Ms Lillian Phiri, Mr Bruce 'Matches' Brockett, Ms Kate Parr, Mr Johnson Maoke and the staff of the Pilanesberg National Park, Mr Sam Otto and family, the staff of Agricor, Mr Xu Yong Xin and Mr Farouk Mangera.

The completion of the project was only possible with the co-operation of many other individuals and institutions. The authors wish to record their sincere thanks to the following:

Dr Andres Bartha of the Bophuthatswana Geological Survey who kindly carried out trace element analyses and is thanked for his enthusiasm and patience; Mr 'Jim' Dziembowski is specifically thanked for providing access to the S.A. National Groundwater Database; Prof John Kalk of the University of the Witwatersrand Medical School organised and paid for the analysis of water samples for iodide; Prof Frank Hodgson of the University of the Orange Free State provided a copy of HYDROBASE free of charge; Prof Balthazar Verhagen provided access to his laboratory and the help of his assistants.

Prof J B du Plessis and Ms Susanna Zietsman are thanked for general discussions and their willingness to share their extensive medical knowledge of the study area.

The Computing Centre for Water Research at the University of Natal is thanked for providing a copy of MINTEQA2.

Mr Dan Wilson helped in implementing the project on ARC/INFO at UCT. Particular thanks are due to the staff of the Department of Geological Sciences at UCT where most of the analyses were carried out, specifically Dr Chris Harris for his time and patience with instructions for the preparation and analysis of samples for stable isotopes; Dr Steve Richardson and Mr Justin Underwood for preparing and analysing samples for Sr isotopes; Dr Martin Fey for instruction on the use of MINTEQA2; Ms Nicky Grant for instructions on the use of the XRF preparation laboratories; Mr Dick Rickard for ensuring smooth running of electron microprobe sessions; Mr Patrick Sieas for his able assistance in the ion chromatography laboratory; and the general helpfulness of Mr Leon Myburg, Mr Ernest Stout and Mr Neville Buchanan.

The original project proposal was finalised by Dr Ron Watkins, then at the Department of Geological Sciences, University of Cape Town and now at the Department of Geological Sciences, Curtin University, Perth, Australia. His continued enthusiasm and advice has been greatly appreciated.

ABBREVIATIONS AND DEFINITIONS

α	(alpha) Fractionation factor for a particular isotope between two phases
BOP	Bophuthatswana
CDTA	1,2,Cyclohexylene Dinitrilo Tetraacetic Acid or 1,2,Cyclohexane Diamine N,N,N,N-Tetraacetic Acid, known commercially as Titriplex IV
C_o	initial ^{14}C activity
C_s	measured ^{14}C activity of a sample
CRF	Crocodile River fragment
δ	(delta) Defined as, for example, $\delta^{18}O = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
Ion balance	Calculated using the equation $\% \ difference = \frac{(\Sigma_{cations} - \Sigma_{anions})}{(\Sigma_{cations} + \Sigma_{anions})} \times 100$
kg	kilogram
pK or K_{sp}	Solubility product
$pK_{25°C}$	Solubility product at 25 °C
kyrs	Kilo years, one thousand years or one millennium.
λ	(lambda) the decay constant of a radioactive substance
LGS	Lebowa Granite Suite
LLD	lower limit of detection
LOI	loss on ignition
ℓ	litre
MMT	Mean maximum temperature
MWL	meteoric water line
μg	microgram (0.000 001 g)
mg	milligram (0.001 g)
ng	nanogram (0.000 000 001 g)
PDB	Peedee belemnite
pmc	percent modern Carbon, measured relative to wood grown in 1850 and related to 1950. The standard is taken to be 100 pmc.
ppb	parts per billion or μg/kg, solid equivalent to 1 μg/ℓ in solution.
ppm	parts per million or mg/kg, solid equivalent to 1 mg/ℓ in solution.
R	Ratio of atomic abundances of heavy isotope to light isotope
RLS	Rustenburg Layered Suite
$\Sigma_{cations,\ anions}$	Sum of cations or anions, as molar equivalents.
SMOW	Standard mean ocean water
T	Temperature, in °C
$t_{½}$	Half life of a radioactive substance.
TISAB	Total ionic strength adjustment buffer.
$V_{A,B}$	Volumes of mixing groundwaters A and B.
wt%	weight percentage
X	Mole fraction
XRF, XRFS	X-ray Fluorescence Spectrometry

1 INTRODUCTION

1.1 Purpose of this study

The concentration of fluoride in groundwater has adversely affected the lives of millions of South Africans. This happens through the action of the fluoride ion (F^-) on teeth (causing dental fluorosis) and bones (causing skeletal fluorosis). The main source of F^- in the human diet is drinking water. Numerous studies have shown that ingestion of drinking water with elevated concentrations of F^- causes dental fluorosis (e.g. Driscoll *et al.*, 1983; Senewiratne *et al.*, 1973). Examples of African studies include those of Van Wyk *et al.* (1983); Ng'ang'a and Valderhaug (1993); Tobayiwa *et al.* (1991); Manji *et al.* (1986); McInnes *et al.* (1982). Very high concentrations of F^- in drinking water have been shown to cause skeletal fluorosis (e.g. Boyle and Chagnon, 1995; Felsenfeld and Roberts, 1991). Excess F^- in the diet has been implicated as one of the causes of goitre (Day and Powell-Jackson, 1972). One of the areas in South Africa where high F^- concentrations in drinking water has caused dental and skeletal fluorosis in humans is the western Bushveld, the subject area of this study.

Although the prevalence of dental and skeletal fluorosis in the area was recognised much earlier this century (Ockerse, 1941; Ockerse and Meyer, 1941), the implementation of the 'apartheid' system of government, starting in 1947, ensured that scant research was undertaken on the mainly black sufferers. Sporadic and small scale studies were undertaken by independent medical researchers (e.g. Zietsman, 1991; Rudolph *et al.*, 1995). Whilst a Government enquiry investigated fluoridation of drinking water supplies (McKenzie *et al.*, 1966), it was concerned only with urban (mainly white residents) water supplies. The majority of dental fluorosis sufferers (mainly black) live in rural areas. At the time of writing, no comprehensive survey of dental and skeletal fluorosis has been undertaken or is planned in the region.

Epidemiological studies around the world have tended to concentrate on the prevalence and severity of fluorosis, rather than study the distribution of high F^- groundwater, the main etiological factor. Without exception, previous studies of the distribution of high F^- groundwater in the Bushveld have relied on very few sampling sites. Zietsman (1991) evaluated the greatest number of boreholes (120) in one study, but her study covered only 7 villages. The data which these researchers needed did exist: routine sampling and analysis of groundwater has been undertaken for decades by Government bodies. However, the area had been fragmented politically by the formation of the nominally independent homeland of Bophuthatswana in 1977. Exchange of data between Bophuthatswana and South Africa seldom took place, and the political boundaries limited and compromised studies which excluded one or other of the countries. The amalgamation of Bophuthatswana back into South Africa, beginning in practice in 1993, has allowed the present study to use the combined hydrochemical data set for the first time. The change of government in South Africa in 1994 has given impetus to calls for the introduction of fluoridation in the country (Moola, 1996), and the present study is of importance in determining areas which do not require further fluoridation.

The study has had two main objectives: to delineate F^- concentrations in groundwater in the study area, so that regions of high F^- concentration may be identified; and to investigate the cause(s) of high F^- groundwater. The study area covers all of the endemic fluorosis areas in the region, and is not constrained by artificial political boundaries. The study also aimed to investigate the following hypotheses: that groundwater F^- concentration is correlated to aquifer composition, especially the content of fluorine-bearing minerals and is controlled by the solubility of these minerals; that F^- concentration is also correlated to the residence time of groundwater; and that very high levels of F^- in groundwater are caused by processes in addition to simple dissolution of fluorine-bearing rock, for instance ion exchange and evaporation.

In this study the distribution of high F^- groundwater has been investigated by collection and analysis of groundwater samples, and the integration of this new data with pre-existing databases. Groundwater has been analysed for the major anions and cations as well as trace metals so that correlations between those elements and F^- can be evaluated, and so that full speciation calculations can be performed on the analyses. Groundwater-mineral equilibria were modelled using a computer program to clarify the mineral controls on water composition and possibly the extent of water-rock interaction. A limited number of water samples were analysed for iodide, as parts of the study area are afflicted with endemic goitre and it has been suggested that F interferes with thyroid function. Iodide in groundwater was analysed to determine whether goitre was likely to be caused by low iodide or high F concentrations in groundwaters. The causes of high F^- groundwater have been investigated by using chemical and mineralogical analyses of rocks, soils and minerals to ascertain the F^- content of these materials. Studies of the stable and radioactive isotopes present in groundwater were used to try to define the origin, environmental history and residence time of the groundwater.

The completion of this study will yield numerous benefits. It will increase knowledge about one of the world's largest areas of endemic fluorosis, and the processes which enrich F^- in groundwaters. For the first time in South Africa, areas of fluorosis risk will be accurately delineated. The study will also estimate for the first time the number of people likely to be affected by fluorosis in the region, highlighting the serious health consequences of high F^- groundwaters. Health authorities and water supply planners will now be able to take action to guard against dental fluorosis in these areas. The study will add to the knowledge of the concentration and distribution of health-related trace elements in Bushveld groundwaters. The increased knowledge of geohydrological and geohydrochemical systems at work in the area will be of use in the planning of water supplies to a previously neglected region, and will be of use in the exploration for low-F^- groundwater supplies. The study will contribute to knowledge of the stable and radioactive isotope systems at work in groundwaters of the Bushveld area. It will show for the first time that the usefulness of strontium isotope studies of groundwater may be limited by the natural variability of the source minerals, and that radiocarbon studies of Bushveld groundwaters may provide information on mineral reaction rates.

1.2 Structure of this report

The report is divided into seven chapters. This introductory chapter contains an outline of the study; the reasons for, and benefits of, undertaking it; the social and human context in which it was undertaken; and a review of previous work on the geology of the field area and its physical characteristics. Chapter 1 also contains a review of the behaviour of the isotope systems used. Chapter 2 is a description of the methods used in the collection and analysis of materials. Chapters 3 and 4 contain descriptions of the results of these analyses on rocks, soils and minerals, and groundwater, respectively. Chapter 5 is a discussion of the data, including a review of the geochemistry of fluorine and the effect that F has on human health, and puts the results into a human health and geochemical perspective. Chapter 6 summarises the report and chapter 7 proposes further areas of research.

1.3 Field area

1.3.1 Extent

The field area was defined initially in relation to the now defunct homeland of Bophuthatswana (Figure 1.1), and then redefined in terms of district boundaries after 27th April 1994 (the date when Bophuthatswana officially ceased to exist). Data covering an oblong area was provided by various Government departments and this area (shown in Figure 1.1) is termed the extended field area. It has an areal extent of approximately 150,000 km^2, three times that of the Netherlands.

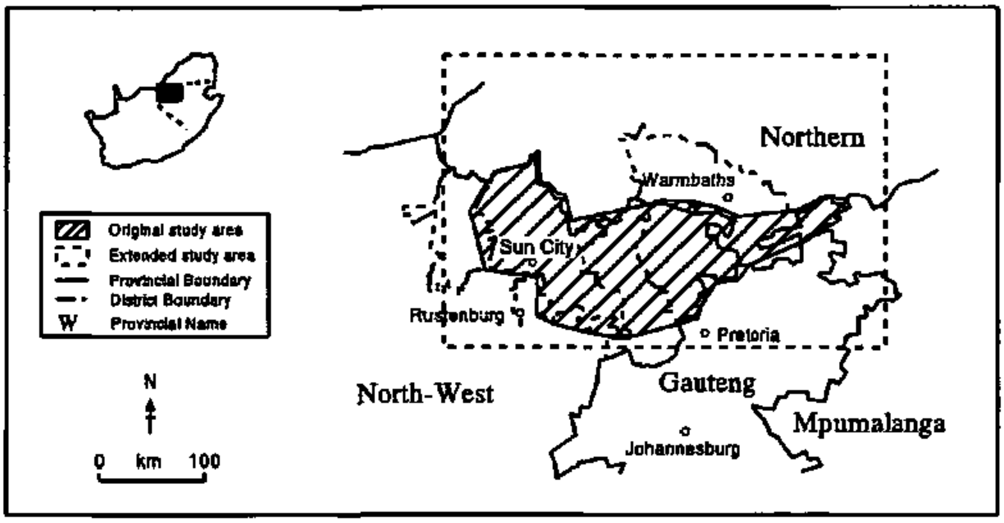


Figure 1.1 Location and extent of the field area.

1.3.2 Geography

A map of the principal physical features in the field area is shown in Figure 1.2. Much of the area is above 1000 meters in elevation, with several notable mountain ranges and blocks. In the south, the

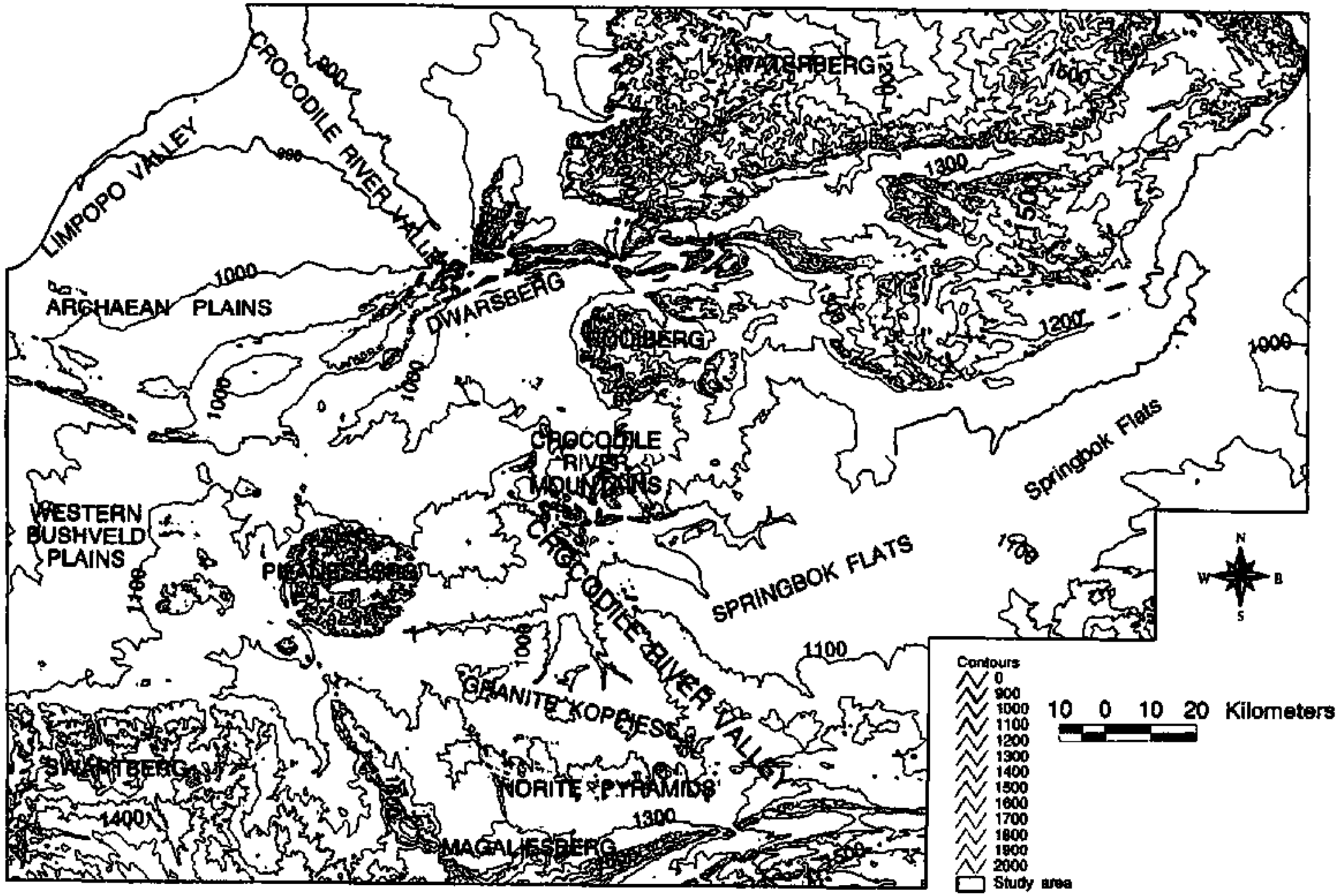


Figure 1.2 Principal physical features of the field area.

Magaliesberg range runs almost continuously from west of Rustenburg to the north of Pretoria. This is in effect the southern boundary of the field area. North of these hills are the flat plains of the Bushveld, occasionally broken by isolated hillocks ('koppies'). A prominent line of koppies 10 km north of the Magaliesberg, and running parallel to them, belongs to the Pyramid Gabbro-Norite member. Further to the north are the rolling plains and subdued hills of the Nebo Granite. Prominent mountain blocks include the circular ring-complex of the Pilanesberg Complex and the oblong Crocodile River Fragment. Koppies occurring to the west of the Pilanesberg are subdued versions of the Magaliesberg and are not as coherent in structure. The rolling landscape of the granites gives way in the east to the featureless plains of the Springbok Flats, which are broken occasionally by small sandstone knolls, seldom higher than 50 meters.

1.3.3 Geology

An outline of the geology of the field area is contained in the guides to the 1:250000 geological maps covering the area, most importantly the 2526 Rustenburg map (Walraven, 1981). Rocks of the Transvaal Sequence and Bushveld Complex comprise much of the field area and the geology of these formations have recently been reviewed by Eriksson *et al.* (1995). The main geological features of the field area are shown in Figure 1.3. The stratigraphic names used here are generally in accordance with the South African Committee on Stratigraphy (SACS, 1980).

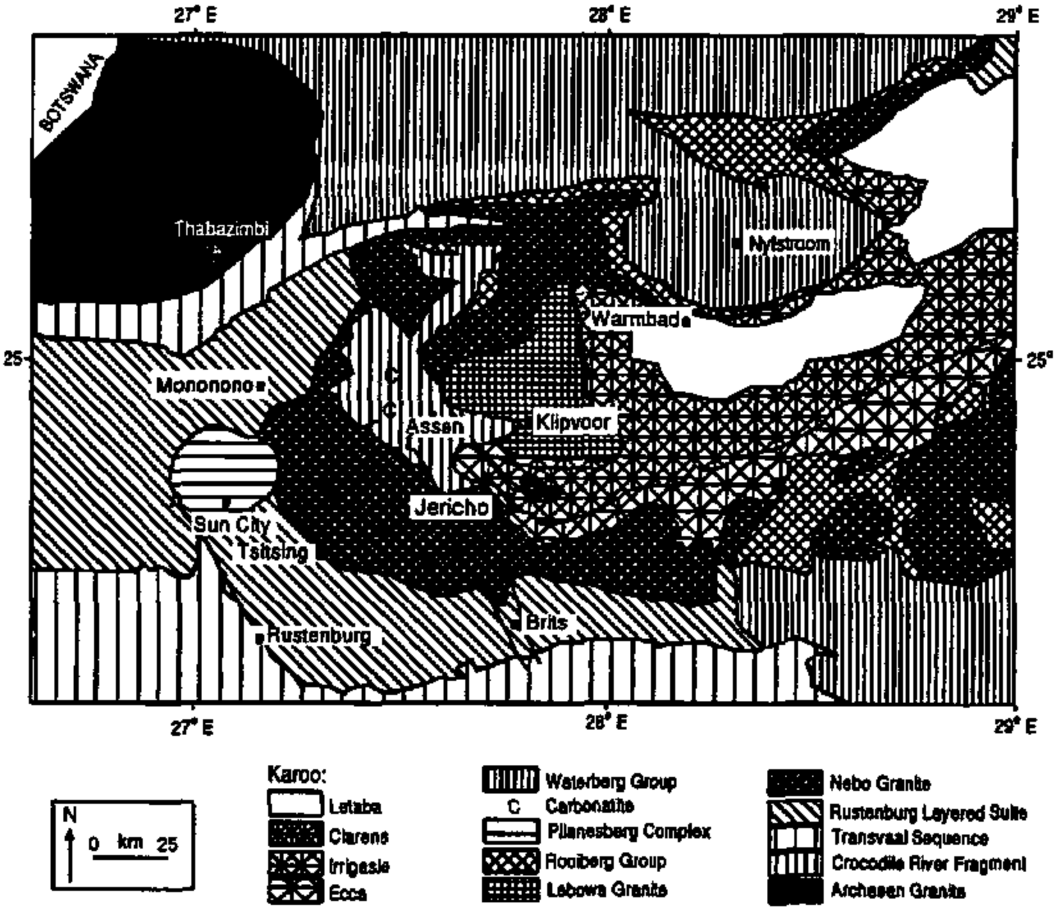


Figure 1.3 Sketch map of the geology of the extended field area.

1.3.3.1 Lithology

The geology of the area is complex and is covered in detail in many publications (e.g. Eriksson *et al.*, 1995). A simple summary is provided here, starting from the oldest rocks. Archaean Granite occurs in the northwest and south of the area, overlain by dolomites of the Chuniespoort Group and clastic sediments of the Pretoria Group, both of the Transvaal Sequence.

Much of the area is underlain by rocks of the Bushveld Igneous Complex (BIC), which in this area was emplaced into the Pretoria Group, most prominently the Magaliesberg Quartzite Formation. The BIC is divided into the mafic rocks of the Rustenburg Layered Suite (RLS), comprising pyroxenites, anorthosites, norites and gabbros; the Rashoop Granophyre Suite; and the Lebowa Granite Suite (LGS). The LGS has most recently been reviewed by Hill *et al.* (1996). The LGS has two principal components in the field area - the Nebo Granite and the Lebowa Granite, the latter being more mineralogically variable and mineralised. The Lebowa Granite is also known as the Bobbejaankop Granite. Sedimentary rocks of the Crocodile River Fragment (CRF), dominantly carbonates, shales and ironstones, are located near Assen. The Rooiberg Group make up the roof rocks of the BIC. They are predominantly siliciclastic volcanic rocks and are often highly mineralised with Zn, Sn and F (Rozendaal *et al.*, 1986; Schweitzer *et al.*, 1995). Clastic and carbonate sediments of Karoo age overlie the eastern parts of the BIC in the field area.

Several alkaline intrusions occur, including the Pilanesberg Complex nepheline syenite (Molengraaff, 1905; Humphrey, 1913; Shand, 1928; Retief, 1962 and 1963; Ferguson, 1973; Lurie, 1974), the associated Pilanesberg Dyke Swarm and several carbonatite complexes, such as Kruidfontein, Bulhoek and Tweerivier (Verwoerd, 1967 and 1993). Two kimberlite pipes have been found in and around the Pilanesberg Complex (Cawthorn, 1988). Ferguson (1973) proposed the Pilanesberg alkaline province. It consists of dykes, small plutonic bodies and the large Pilanesberg Complex nepheline syenite pluton. Several intrusions belonging to the province are carbonatites or are carbonatitic, e.g. those at Spitskop, Kruidfontein and Bulhoek (Harmer, 1992), yet the Pilanesberg Complex has so far been described as being devoid of carbonatite (Verwoerd, 1993). Given the large volume of undersaturated alkaline rocks (probably in excess of 500 km^3), the highly evolved nature of the Pilanesberg Complex, and the occurrence of carbonatite associated with many other southern African nepheline syenites, e.g. those at Schiel, Lofdal and Okorusu (Verwoerd, 1993), it is unusual that no carbonate rocks of igneous origin have been found in close association with the Pilanesberg.

1.3.3.2 Structure

The BIC occurs as a series of lobes of large dimensions, fed by postulated 'abyssal fractures' (Ferguson, 1973). Hamilton (1970) suggested that the BIC was formed by meteorite impact, although this has now been shown to be unlikely because of the absence of shock metamorphic effects in the rocks underlying the Bushveld (French, 1990). Intrusion of the complex has resulted in deformation of the Transvaal Sequence country rocks, so that dips of around 30° towards the centre of the complex occur in the underlying sediments. An extension of the main BIC body is found to the west of the Pilanesberg and is termed the 'western lobe'. The stratigraphy of the BIC is essentially conformable, with local unconformities. Granite overlies granophyre, which in turn overlies the RLS. Meyer and de Beer (1987) used deep resistivity methods to model the structure of the BIC. They confirmed earlier models that the BIC is not one single lopolith, but is instead comprised of separate lobes. They concluded that the RLS directly overlies Transvaal Sequence rocks in the eastern and western Transvaal, but rests on Archaean Granite in the centre of the complex. Walraven (1976) showed that long-wavelength folding of the complex has occurred, with fold hinges trending northwest-southeast in the area around Tsitsing. Faulted contacts of BIC and Pretoria Group sediments occur occasionally, such as the large Rustenburg Fault and the Brits Graben. The contact of the Lebowa and Nebo Granites is obscured by younger Karoo rocks and the nature and location of the contact is uncertain.

The Crocodile River Fragment, correlated in part with the Transvaal Sequence, occurs within the body of the BIC and is variously interpreted as a mega-xenolith, as upfaulted floor rocks or as a roof pendant (Walraven, 1981). An extension of the Brits Graben to the northeast has been traced and appears to link up with the western edge of the Crocodile River Fragment (R. Holdsworth, Council for Geoscience, *pers. comm.*). The Karoo sediments in the area have their deepest extent near the village of Sephai, where they are approximately 430 m thick. The sediments are characterised by a lack of outcrop and flat topography and there is a marked decrease in altitude across the Lebowa Granite/Karoo contact. The Saltpan Crater 40 km northwest of Pretoria had previously been ascribed a volcanic origin (Wagner, 1920, 1922; Feuchtwanger, 1973; Fudali *et al.*, 1973), before a borehole penetrating the structure gave unambiguous evidence for a meteoritic origin (Reimold *et al.*, 1991, 1992). Brandt and Reimold (1995) showed that the fracture patterns in the Nebo Granite around the Pretoria Saltpan impact structure were not significantly different from regional lineations. This indicates that the cratering process has not significantly overprinted the regional fracture system, one of the most important of which has a horizontal to sub-horizontal orientation.

1.3.4 Meteorology

The area is semi-arid, with mean annual potential evaporation (2135 mm) far exceeding mean annual precipitation (MAP) of 622 mm. Figure 1.4 illustrates the variation in MAP over the field area. It will be seen that MAP increases from approximately 500 mm/yr in the west to almost 900 mm/yr in the east. MAP increases towards the southeastern corner (in the vicinity of Pretoria and the Magaliesberg Mountains) and towards the northeast (in the Waterberg Mountains). Increased rainfall station density around Pretoria is apparent, as well as a paucity of stations in the central Bushveld. Figure 1.5 shows the correlation of MAP with elevation - an indication that rainfall has an orographic component. This may explain high MAP values in the Magaliesberg and Waterberg.

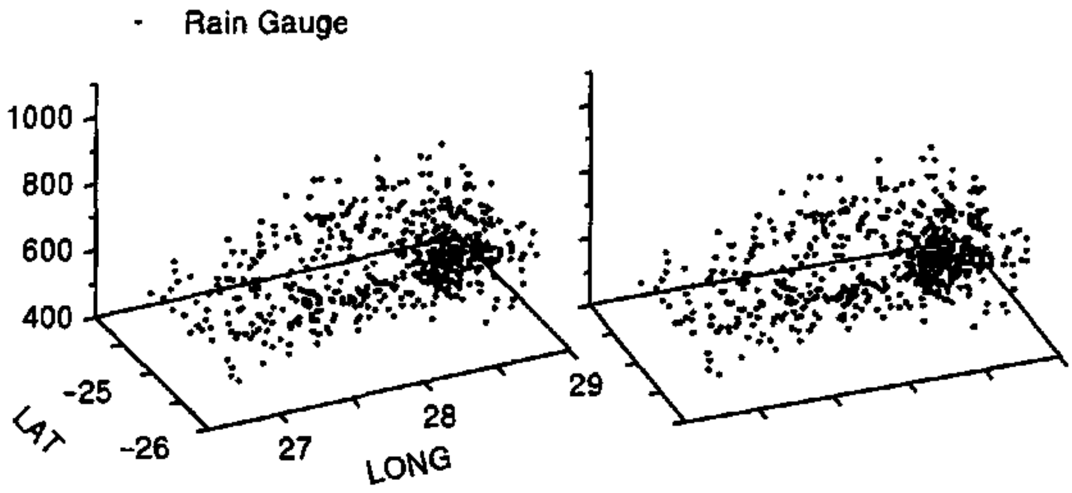


Figure 1.4 *Stereographic* representation of mean annual precipitation (MAP) in the study area.

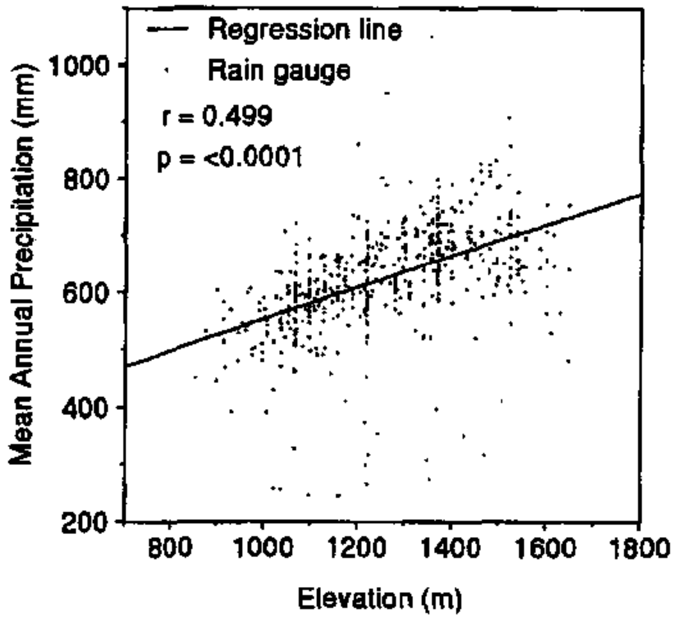


Figure 1.5 Correlation of mean annual precipitation with elevation, indicating an orographic influence.

Mean maximum temperature (MMT) has been found to be of importance in the epidemiology of fluorosis, as water is consumed in greater quantities in warmer climates. MMT is highly correlated with elevation, and this is shown graphically in Figure 1.6. Also shown in Figure 1.6 is the variation of MMT with latitude south. It is apparent that the correlation with latitude is poor, and so in the field area MMT is dominated by the effect of elevation.

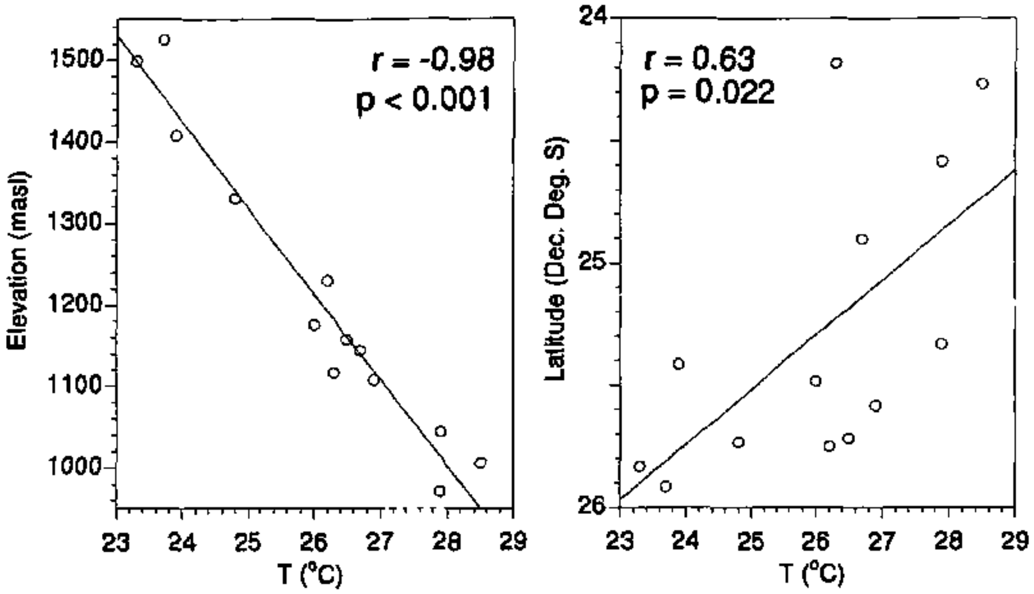


Figure 1.6 Correlation of mean maximum temperature (T) with elevation (in metres above sea level: masl) and latitude (in decimal degrees South). Raw data obtained from the Weather Bureau, Pretoria.

1.3.5 Hydrology

The river system is shown in Figure 1.7. Several perennial rivers cross the area, the Crocodile River being the largest, flowing south to north and eventually joining the Molopo river. Major tributaries of the Crocodile River include the Elands and Tolwane rivers. Many non-perennial streams occur.

1.3.6 Geohydrology

The geohydrology of the field area as a whole has been the subject of few academic studies, although a wealth of unpublished raw data of mixed quality exists in government drilling records. Historically the area had a higher water table than at present, as many of the farms are named after springs which are long since dry. Frommurze (1937) analysed drilling records from the area and drew a series of water yield - water depth curves for each lithology, but these curves are meaningless because of the small number of boreholes which were studied for each lithology. McCaffrey (1993) described the geohydrology of the Pilanesberg Complex as being characterised by surface weathering, fractures and faults in igneous rock, permeable tuff aquifers and lava aquitards. The water table had steep gradients because of the very low transmissivity of the rock mass as a whole.

The review of continental-scale groundwater flow processes by Garven (1995) is of interest. Although based primarily on sedimentary basins, the review is applicable at times to large areas of basement rock. He notes that topographic relief is the dominant mechanism of groundwater flow, with a water table that is a subdued replica of the landscape. Convection cells may operate, driven

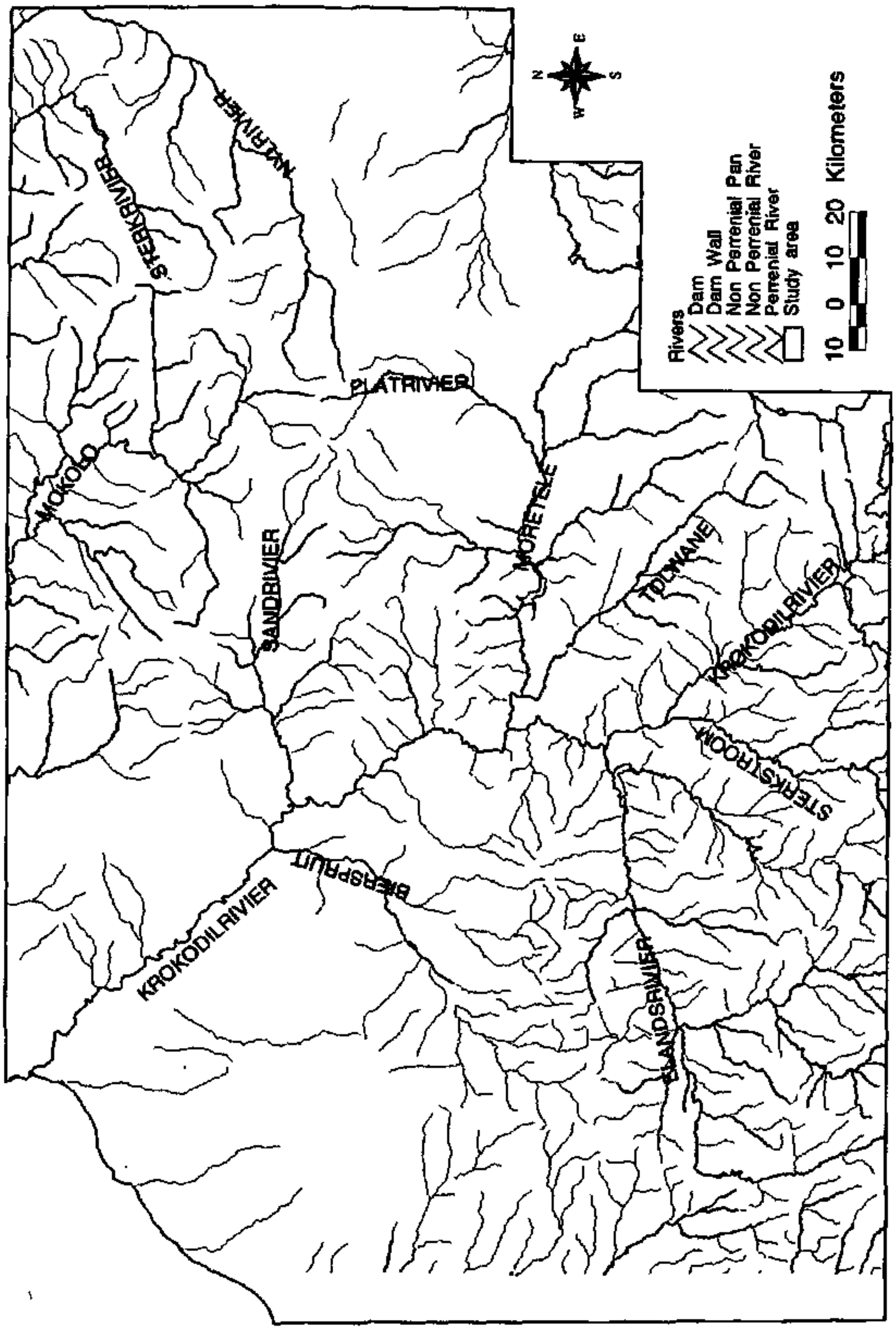


Figure 1.7 Hydrology of the field area. Data supplied by DWAF.

by temperature and salinity gradients. Garven quotes a maximum flow rate in these cells of 1 m/yr, and this seems feasible for large fractures and faults in the Bushveld and Pilanesberg Complexes. The Bushveld Igneous Complex is probably closest to Garven's 'pressure compartments' model, where there is little or no flow between compartments (Figure 1.8).

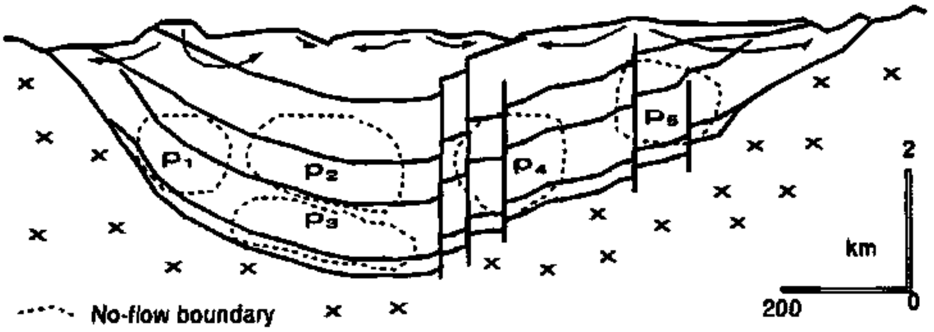


Figure 1.8 Compartmentalisation of a basin with no deep flow. $P_{1\text{-}5}$ refer to hydrogeological compartments. After Garven (1995).

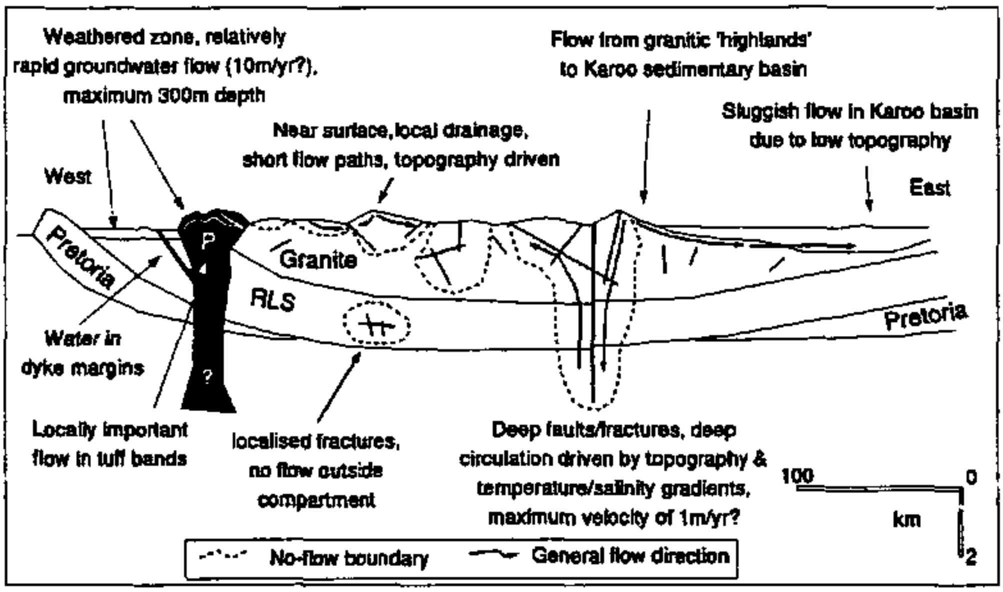


Figure 1.9 . Schematic diagram of geohydrological conditions in the Bushveld area. 'P' is the Pilanesberg Complex.

A conceptual model of groundwater occurrence and flow in the Bushveld area is shown in Figure 1.9. Porosity, permeability and transmissivity is likely to be very low in the rocks of the Bushveld Igneous Complex. Groundwater is generally confined to the upper 150m and is hosted in shallow weathering zones, fractures and faults. Fractures are scarce and the system has a very high rock/water ratio. At greater depths virtually impermeable rocks are encountered. For instance, the platinum mines at Rustenburg, hosted in the southern outcrop of the RLS, are completely dry at 700m and below.

Water-bearing fractures do occur occasionally at great depths: Northam Platinum Mine on the northern outcrop of the RLS has serious development difficulties because of water ingress at depth. The water is contained in three types of features: type I fractures, type II fractures and dyke margins. Type I fractures contain salty water which flows very strongly (10 ℓ/s) when first intersected, but quickly run dry. Type II fractures cause the most disruption, as they continue to flow strongly (25 ℓ/s) for long periods after intersection. The temperature of the water at 1450m depth (approximately sea level) was 55 °C when first intersected, but decreased in temperature steadily over several months. Water has also been encountered around a dyke belonging to the Pilanesberg Dyke Swarm. The mine has intersected all of these aquifer types down to 2000m below the surface, with water temperatures up to 60 °C. A geohydrological interpretation of the type I and II fractures could be that type I fractures are relatively limited in size and do not tap into surface groundwater reservoirs. They are effectively closed fractures; the 'saltiness' of the water (not analysed in this study) suggests they may be remnant igneous fluids. Type II fractures probably continue to the surface, allowing them to drain the 'perched' water table within the first 300m of the surface. Decreasing temperatures with continuous flow suggest that the fractures are supplied from higher, large scale sources.

1.4 Isotope Hydrogeochemistry

1.4.1 Introduction

Although the principal subject of this report is fluoride, it is crucial to understand the behaviour of the groundwaters in which it occurs. Isotope studies in other areas have provided information on the origin of groundwater, the degree to which it has been evaporated, exchanged chemically with carbonates and sulphates, and in some cases its residence time and the identity of the main aquifers through which it has flowed.

Naturally occurring and anthropogenic isotopes provide valuable insights into geohydrological processes (*e.g.* Verhagen *et al.*, 1991, 1974; Blavoux and Letolle, 1995). Determinations of ^{18}O and ^{2}H (also known as Deuterium, D) have been used in conjunction with hydrological modelling and radiogenic isotopes (^{14}C) to estimate palaeoclimates (Heaton *et al.*, 1986), for the location of recharge areas and for modelling water-rock interaction both terrestrially and extraterrestrially (Jakosky and Jones, 1994). McCaffrey (1993) used the isotopes of oxygen and hydrogen to investigate the origin and behaviour of the groundwaters of the Pilanesberg. Other radiogenic isotopes studies, principally ^{3}H, ^{14}C and ^{36}Cl, have concentrated on the estimation of recharge rates in sedimentary basins (e.g.. Verhagen *et al.*, 1974) and continental scale groundwater flow. Measurements of ^{87}Sr/^{86}Sr ratios have been used for several purposes in the earth sciences, chiefly in dating rocks. Increasing use is being made of Sr isotopes for environmental geological purposes, such as dating glacial influences on landscapes (Blum *et al.*, 1994), investigation of water/rock interaction (Collerson *et al.*, 1988; Dia *et al.*, 1995), nuclear waste safety studies (Stuckless, *et al.*, 1991) and for groundwater provenance studies (Verdoux *et al.*, 1995; Banner *et al.*, 1994). No references to strontium isotope studies of groundwaters from the Bushveld could be found in the literature.

The use of ^{3}H as a recharge rate indicator is now limited, due to the decrease in ^{3}H activities, resulting from radioactive decay, to below natural background levels after the ending of atmospheric thermonuclear weapons testing in the 1960's. Blavoux and Letolle (1995) predict that anthropogenic ^{36}Cl, produced during thermonuclear tests in atolls of the Pacific between the years of 1952 and 1958, will supersede tritium as the tracer of choice. This will be due mainly to the large amounts of ^{36}Cl produced in these tests and the longevity of its half life ($\approx$300 kyrs). Although the analysis of ^{36}Cl may have proved useful, no arrangements exist for its determination in South Africa at present.

1.4.1.1 Stable Isotopes of oxygen and hydrogen

The constituent elements of water, hydrogen and oxygen, each have several naturally occurring isotopes. They are used in this report as indicators of processes which have acted on surface and ground water. Analyses of ^{18}O and ^{2}H analyses are expressed in terms of an international standard known as Standard Mean Ocean Water (SMOW), as a δ value in parts per thousand. For instance, for ^{18}O:

$$\delta^{18}O = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \qquad (eq.\ 1.1)$$

where R is the ratio of atomic abundances of ^{18}O to ^{16}O. Most water molecules have a relative atomic mass of 18, composed of $^1H_2{}^{16}O$. The isotopes ^{18}O and ^{2}H have significant natural abundances (0.2% and 0.015%, respectively; Verhagen *et al.*, 1991) and so molecules of $^2H^1H^{16}O$ and $^1H_2{}^{18}O$ also occur. Since these molecules have differing vapour pressures, enrichment of the lighter isotope will occur in the most volatile phase during evaporation, condensation or sublimation. This fractionation effect depends strongly on temperature, which gives rise to seasonal, altitudinal and latitudinal variations in ^{18}O and ^{2}H content of precipitation. For ^{18}O, the effect has been estimated to be between 0.28‰/°C and 0.70‰/°C (Suzuki and Endo, 1995; Yurtsever and Gat, 1981; Heaton *et al.*, 1986; Broecker, 1995). Global δ^{18}O and δ^2H values are linearly related in continental precipitation, as described by the equation

$$\delta^2H = s\ \delta^{18}O + d \qquad (eq.\ 1.2)$$

where s is the slope of the line (with a value of 8 for continental rain) and d is the deuterium excess, defined as the measured δ^2H value minus $8\times\delta^{18}$O and calculated to be between 10‰ and 5‰ (Craig, 1961; Taylor, 1974). The line describing average isotopic content of continental precipitation is known as the meteoric water line (MWL). Most meteoric water has negative δ values, since water vapour is enriched in the lighter isotopes upon evaporation from the ocean surface. Upon evaporation from continental surface water bodies, isotope fractionation increases the proportion of heavier isotopes in the residuum, producing an evaporation line with a slope as low as 2. During the last glacial period, when temperatures were lower on average than they are at present, precipitation was isotopically lighter (Heaton *et al.*, 1986). Because temperature generally decreases with increasing elevation, $\delta^{18}O$ gradients occur in rainfall of between -0.15 to -0.40 ‰ per 100 m elevation. The temperature and elevation effects in isotope hydrology are well known (Craig, 1961; Dansgaard, 1964). More recently, Thorsden *et al.* (1992) found $\delta^{18}O$ to be well correlated with elevation, being between 0.3 and 0.35 ‰/100 m, and for elevation to be the dominant factor in determining $\delta^{18}O$. No correlation coefficient for their regression is quoted. Chemical effects, such as exchange of ^{18}O with $C^{16}O_2$ and $CaC^{16}O_3$, and exchange of ^2H with ^1H_2S, alter the position of the sample on a $\delta^{18}O/\delta^2H$ diagram, Figure 1.10.

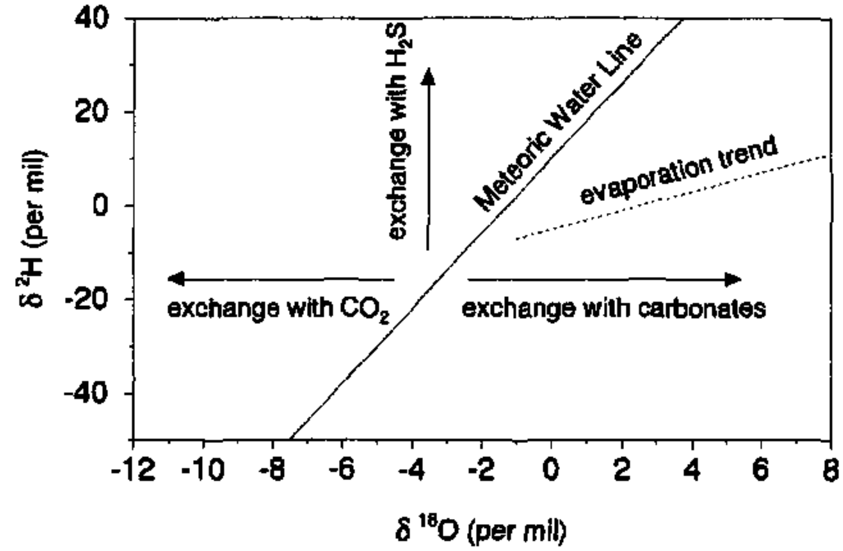


Figure 1.10 $\delta^{18}O/\delta^2H$ diagram for continental precipitation. The meteoric water line is that of Craig (1961). The evaporation trend is hypothetical. ^{18}O is displaced upon interaction with carbonates and volcanic CO_2, whilst ^2H values shift upon exchange with H_2S. After Verhagen *et al.*, 1991.

Few studies have linked the study of high F^- and stable isotopes in groundwater. However, the study by Datta *et al.* (1996) showed that ^{18}O and F^- were positively correlated in some groundwaters in the region of Delhi, India. It was theorised that soil moisture with a long residence time dissolved F^- salts in the soil and, at the same time, underwent partial evaporation, before infiltrating to the water table.

1.4.1.2 Strontium isotopes

It is hypothesised in this report that Sr isotopes can be used to characterise a groundwater body, and can thus be used to trace the movement of groundwater from one aquifer to another. It is necessary, therefore, to review the geochemistry of Sr and its geochemical analogue Ca, as well as the element which gives rise to radiogenic Sr, namely Rb. Ionic radii values are from Ahrens (1952). The ionic which gives rise to radiogenic Sr, namely Rb. Ionic radii values are from Ahrens (1952). The ionic radius of Sr^{2+} (112 pm) is only slightly larger than that of Ca^{2+} (99 pm), and both are divalent cations, thus allowing Sr to replace Ca in many minerals. Strontium is therefore present in many Ca-bearing minerals such as plagioclase, apatite and calcite. Strontium has four naturally occurring isotopes, all stable, namely ^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr, but Sr isotope abundances are variable due to the decay of the naturally occurring radioactive ^{87}Rb to ^{87}Sr. The accepted decay constant for ^{87}Rb is $1.42\times10^{-11}yr^{-1}$, equivalent to a half life ($T_{½}$) of 4.88×10^{10} years (Faure, 1987). The Rb^+ ion has similar ionic radius (147 pm) to K^+ (133 pm) so that Rb can substitute for K in all K-bearing minerals, such as the micas and K-feldspar. Since Sr will partition into plagioclase and Rb will stay in the melt during fractional crystallization of plagioclase from a silicate magma, late stage differentiates tend to have high Rb/Sr ratios. Rocks and minerals with high Rb/Sr ratios will acquire progressively higher $^{87}Sr/^{86}Sr$ ratios over geological time. High $^{87}Sr/^{86}Sr$ ratios are said to be 'radiogenic' (Faure, 1987).

In groundwater, Sr actively participates in carbonate-water reactions in substitution for Ca and is not a conservative tracer. However, several characteristics of Sr can be useful in groundwater studies: different rocks can have very different Sr isotope ratios; Sr is relatively abundant in groundwater; and its isotopic composition can be measured accurately and precisely. For these latter reasons Sr isotopes have been used extensively as tracers of groundwater flow (e.g. Collerson *et al.*, 1988; Stuckless *et al.*, 1991; Banner *et al.*, 1994; Dia *et al.*, 1995; Verdoux *et al.*, 1995). The isotope ratio of dissolved Sr is attained in flowing groundwaters by dissolution of, or exchange with, aquifer materials. The resulting $^{87}Sr/^{86}Sr$ ratio is an integration of all ratios sampled along the flow path. It has been noted that for many water-rock pairs, groundwater Sr is not as radiogenic as its host (McNutt *et al.*, 1990). These differences between Sr ratios in groundwater and bulk aquifer can result from the preferential dissolution of minerals with differing $^{87}Sr/^{86}Sr$ ratios. For instance, mica and K-feldspar both have high Rb/Sr ratios (so that in Bushveld minerals the $^{87}Sr/^{86}Sr$ will be high) and dissolution of these minerals will result in groundwater with a high $^{87}Sr/^{86}Sr$ ratio. Conversely, anorthite has a low Rb content and low $^{87}Sr/^{86}Sr$ ratios: dissolution of anorthite will result in groundwater with low $^{87}Sr/^{86}Sr$ ratios. Of importance to this study is that fluorite and apatite are Sr-rich and Rb-poor (McNutt *et al.*, 1990), are common accessory minerals and are relatively abundant in the fractionated rocks of the study area. Dissolution of these mineral phases will result in a groundwater with a low $^{87}Sr/^{86}Sr$ ratio. No significant fractionation of Sr isotopes occurs during precipitation of minerals, such that the $^{87}Sr/^{86}Sr$ ratios of water and precipitate are virtually identical.

For very young groundwater, mineral dissolution rates will be an important factor in determining $^{87}Sr/^{86}Sr$ ratios, since readily soluble minerals will contribute their Sr first, regardless of Sr content. Table 1.1 shows that Ca-rich feldspar (anorthite) is quickly dissolved, followed by Na-feldspar (albite), K-feldspar and muscovite. Because of the relatively high Sr concentration and rapid dissolution of feldspar, especially anorthite, Sr isotope ratios in groundwater with a short residence time in contact with rock containing anorthite should be low. With time the Sr isotope ratio will increase, due to the dissolution of K-feldspar and mica.

Table 1.1 Dissolution time and typical $^{87}Sr/^{86}Sr$ ratios for 2.05×10^9 yrs old minerals. Weathering rates are for dissolution of a 1 mm crystal at T = 298 K and pH = 5.0, from Lasaga (1984). Sr isotope ratios for muscovite, K-feldspar and diopside from McNutt *et al.* (1990); for biotite and unspecified 'plagioclase' from Hamilton (1977) from the Main Zone of the RLS.

Mineral	Dissolution Time	Relative Concentration		$^{87}Sr/^{86}Sr$
	yrs $\times10^3$	Rb	Sr	
Biotite	*n/a*	very high	very low	1.6067
Muscovite	2,700	very high	very low	>>1.0
K-Feldspar	520	moderate	moderate	0.730-0.800
Albite	80	low	moderate	0.706
Anorthite	0.11	very low	high	
Diopside	6.8	low	low	0.701-0.703

1.4.1.3 Radiocarbon

Libby and others in the 1950's showed that radiocarbon (^{14}C) is present in natural samples in sufficient quantities to allow relatively easy analysis (Libby, 1955). Today the dating of objects by measurement of radiocarbon is now a routine procedure. Analysis of the radiocarbon activity of groundwater has been used extensively to model groundwater residence time and has been reviewed by Mook (1980). The relative simplicity of dating a solid, carbon-bearing object is in contrast to the corrections and assumptions needed when attempting to date groundwaters. As Mook (1980) put it, "*there are many geohydrologists who feel that* ^{14}C *will never provide us with ..... accurate groundwater ages*". Nevertheless, dating of groundwater is frequently attempted and the basic assumptions are summarised here.

The activity of the sample, *a*, is expressed in pmc (percent modern carbon) calculated by comparing the activity of the sample to that of an oxalic acid standard:

$$a = \frac{A}{A_{ox}}\times 100 \qquad \textit{(eq. 1.3)}$$

where A is the measured activity of the sample in disintegrations per minute per gram (dpm/g) and where A_{ox} is 0.95 times the specific activity of NBS oxalic acid (0.95 × 13.56 dpm/g carbon in the year 1950).

Radiocarbon is produced naturally in the atmosphere at a rate of approximately 2.5 atoms/cm^2/s by the reaction of slow cosmic ray neutrons with stable ^{14}N. The variation of the cosmic ray flux over long time periods (Sonnet and Finney, 1990) means that radiocarbon production has not been entirely constant. For geohydrological studies, this variation is swamped by other uncertainties and can safely be ignored.

Anthropogenic alteration of atmospheric radiocarbon activities has occurred. Firstly, combustion of fossil fuels has reduced tropospheric ^{14}C levels by about 10%. Secondly, since the 1960's, atmospheric thermonuclear weapons testing has radically increased the radiocarbon activity of the world's atmosphere. Groundwater samples with greater than 100 pmc are now quite possible.

1.5 Workshop on Fluoride and Fluorosis

A one-and-a-half day workshop on the status of South African research on fluoride and fluorosis was organised by Mr L. McCaffrey as part of this project. The workshop was held on the 10-11th August, 1995 at the Manyane Conference Centre, Pilanesberg National Park, North West Province. On the first day ten papers were presented on a very wide range of topics dealing with fluoride and fluorosis, and the meeting was attended by thirty-three delegates. On the 11th August a half-day field trip provided delegates with an opportunity to visit sites of geochemical, geological and geohydrological interest in the Pilanesberg National Park.

A copy of the programme, abstracts and a list of delegates is included in Appendix A12. Only two of the authors (Mr B Mothusi and Dr JB du Plessis) submitted copies of their papers, and these are also included in Appendix A12.

2 MATERIALS AND METHODS

This chapter describes the methods used in sampling, preparation and analysis of water, rock and soil samples.

2.1 Groundwater

2.1.1 Sampling and field tests

Groundwater sampling took place during July and September 1993 and in October 1994. Sample locations were selected primarily to give an even spread over the field area and secondly to fill in spatial gaps in the existing Department of Water Affairs of the former Bophuthatswana groundwater database. This effectively meant sampling took place in agricultural areas rather than villages. Because of the tribal system of government in the area, the Paramount Chief of each area had to be consulted before moving into his territory. On two occasions a full tribal *Kgotla* was called, which delayed sampling for several days. A headman or tribal policeman was often assigned to help in locating isolated boreholes and an interpreter was employed in the first field season to assist in communication. A two-wheel-drive saloon car was used as transport.

2.1.1.1 Sampling protocol

A protocol for water sampling was formulated before entering the field and was adhered to as much as possible. Details of the sampling protocol are given in Appendix A11.

2.1.1.2 Field tests

Groundwater was analysed in the field for pH, Electrical Conductivity (EC) and Dissolved Oxygen (DO) using solid state probes and a voltmeter. A Corning 'general purpose combination electrode', a 'conductivity/TDS sensor' and 'DO sensor' probes connected to a Ciba-Corning 'Checkmate 90' portable millivoltmeter were used for pH, EC and DO measurement, respectively. Standards used were Ciba-Corning pH buffers at 4.00, 7.00 and 10.01; Corning 12.88 mS conductivity standard; and Ciba-Corning zero oxygen solution. Each day the pH probe was recalibrated using a 2 point calibration, the DO meter was calibrated whenever near fresh water, and the EC probe was recalibrated every morning. To measure pH, EC and DO, a 50 ml beaker was rinsed with deionised water, rinsed with groundwater in order to reduce cross-contamination, then filled with 50 ml of groundwater. Groundwater was prepared for temperature measurement by filling a 50 ml glass beaker full of fresh, unfiltered ground water, allowing the glass of the beaker and thermometer to equilibrate to the water temperature, then refilling with fresh groundwater and quickly measuring temperature, all out of direct sunlight. To measure total alkalinity, two drops of screened methyl orange indicator were added to 50 ml of groundwater in a conical flask. The mixture was then titrated to the green/purple colour change using an automatic levelling pipette filled with 0.1 M hydrochloric acid. Fluoride was measured each evening at the field base (see sections 2.1.2.2 and 2.1.3.1).

2.1.2 Sample preparation

2.1.2.1 High Pressure Ion Chromatography (HPIC)

Samples with a high EC, as determined from field measurements, were diluted so that their EC was reduced to less than 200 mS/m. This was done to prevent overloading of the analytical column and conductivity detector. Highly coloured samples were passed through a Dionex 'Onguard P' filter to remove organic acids which might degrade the column.

2.1.2.2 Fluoride ion selective electrode

A Total Ionic Strength Adjustment Buffer (TISAB) was used to bring all samples to approximately the same ionic strength and pH (Frant and Ross, 1968; Harwood, 1969; Campbell, 1987). The TISAB used in the field contained 1 mg/ℓ CDTA (1,2,Cyclohexylene Dinitrilo Tetraacetic Acid or 1,2,Cyclohexane Diamine N,N,N,N-Tetraacetic Acid, known commercially as Titriplex IV) as a chelating agent to break up aluminium fluoride complexes (Harwood, 1969). In later experiments CDTA was omitted from the TISAB in order to gauge its effect (discussed in a later section). The other components of the TISAB were 58.5 g/ℓ NaCl, 15 g/ℓ glacial acetic acid and 66 g/ℓ sodium acetate.

2.1.2.3 Iodide

A 5 ml sample of the acidified water sample was put into sample-rinsed plastic 5 ml phials and sent to the South African Institute for Medical Research (SAIMR) for analysis.

2.1.2.4 Stable isotopes

Preparation took place in the stable isotope laboratory at UCT, supervised by Dr. Chris Harris. The preparation technique used for O was that of Socki *et al.* (1992). Approximately 1.5 ml of sample was frozen into a pre-evacuated glass phial and then evacuated. The phial was then filled with 0.5 atmospheres of CO_2 and put into a water bath at 25°C for 4 hours to allow equilibration between O in the CO_2 and H_2O. The CO_2 was then sub-sampled into a break-seal glass tube. Hydrogen was obtained by reduction of 1 µl of water sample by Zn at 450°C for 30 minutes, and the resulting H_2 sealed in a break-seal glass tube.

2.1.2.5 Radiocarbon

Preparation took place in the Schonland Nuclear Research Centre at Wits University, under the supervision of Professor Balt Verhagen. The precipitate had to be converted to ethane, which is easily ionised in the detectors. The $BaCO_3$ in the precipitate was first converted to CO_2 using orthophosphoric acid. The gas was then converted to acetylene using lithium at 600°C. Acetylene was catalysed to ethane by palladium metal and stored in large glass bulbs for analysis.

2.1.2.6 Strontium isotopes

All preparation took place in the clean laboratory in the radiogenic isotope facility at UCT, and was performed by Mr. Justin Underwood. The cations in the samples were converted to chloride salts by repeated drying and dilution with 5 ml of 6.2N HCl. The dry residue was dissolved in 0.7 ml of 2.5N HCl and centrifuged to remove insoluble matter. Sr was separated from other cations by ion chromatography. The separation of Sr from other cations had been calibrated using chloride salts. The resulting Sr chloride solution was converted to a nitrate solution by repeated drying and addition of 7M nitric acid. The solution was finally diluted with 0.5N phosphoric acid and 2% nitric acid and evaporated onto a tantalum filament.

2.1.3 Analysis

2.1.3.1 Fluoride ion selective electrode

Groundwater F^- concentration was measured every evening at the base camp, where a rudimentary laboratory was established. A Corning fluoride ion selective electrode (FISE) was used (Frant and Ross, 1966), connected to a Corning 'Ion Analyser 255' digital millivoltmeter. Fluoride was remeasured at UCT using TISAB with and without CDTA.

2.1.3.2 Major ions

High pressure ion chromatography (HPIC) was used to determine the concentration of major ions in groundwater. Tables 2.1 and 2.2 show the experimental conditions used for anions and cations, respectively. A Dionex DX300 ion chromatography system controlled by AI-450 software was used. The analytical column used for the majority of anion analyses was an AS4A separator column with AG4A guard column, supplemented on occasion by an AS11 separator column, and recently replaced by an AS4AC column.

2.1.3.3 Iodide

Analysis for iodide was conducted by the South African Institute for Medical Research using a Waters High Pressure Liquid Chromatograph, with a Ag electrode as a detector. Standard stock solution was 1000 ppm I^-, prepared by dissolving 0.118 ± 0.001 g NaI in 100 ml Milli-Q water.

2.1.3.4 Stable isotopes

Stable isotopes were measured on a VG 602E gas-source mass spectrometer. The external standards used were provided by Dr T. Venneman of the University of Michigan, and were deionised water and snow from Michigan.

2.1.3.5 Radiocarbon

A gas-proportional counter was used to analyse for radiocarbon. Measurement of each sample took place on three occasions separated by approximately a week, to differentiate between disintegrations due to radiocarbon and those due to radon, which have the same energies. Since radon has a much shorter half life than radiocarbon, the radon content is that part of the scintillation count which measurably reduces over a month or two and can therefore be corrected for. Standards were radiocarbon-free groundwater from dolomites in the Pretoria area.

Table 2.1 Experimental conditions used in the determination of anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}). ASRS = Anion Self Regenerating Suppressor. The Waters HPLC method was used by the South African Institute of Medical Research.

Instrument	**Dionex DX300 HPIC**			**Waters HPLC**
Experimental conditions\Method	Sodium tetraborate	Sodium carbonate/ bicarbonate	Sodium hydroxide	
Eluent 1	5.0 mM $Na_2B_4O_7$	1.7 mM Na_2CO_3 1.8 mM $NaHCO_3$	21 mM NaOH	4 mM potassium hydrogen pthalate
Eluent 2	50 mM $Na_2B_4O_7$	none	none	none
Column	AS4A	AS4A*	AS11	IC-pak A
Flow rate (ml/min)	2.0	2.0	1.0	2.0
Detector	Conductivity	Conductivity	Conductivity	Electrochemical
Suppressor	ASRS	ASRS	ASRS	none
Run Time (min)	10	7	7	15
Sample Loop Volume (µl)	50	50	50	100
Best For:	Accurate fluoride analysis	Routine analysis of major anions	fast analysis of major anions in low carbonate sample	Analysis for iodide

* Replaced in later analyses by an AS4A-SC column

Table 2.2 Experimental conditions used in the determination of cations (Ca^{2+}, Na^+, Mg^{2+} and K^+). CSRS = Cation Self Regenerating Suppressor. MSA = Methyl sulphonic acid.

Experimental conditions\Method	A	B
Eluent	20 mM MSA	22 mM MSA
Column	CS12	CS12A
Flow rate (ml/min)	1	1
Detector	Conductivity	Conductivity
Suppressor	CSRS	CSRS
Run time (min)	15	14
Sample loop volume (µl)	25	25

2.1.3.6 Strontium isotopes

The isotopes of strontium were analysed using a VG Sector solid-source mass spectrometer, run in dynamic multi-collector mode. The measured $^{87}Sr/^{86}Sr$ values were normalised to $^{88}Sr/^{86}Sr = 0.1194$, to correct for mass fractionation.

2.2 Rock and soil

2.2.1 Sampling

Rock and soil sampling took place during June 1994. The objective was to collect at least three samples of each major rock type and associated soil in the area, to provide an indication of the variability of the lithology and geochemistry of each rock and soil type.

Rock and soil samples were taken in pairs, with the samples usually located not more than 10 m from each other. Whenever possible, samples from road-cut profiles were taken, so that soil directly overlying fresh rock could be taken. More often the soil sample was taken in the vicinity of a fresh outcrop of rock. At least 1 kg of rock sample was taken, and this was increased up to 5 kg when the rock became coarse grained. A 5 kg sledgehammer and 'Estwing' geological hammer were used in the field. The rocks were broken into pieces with long axes not greater than 20 cm and with all weathered surfaces trimmed off by hammer. Soils were sampled from the top 20 cm either by spade or hand-held auger. No attempt was made to sample vertically. The rationale for taking a sample from the surface was that it would be the most easily accessible and the driest part of the soil. The disadvantage of taking a topsoil sample was that it is the part of the soil subject to the most transport and input of anthropogenic, aeolian and fluvial material (Schloemann, 1995). Forty two rock samples and 40 soil samples were obtained by this method. Difficulties were encountered in sampling Karoo rocks, since they produce a flat relief with few rock outcrops. Only two samples from the Karoo Sequence were collected. Sample site details are shown in Appendix A2.

2.2.2 Sample preparation

2.2.2.1 Drying

The samples were taken in the middle of the Transvaal winter (the dry season), in the heat of the day, and were therefore thoroughly dry; no artificial drying took place before crushing. Indeed, to 'air dry' samples from so far inland at a coastal site may very well have caused gross contamination from airborne salt particles. Contamination in this manner was guarded against for the duration of the analyses.

2.2.2.2 Crushing and milling

Rock samples were first split into sub 2 cm chips using a hydraulic splitter, then crushed to sub 5 mm chips in a jaw crusher (Mn steel ribbed plates). Soil samples were generally fine grained and when pebbles were present, they were broken into sub 5 mm pieces using a geological hammer. Both rock and soil samples were then milled for 3 minutes at high speed in either a carbon steel or Ni-Cr alloy Siebtechnik swing mill. This reduced all grains to less than 50 µm diameter. Problems were experienced with the milling of soil from sites 7 and 9, both of which are examples of 'black turf'.

The plastic nature of these soils caused the mill to smear the material onto the side wall, rather than to disaggregate it. The samples were therefore disaggregated manually with a geological hammer.

2.2.2.3 XRFS briquettes

For trace element analysis using X-ray fluorescence spectrometry, 6 g of the powdered sample were pressed into a 30 mm diameter boric-acid backed briquette using a hydraulic press and 7-10 tons pressure on the ram. For sandy samples, which tended to disintegrate under vacuum, one drop of a Mowiol solution (2% Hoechst Mowiol N 70-80 in distilled water) per gram of sample powder was added as a binder. The Mowiol solution was mixed thoroughly with the sample powder in an agate mortar and pestle before pressing. Before XRFS analysis all briquettes were placed under vacuum in a vacuum desiccator for at least an hour to both degas them and to induce failure in the desiccator rather than inside the spectrometer. The soil briquettes were observed to be generally more water absorbent than the rock briquettes, as shown by the longer times taken for the vacuum in the spectrometer to reach the specified level.

2.2.2.4 XRF fusion disks

Fusion disks were prepared according to the method of Norrish and Hutton (1969). Approximately two grams of the sample powder were weighed out accurately to 5 decimal places into a clean weighed platinum crucible. To determine loss of adsorbed water (H_2O^-), the sample was dried at 110°C for at least 4 hours, cooled, and the mass was measured again. To determine the combined water, CO_2 and organic material lost on ignition (LOI), the crucible was then placed into a furnace at 850°C overnight, cooled and the mass recorded. Other preparation schemes undertake the latter step at 950°C or 1000°C, but because several samples were syenitic with large amounts of fluorine and such samples melt at temperatures >950°C, it was decided to roast all samples at temperatures below the melting point of these rocks.

Duplicate fusion disks were made by mixing 0.28 ± 0.002 g of sample with 1.5 g (± 0.02 g) Johnson Matthey Spectroflux 105 and 0.02 g $NaNO_3$ (as oxidant). The mixture was fused for approximately 10 minutes and thoroughly mixed in a platinum crucible before being poured onto a heated graphite mould and compressed with an aluminium plunger. Only sample RO19 required an extra long period of fusion.

2.2.2.5 XRD

An excess of the $-50\ \mu m$ powdered sample was loaded onto an indented aluminium holder and pressed into place with a spatula. The excess was removed using the edge of the spatula, so that the powder surface was level with that of the holder.

2.2.2.6 Electron microprobe

The rock was cut into thin sections, polished, then washed in soapy water, deionised water and acetone and air dried. Minerals of interest were identified using a petrographic microscope and were circled with a technical drawing pen. A sketch of each section was made, identifying mineral locations. The section was then coated with carbon in an electric arc coater and mounted in a conducting frame for analysis.

2.2.2.7 Stable isotopes

Carbon and oxygen isotope ratio analyses of the bulk carbonate were made using the method of McCrea (1950). Powdered samples were reacted with orthophosphoric acid at 50°C overnight and a value of $\alpha_{CO2\text{-}calcite}$ of 1.009 was assumed (Al-Aasm et al., 1990). The $\alpha_{CO2\text{-}strontianite}$ would be expected to be similar to $\alpha_{CO2\text{-}calcite}$, given the geochemical similarity of the two minerals and the closeness of the α *vs.* temperature curves for the two minerals equilibrium with water (Figure 13, Friedman and O'Neil, 1977). An internal standard (Namaqualand Marble) was used to normalise the data to the V-SMOW and V-PDB scales (Coplen, 1995).

2.2.3 Analysis

2.2.3.1 X-Ray Fluorescence Spectrometry (XRFS)

Major and trace element concentrations were measured using a Siemens SRS303AS XRF spectrometer. Standard instrumental conditions (Willis, 1995, listed in Appendix A3) and in-house and certified reference materials were used for calibration. A special calibration fusion disk containing 6% SrO was prepared using $SrCO_3$, NIM-G and the method outline above, for the analysis of the high Sr samples.

2.2.3.2 X-Ray Diffraction (XRD)

Mineral phases were qualitatively determined using a Philips PW1130/90 X-ray diffractometer using CuKα radiation, a LiF(200) monochromator, a NaI scintillation counter, pulse height selection, and generator settings at 25 kV and 40 mA. The JCPDS PDF-2 computer database was used to identify mineral phases based on d-values and relative peak intensities.

2.2.3.3 Carbon dioxide (CO_2)

The equivalent CO_2 contents of several samples were determined using the "Karbonat-bombe" method of Birch (1981). Concentrated hydrochloric acid was added to a powdered rock sample in an airtight perspex pressure vessel, liberating CO_2 from the carbonate minerals. The resultant CO_2 pressure, measured within 1 minute of the addition of acid, is proportional to the $CaCO_3$ and $SrCO_3$ content of the sample. Dolomite [$(CaMg)CO_3$], if present, reacts more slowly and so does not contribute significantly to the initial pressure increase.

2.2.3.4 Gas-source Mass Spectrometer

Two different mass spectrometers were used: a VG602E gas source mass spectrometer with dual inlet and double collectors; and a Finnigan MAT252 multi-collector instrument.

2.2.3.5 Solid-Source Mass Spectrometer

The instrumentation used was a VG Sector 7-collector thermal-ionisation mass spectrometer, at the Radiogenic Isotope Facility at UCT, operated by Dr Steve Richardson and Justin Underwood. 200 ratios were measured per bead (*i.e.* per sample) and approximately 170 ratios were accepted for calculating the final Sr isotope ratios.

2.2.3.6 Electron microprobe

Analysis of mineral phases was undertaken using a CAMECA Camebax Microbeam electron microprobe. Carbonate minerals were analysed according to the parameters of Lane and Dalton (1994), with an accelerating voltage of 15 kV, a final beam current of 14 nA and a beam diameter of 10 µm. Silicate minerals were analysed using the same accelerating voltage, but with a beam current of 40 nA. Data from both mineral types were reduced using a ZAF correction algorithm.

2.3 Leaching experiments

The solubility of fluoride bearing phases in rock and soil samples from the field area was investigated using leaching experiments. Many different methods have been published for the leaching of soil, and there is no widely accepted standard. Various preparation methods prior to leaching of soil were evaluated by Schloemann (1995); all techniques have advantages and disadvantages associated with them and it is apparent that no technique is universally optimal (Table 2.3). For this reason it was decided not to use published experimental conditions, but rather to optimise the conditions for the current set of sample compositions, method of analysis and detection limits. The philosophy behind the selection of the experimental conditions is discussed below.

Table 2.3. Comparison of sample preparation techniques prior to the extraction of soluble elements from soil samples (modified after Schloemann, 1995).

Method	**Sieved soil, coarse fraction discarded**	**Sieved soil, coarse fraction crushed to ~2 mm**	**Untreated soil**	**Powdered soil (this study)**
Comparison with literature	good	reasonable	impossible	impossible
Comparison with whole-soil analysis	limited	good	good	good
Pretreatment time	little	long	none	none for this study
Representative subsampling	possible	difficult to possible	difficult to impossible	easy
Increases relative surface area	limited	yes	no	yes
Simulation of *in situ* conditions	limited	reasonable to limited	reasonable	limited

The *maximum* concentration of fluoride soluble by natural water from rock and soil was of prime interest. Powders of rock and soil had already been prepared for XRF analysis and so it was decided to use these powders as the raw material for the experiment. Because the powders have been milled to nominally the same grain size (~50 microns), it was possible to add constant volumes of leachate and be able to assume a constant surface-area to leachate-volume ratio. This is the assumption in 'saturated paste' leaching experiments.

A suitable mass of sample (10 ± 0.1 g) was chosen to fit into the 125 ml plastic bottles in which the experiment was carried out. It was decided that a 1:2 ratio of sample to leachate was optimal. A lesser ratio would mean that although fluoride concentrations might be higher, lengthy vacuum extraction of leachate would be needed to achieve conveniently sized samples for analysis. A higher ratio would entail lower concentrations of fluoride and more samples below the detection limit. The volume of leachate (20 ± 0.05 ml) was added to the sample using a digital burette. This volume of leachate gave a convenient volume (between 5 and 15 ml) for analysis after filtration.

Selection of the leachate composition was of importance. Since the leaching experiment was an attempt to *broadly* simulate natural conditions, an 'artificial rainwater' leachate was formulated and used. Two litres of deionised water were left to equilibrate with the atmosphere for 24 hours at approximately 20°C in a beaker covered with perforated polyethylene film on a shaking-table, becoming weak carbonic acid through the solution of atmospheric carbon dioxide. Because of the spatial constancy of carbon dioxide concentrations in the sea-level atmosphere throughout the world, this would be an ideal method of preparation of leachate for standard leaching experiments, were it not for the variation in salt particle flux from site to site and short-term temporal variation in barometric pressure.

The duration of the leaching experiment was set at 96 hours, which, although not allowing for full equilibrium dissolution (Brown and Roberson, 1977), would allow the dissolution of soluble and sparingly soluble phases.

The sample containers were shaken vigorously along their long axes on a shaking table to facilitate mixing of solid and leachate. The temperature was not controlled, but probably varied between 15 and 25°C. After 96 hours the samples were allowed to settle for 2 hours, the supernatant liquid was filtered through 'Whatman qualitative medium crystalline' filter paper, then centrifuged for 20 minutes at 3000 revolutions per minute, corked and stored upright. Analysis for fluoride using FISE took place within 4 hours of the end of the leaching period.

A pilot experiment was undertaken with a variety of soils with high- to low-fluorine concentrations as determined by XRFS. The experimental conditions were as detailed above, apart from the sample to leachate ratio, which was 1:1, and the duration of leaching, which was 48 hours. The results shown in Table 2.4 indicated that even samples with very low total fluorine concentrations would yield a fluoride concentration in leachate above the detection limit, when using the experimental conditions detailed above.

Table 2.4. Results of a pilot experiment showing feasibility of the experimental conditions for rock and soil leaching experiments.

Sample No.	SO3	SO8	SO20	SO2	Blank
Lithology	Foyaite	Granophyre	Granite	Norite	Quartz
Total F (ppm)	2340	1130	177	<62	<62
Leachate pH	6.67	7.32	7.28	7.24	6.23
Leachate F^- (mg/ℓ)	0.51	1.03	0.15	0.07	0.06

2.4 Data quality

2.4.1 Groundwater Data Quality

2.4.1.1 Ionic analysis

Frant and Ross (1966) proposed the use of an ion selective electrode to measure fluoride activity in solution. The use of a total ionic strength adjustment buffer (TISAB) brings all solutions to approximately the same ionic strength and pH (≈5.5) and is intended to break up aluminium-fluoride complexes which might otherwise reduce the fluoride activity. Cyclohexane diamine tetraacetic acid (CDTA) was proposed by Harwood (1969) as an effective de-complexing agent. It is manufactured by Merck and costs approximately R7 000/kg.

The detection limit when using standards at 1 and 0.5 mg/ℓ is approximately 0.1 mg/ℓ (Figure 2.1). Accuracy at this concentration is within 25% relative, whilst precision is approximately 1% (Figure 2.1). In the field the lowest routinely used standard was 0.1, implying that the detection limit in the field was approximately 0.05 mg/ℓ. Other studies (Barnard and Nordstrom, 1982a) have shown that under ideal circumstances the lower limit of detection for the FISE is between 0.3 and 1 µg/l. Such low limits of detection had no relevance in this study.

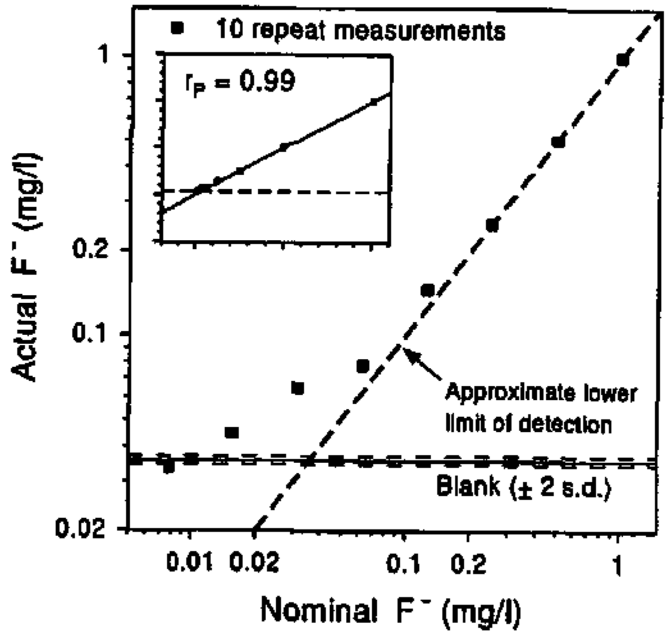


Figure 2.1. Accuracy, precision and lower limit of detection of FISE using standards at 1 and 0.5 mg/l. Instrumental precision error bars are smaller than the markers.

Fluoride was measured in fifty acid-preserved samples using FISE with CDTA in the TISAB and without. The results are shown in Figure 2.2.

It can be seen that the results are in excellent agreement, although at higher concentrations (> ~0.3 mg/ℓ) there is a consistent and slightly higher determination of F^- using CDTA. When the differences between the two analyses are plotted against Al concentrations, however, many of the samples with significant differences have very low Al concentrations (Figure 2.3).

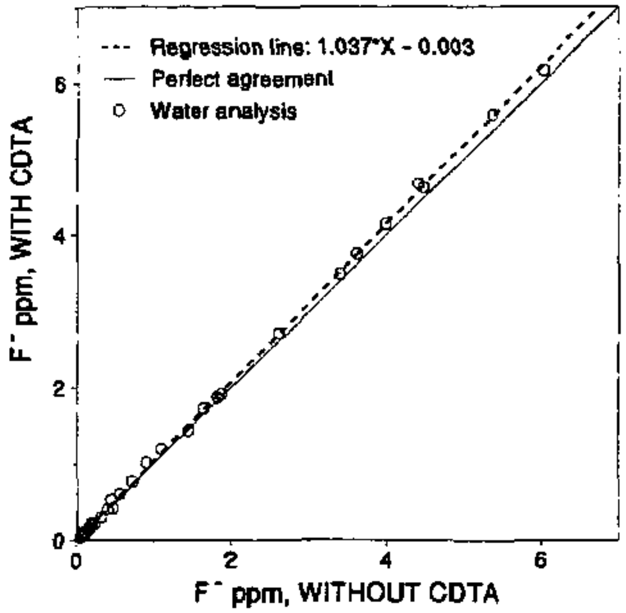


Figure 2.2 Fluoride concentration determined by ion selective electrode, using TISAB with and without CDTA.

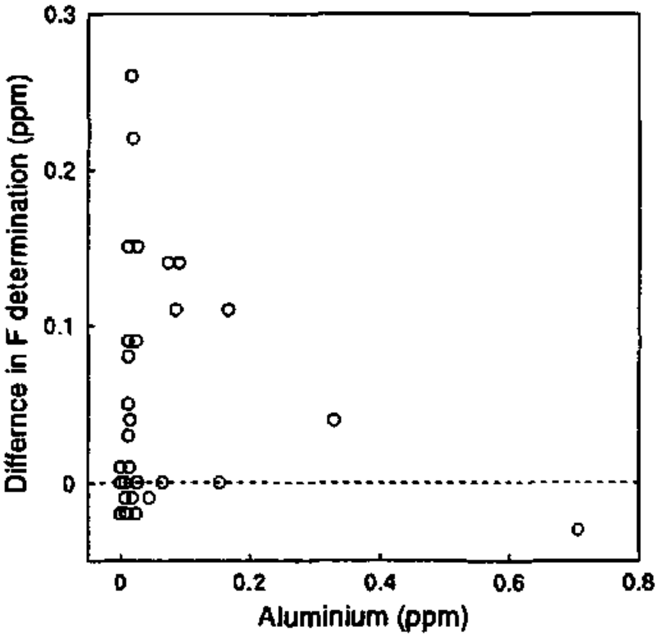


Figure 2.3. Difference in fluoride determination when using a buffer with and without CDTA on samples with differing Al concentrations.

There is no correlation between the difference in F^- determinations and the Al content of the water sample. Differences in F^- determination, therefore, can not be attributed to Al complexation in these samples.

Al solubility increases at both high and low pH levels, and is lowest between pH 5-8 (Mason and Moore, 1966). Since the subset of samples was acidified only *after* filtration, Al concentration could not have been increased by solution of suspended aluminium-containing sediment particles. Groundwaters in the field area have a near-neutral pH and so are unlikely to have high Al concentrations. This implies that Al complexation is unimportant in the determination of unacidified samples with an original pH close to 7. It is suggested that only in more acidic and basic groundwater, where aluminium solubility is enhanced, will CDTA be a useful and cost-effective additive to TISAB.

High pressure ion-chromatography (HPIC) has been used extensively in this project for the routine determination of major anions and cations. A sample chromatogram for anions is shown in Figure 2.4, using a Dionex AS4A analytical column. It can be seen that when a sodium carbonate-bicarbonate eluent is used, the chloride peak is invariably well defined and chloride concentration is easily determined. Nitrate and nitrite are also resolved with sharp peaks. Phosphate occurred in concentrations generally lower than the detection limit. Sulphate was very well resolved, but suffered somewhat from peak broadening. Iodide and bromide occur at very low levels in most of the samples. Iodide elutes as a broad peak after sulphate and was generally below the background variation of the baseline. It was found that, under the operating conditions recommended by the manufacturers, the AS11 separator column suffered from bunching of analytes, reduced peak definition, as well as a severe interference from carbonate.

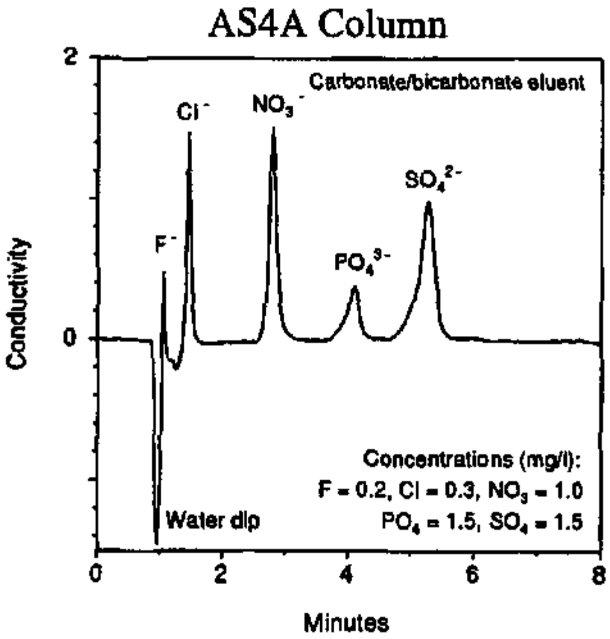


Figure 2.4. A sample of a chromatograph using sodium carbonate and bicarbonate as eluent, showing excellent resolution. However, note the proximity of the water dip to the fluoride peak.

Consistent differences in the determination of fluoride in groundwater by HPIC and FISE have been reported by some laboratories, and so an investigation was undertaken to compare the results of the two methods (McCaffrey, 1994). The results of the two techniques for all water samples taken in this study are shown in Figure 2.5. It will be seen that HPIC using a sodium carbonate/bicarbonate eluent often over-estimated the concentration of fluoride relative to FISE values.

Different standards were used for HPIC and FISE. However, when the HPIC standard was analysed by FISE the measured value was identical to the given value within 1% relative. No normalisation has therefore been applied. The presence of a water dip in the carbonate/bicarbonate chromatogram generally complicates the process of determining a baseline for the fluoride peak and is the probable cause of the overestimation of F⁻.

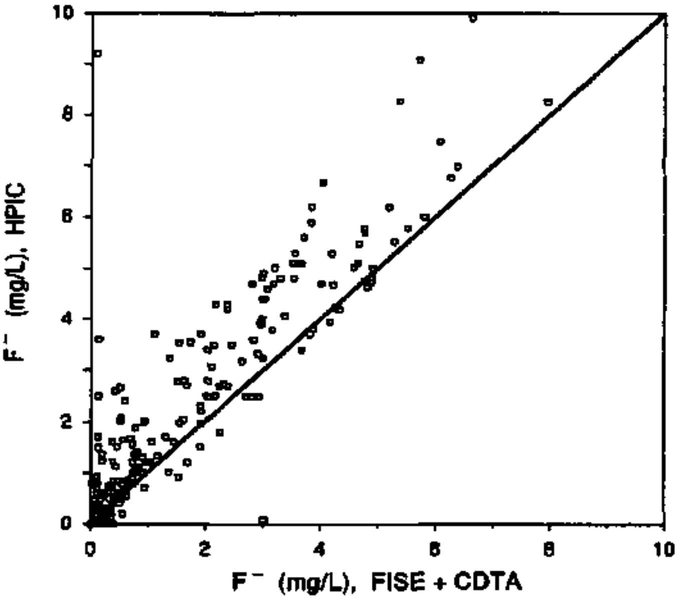


Figure 2.5. Fluoride determinations on the same samples by high pressure ion chromatography and ion selective electrode. HPIC determinations are consistently higher.

The use of sodium tetraborate eluent greatly improves the relationship of HPIC to the FISE determination of F⁻ (Figure 2.6), and was used on the more inaccurate carbonate/bicarbonate determinations. Fluoride elutes well away from the water dip and all other major anions (Figure 2.7). The baseline is even and easy to determine either manually or automatically. Acetate does give a minor interference (on all columns used in this study), but its presence in natural waters is rare and at very low levels and is not considered a serious problem (Figure 2.8). The use of sodium tetraborate as an eluent gives an accurate and precise determination of fluoride in solution but is rather slow and other anions cannot be determined in the same run.

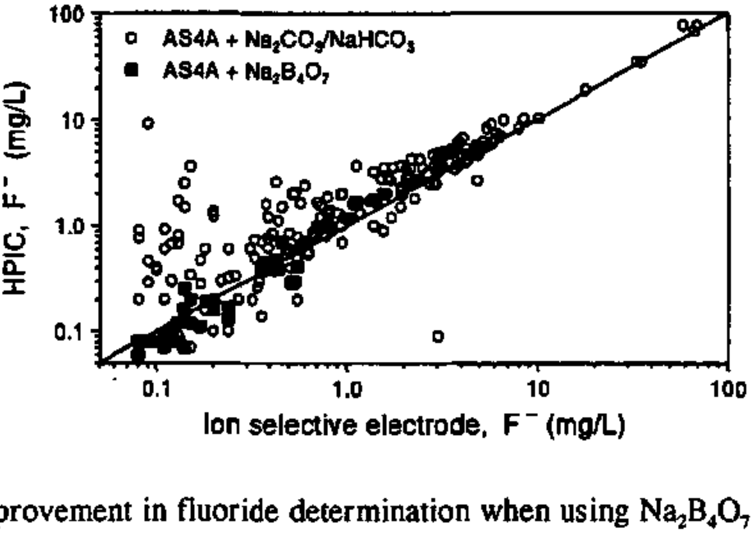


Figure 2.6. Improvement in fluoride determination when using $Na_2B_4O_7$ as an eluent.

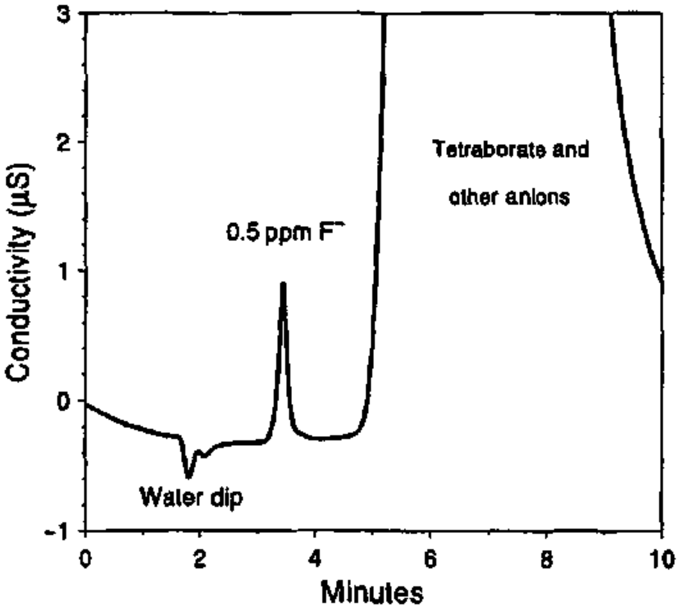


Figure 2.7. Determination of fluoride using sodium tetraborate as the eluent. Note that the water dip and fluoride peak are well separated.

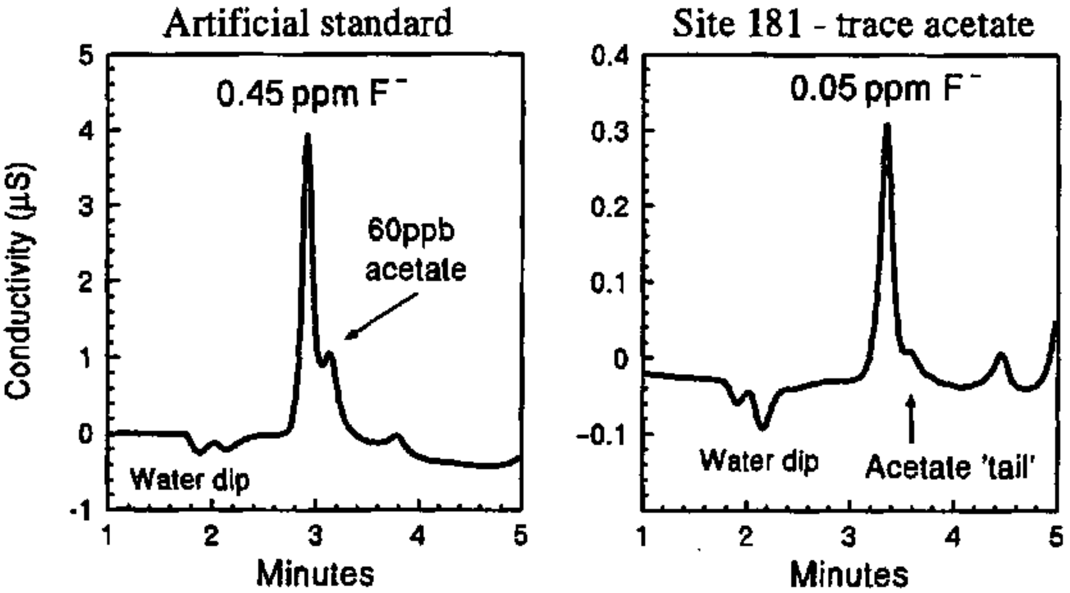


Figure 2.8. Chromatograms showing interference with the fluoride peak by acetate in an artificial solution and an actual sample.

Towards the end of this project an alternative separator column became available, namely the 'Star-Ion' column supplied by phenomenex™. Although the column has somewhat less separation between Cl^- and later anion peaks, it has a greater separation between the water dip and the fluoride peak (Figure 2.9) than the AS4A column (Figure 2.4), allowing better quantisation of the fluoride peak. Operating parameters are identical to those of the Dionex AS4A column, including the use of a sodium carbonate/bicarbonate eluent.

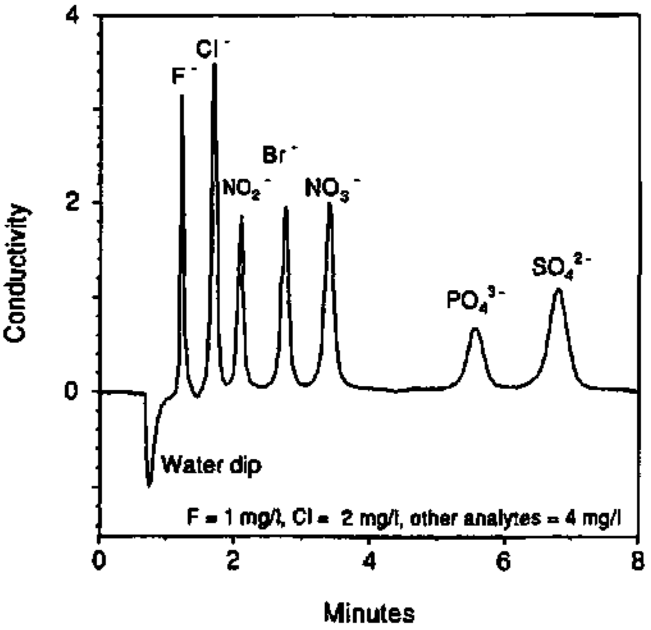


Figure 2.9. Sample chromatogram using a Star-ion analytical column and operating conditions identical to those used for the Dionex AS4A. Note the separation of the fluoride peak from the water dip (cf. Fig. 2.4).

2.4.1.2 Overall quality of water analyses

Since water samples are electrically neutral, total charges on cations and anions should be equivalent. The ion balance error for all samples used in this study has been calculated using the equation of Lloyd and Heathcote (1985):

$$\textit{Ion balance} = \frac{\Sigma\, \textit{cations} - \Sigma\, \textit{anions}}{\Sigma\, \textit{cations} + \Sigma\, \textit{anions}} \times 100 \quad \textit{per cent}$$

Ideally, the ion balance should be less 10% for good quality data. Since all major ions have been determined for the majority of samples, ion balance error cannot be attributed to missing analytes. Figure 2.10 shows an ion balance plot for the samples analysed during this project. It can be seen that the ion balance is generally good, although there is a significant bias towards a cation excess, or anion deficiency. Figure 2.11 shows an ion balance graph for the raw data received from the Department of Water Affairs of South Africa and Figure 2.12 that from the former Bophuthatswana. Distinct differences in ion balance error are seen. South African data is tightly clustered but also shows a bias towards a cation excess. There are only a few data points falling outside acceptable limits. While most of the Bophuthatswana data points are tightly clustered around the 0% ion balance line and show little evidence of bias, there are a significant number of samples falling well outside acceptable ion balance limits.

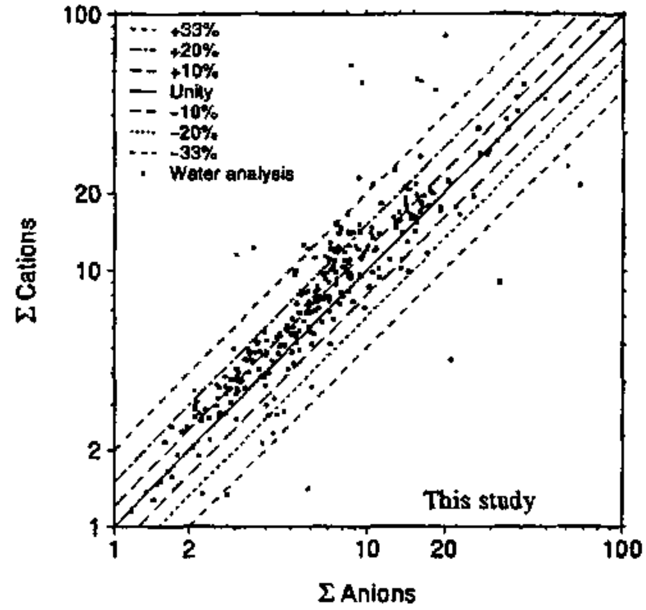


Figure 2.10. Ion balance plot for water analyses performed during this project.

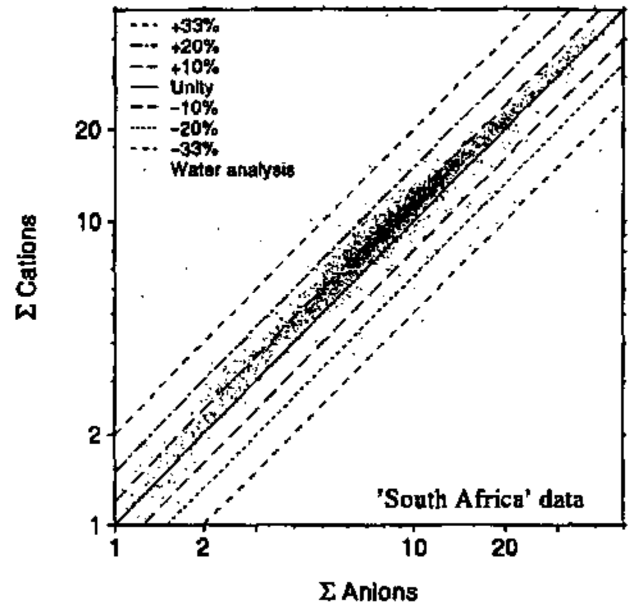


Figure 2.11. Ion balance plot for water analyses from the RSA provided by the Department of Forestry and Water Affairs.

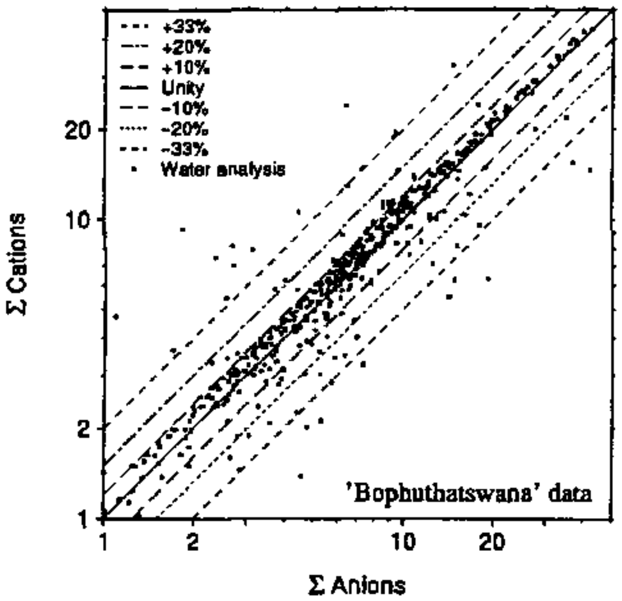


Figure 2.12. Ion balance plot for water analyses from the former Bophuthatswana supplied by the Department of Forestry and Water Affairs.

2.4.1.3 Spatial distribution of water samples

Several factors affect the spatial distribution of the data, which is very variable. In rural areas there is often a 'clustering' of the water samples, since boreholes are most common in villages. In parks such as Pilanesberg and Borakalalo, data is more evenly distributed because of the need for game to have evenly distributed watering points. Groundwater availability (and conversely, the availability of river water) has also modified the sample distribution. Some parts of the study area have a low data-density because of the absence of boreholes, such as the granite areas to the northeast of the Pilanesberg and north of Brits. Boreholes in these areas have low success rates and low yields, and hence are either abandoned after drilling or rapidly fall into disrepair after being equipped, so that samples are unavailable from these areas. Conversely, few boreholes exist in the vicinity of the Apies River, since water is usually available from the river all year round. A third factor influencing data distribution is groundwater quality. Boreholes with good quality water are maintained and more boreholes are drilled in the area. However, boreholes with poor quality water tend to be abandoned after drilling, or are equipped but fall into disrepair, and naturally act as a disincentive for further drilling in the area.

Any data concerning groundwater chemistry collected from rural areas, anywhere in the world, might be affected in these ways. The current data set is therefore highly biased, in that it is "clustered" and biased towards boreholes with high yields and good water quality. The results from this study are, therefore, of the 'best scenario' type; the unbiased reality may show a much worse picture of water quality.

2.4.2 Rock and soil data quality

2.4.2.1 Elemental analysis

Figure 2.13 shows a plot of measured XRFS values *vs* given values for fluorine in standard rocks and soils obtained in this project. The agreement is excellent, despite very small x-ray penetration depths into the powder briquette and potentially large mineralogical effects. The extended counting times for fluorine resulted in an acceptable detection limit of approximately 60 ppm.

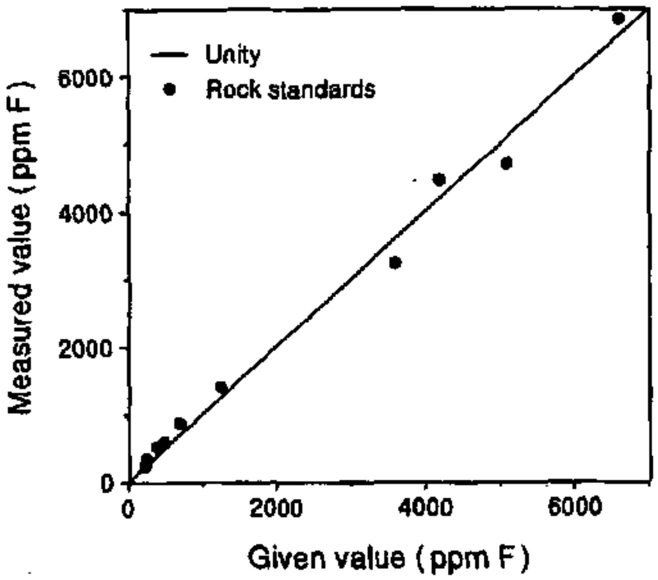


Figure 2.13. Comparison of given and measured values for fluorine in rock standards using XRFS.

2.4.2.2 Spatial distribution of rock and soil samples

With a study area of 150 000 km^2 and only 42 rock and soil samples, data density is very low. No meaningful spatial distribution maps can be drawn from such a small data set. However, an evaluation of the Regional Geochemical Survey maps of the study area (Council for Geoscience, 1995) show that the stream sediments and soil samples derived from a particular lithological unit have similar geochemical characteristics over their full areal extent. For instance, a distribution map of Rb shows lithological boundaries very clearly, because of the contrasting Rb contents of the different rock types. It is inferred from this that in the study area a small number of samples from a particular lithological formation can be taken to be representative of the rock body as a whole. The main rock types were sampled at least three times, and the more important rock types (Pilanesberg foyaites and Lebowa granite) were sampled at least four times.

2.5 Computer manipulation of spatial data

Analysis of data with a spatial component was carried out using a Geographical Information System (GIS) software package called ARC/INFO. Lithological boundaries were digitised from the 1:250000 scale geological maps sheets for Rustenburg, Pretoria and Thabazimbi. The Nelspruit map was unavailable at the time of digitising and so this section of the map was obtained from the 1:1 000 000 scale geological map of South Africa. Digital data on topographic contours, roads, major settlements and rivers were provided by the Department of Forestry and Water Affairs. In order to initially classify groundwater analyses in terms of surface geology, a 'spatial join' was performed between the analyses and the digitised geology. This is a rapid and accurate method of performing such a classification, given the large number of data points. With fewer data points, classification by hand plotting each borehole on a geologic map sheet would be more efficient, and GIS would not be needed.

To produce a 'fluorosis risk map', the F^- concentration of groundwater samples was classified into 4 groups: <0.7, 0.7-1.5, 1.5-3.0 and >3.0 mg/ℓ (Figure 5.6, section 5.2.4.2). These are designated 'no risk', 'low risk', 'medium risk' and 'high risk', respectively. For the origin of these divisions, see Chapter 5. Theissen polygons were generated for each sample point, resulting in approximately 3 000 polygons. Where adjacent polygons had the same classification, they were merged. In this way 300 areas have been delineated where there is a medium or higher risk of fluorosis. Theissen polygons admirably mirror human behaviour, in that people generally fetch water from the nearest borehole: points within a given Theissen polygon are closer to the central point (the borehole) than to any other borehole.

One of the major advantages of this method is that people living within the area of the polygon will probably receive their water from the boreholes within the area represented by the polygon. A further advantage of this method is that it avoids a visually confusing clutter of points, which results if the original 3 500 data points are not reduced in this way. A disadvantage is that geographically isolated boreholes result in very large polygons, which have a visual impact disproportionate to their importance. Borehole locations are given in Figure 4.1.

3 GEOCHEMISTRY OF ROCKS, SOILS AND MINERALS

3.1 Introduction

This chapter discusses the geochemistry of selected rocks, soils and minerals from the field area. The western Bushveld is the main site of South Africa's platinum mining industry, and because of this the economic geology of the area has been intensively studied. However, much of this research has concentrated on elements of economic significance, such as the platinum group elements (PGE's), chromium and vanadium. Comparatively little work has been undertaken on the geochemistry of the halogen elements. This chapter will therefore concentrate on the halogen group of elements and especially fluorine. It will also discuss the geochemistry of elements which affect the distribution of the halogens, in particular some of the alkali metals and the alkaline earth metals. The strontium and oxygen isotopic composition of selected rock samples will also be discussed.

3.2 Chemical composition of rock samples

This section will discuss the results of analyses of rock and soil samples undertaken during the study using the XRF facilities at UCT (Chapter 2).

3.2.1 Major element Geochemistry

3.2.1.1 Previous Work

The field area is one of the most intensively explored and mined areas in the world and a vast amount of geochemical work has been carried out, but very little of relevance to this study.

3.2.1.2 Present work

Rock and soil samples were taken from the field area during May and June 1994. The sample locations are shown in Figure 3.1 in relation to the regional geology and details are listed in Appendix A2.

Despite being from a wide range of rock types, some general trends are still apparent and are shown in Figure 3.2, which shows bivariate plots for three of the four oxides which constitute major cations in groundwater.

In the Na_2O *vs* MgO plot there are two populations: one which has a constant Na_2O concentration and variable MgO, and the other which has a constant MgO but variable Na_2O concentrations. The high MgO rocks come mainly from the Rooiberg suite.

Positive correlations occur for MgO with CaO; CaO with Loss On Ignition (LOI). The inverse correlation of SiO_2 with MgO, CaO and LOI, and of MgO with Na_2O is apparent. K_2O shows an inverse correlation with CaO and MgO and a poor positive correlation with Na_2O. The correlation of K_2O with Na_2O in the Pilanesberg is good, but scattered for the other rock types (Figure 3.3). There is a general scatter when K_2O is plotted against SiO_2.

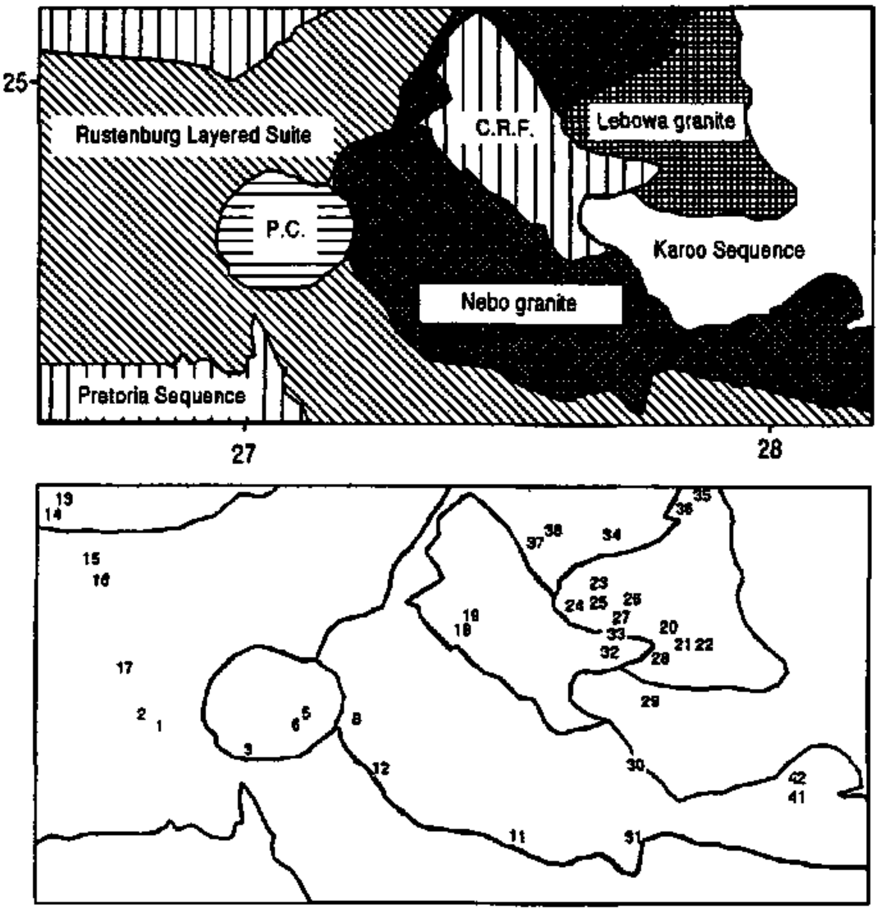


Figure 3.1. Position and sample number of rock and soil samples taken for analysis during this study. P.C. = Pilanesberg Complex; C.R.F. = Crocodile River Fragment.

Possible correlations between CaO, MgO, Na_2O and SiO_2 with F are of interest (Figure 3.4). Bivariate plots of these elements are given in Figure 3.4, which includes inset graphs to show the relationship of high fluorine rocks from the Pilanesberg to the rocks from other lithologies. F and CaO are highly correlated in the Pilanesberg (Figure 3.4). The relative levels of F and CaO in the Nebo granites are very much lower but are also positively correlated, whilst the Lebowa granite has low CaO and widely varying F. The Rustenburg Layered Suite has low F contents and a wide range of CaO values, with no evidence of a correlation between the two variables. The other lithologies have too few samples to draw firm conclusions as to possible correlations. No correlation of F with MgO is apparent for any of the rock types. There is a weak positive correlation of F with Na_2O for the sample set as a whole, but is not present when considering each rock type in isolation. The rocks of the Transvaal System have widely varying SiO_2 but low F, due to the mixture of carbonate and siliceous rocks in the system. The inverse is true for the Lebowa, Nebo and Rooiberg rocks, with SiO_2 in the range of 60-80 %, but with F ranging from 163 ppm to 4980 ppm.

There is no evidence of correlation of F with SiO_2 in the Pilanesberg. Selected analyses of the lithologies sampled taken during 1995 are tabulated in Table 3.1.

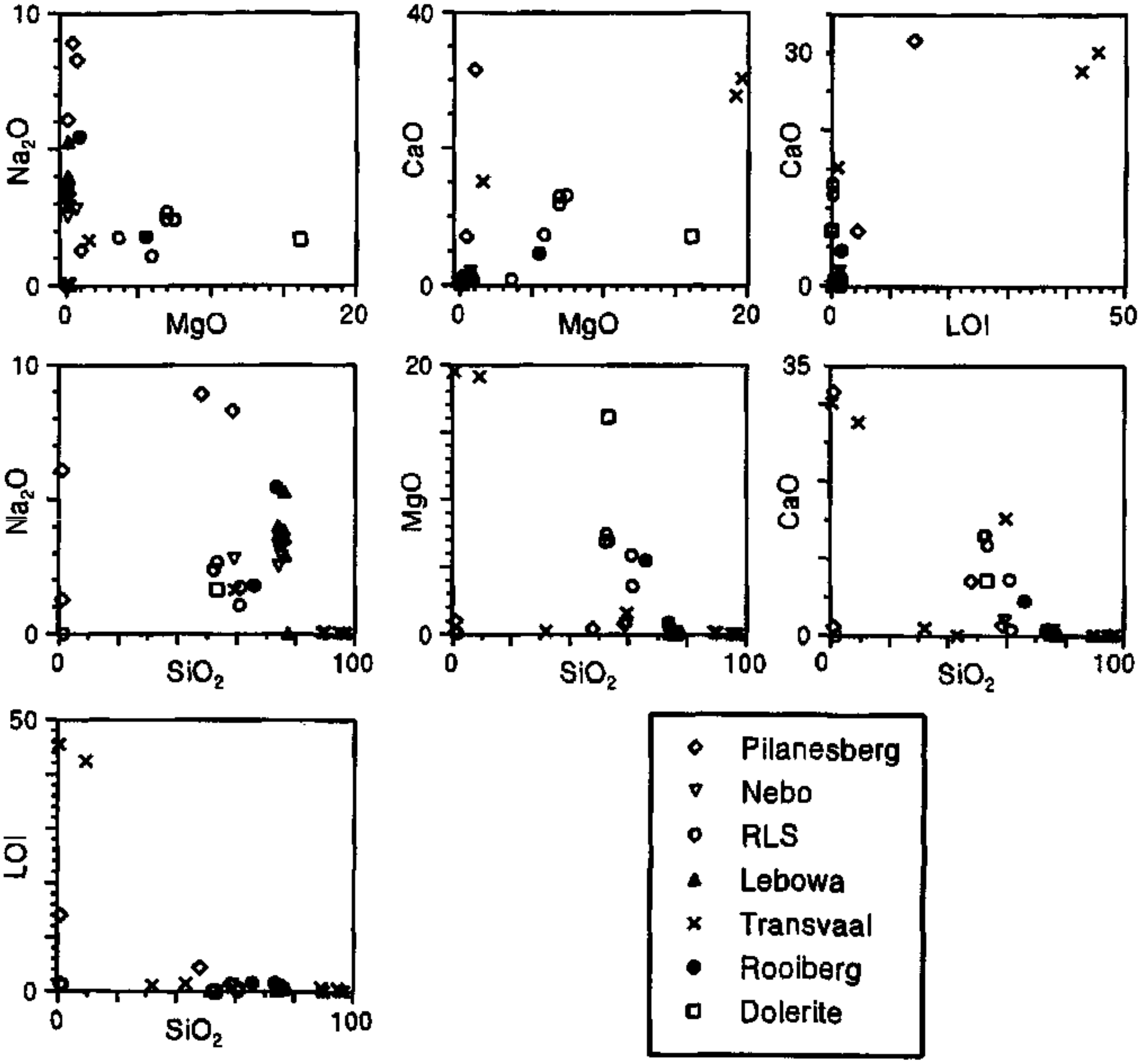


Figure 3.2. Bivariate plots for Na_2O, MgO, CaO, SiO_2 and LOI in rock samples from the study area.

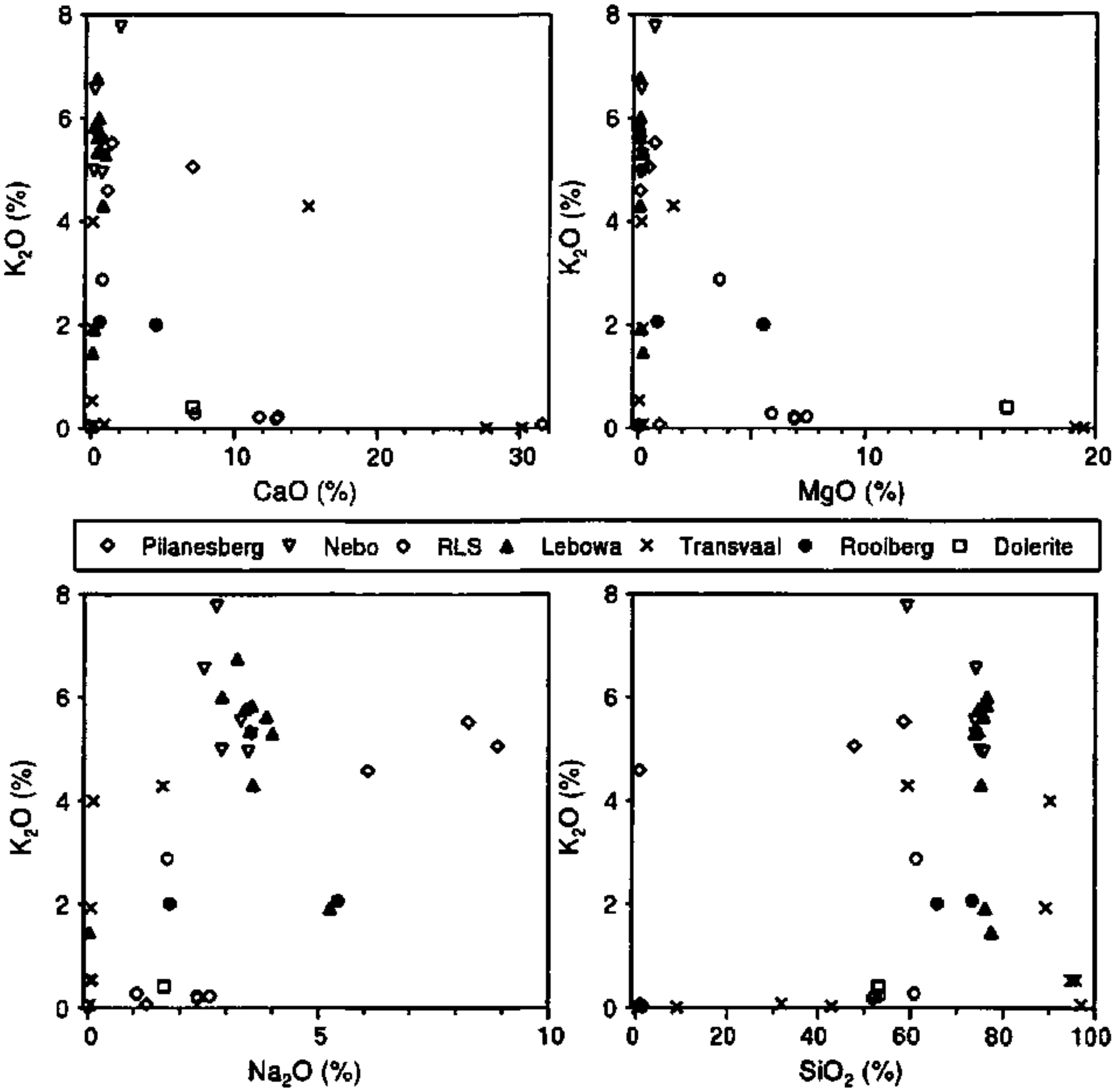


Figure 3.3. Bivariate plots for K_2O *vs* CaO, MgO, Na_2O and SiO_2 in rock samples from the study area.

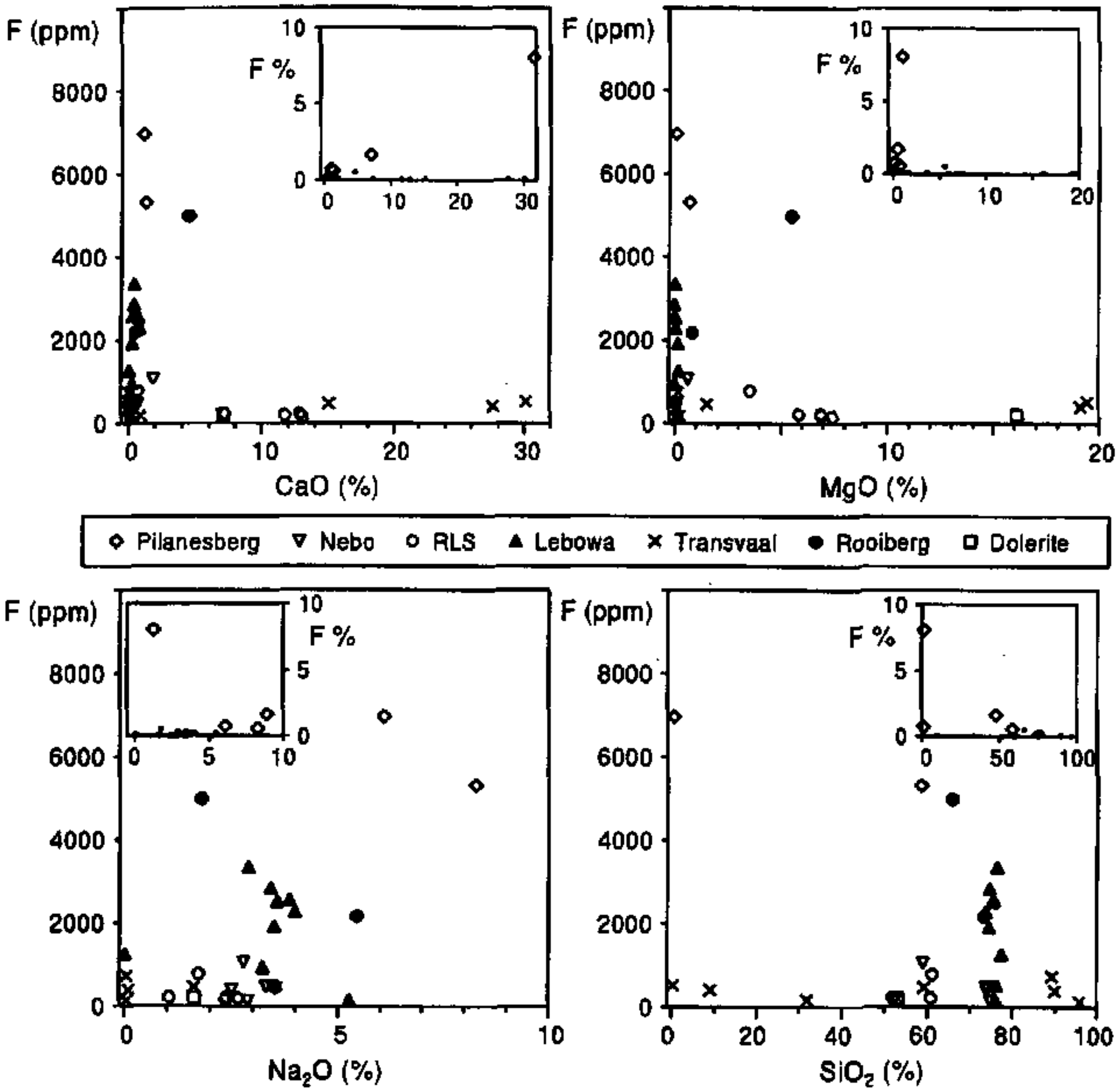


Figure 3.4. Bivariate plots for F *vs* CaO, MgO, Na_2O and SiO_2 in rock samples from the study area.

Table 3.1. Selection of XRF analyses of rock samples from the field area. Results are in weight %, apart from F which is in parts per million. '*n/a*' is not available. SrO and CO_2 contents of the Moepo sample are 6.22 and 13.37 wt%, respectively.

Site Name	Rock Type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	LOI	F	Total
Bapong	Quartzite	96.85	0.06	0.17	1.15	0.01	0.01	0.14	0.02	0.06	0.10	0.07	0.10	<62	98.7
Green Tweed	Foyaite	58.44	1.09	17.17	5.42	0.31	0.73	1.37	8.28	5.52	0.10	0.25	1.36	5310	100.6
Moepo	Fluorite ore	10.67	1.29	2.57	13.55	1.09	1.00	31.60	1.28	0.07	6.94	0.52	14.07	80514	92.7
Lesung	Magnetite Norite	1.53	14.22	4.10	78.87	0.2	0.07	0.03	0	0.03	0	0.34	1.18	<62	100.6
Modike	Nebo Granite	73.88	0.18	12.25	3.33	0.04	0.07	0.62	3.33	5.54	0.04	0.18	0.36	489	99.9
Smaldale	Dolomite	9.09	0	0.08	0.75	0.27	19.09	27.65	*n/a*	0.01	0	0.17	42.38	400	99.5
Makoropeja	Lebowa Granite	76.21	0.12	11.85	3.43	0.02	0.14	0.24	5.27	1.92	0.07	0.22	0.94	163	100.4
Blokspruit	Lebowa Granite	76.58	0.06	12.00	1.59	0.01	0.08	0.49	2.92	6.00	0	0.33	0.56	3351	101.0
Borakalalo	sandstone	89.23	0.17	6.17	1.08	0.01	0.19	0.03	0.05	1.93	0.02	0.21	0.78	735	99.9
Sephai	Limestone	6.02	0.05	0.74	0.42	0.03	2.84	47.87	*n/a*	0.08	0	1.52	39.79	858	99.4
GaTsogwe	Nebo Granite	75.81	0.21	11.35	3.29	0.04	0.10	0.72	3.49	4.95	0.02	0.16	0.32	480	100.5
Mpatsetlha	mudstone	59.27	0.57	11.99	4.43	0.16	1.55	15.15	1.62	4.29	0.12	0.18	0.81	464	100.2
Leeupoort	Felsite	73.40	0.48	13.05	2.15	0.04	0.88	0.61	5.44	2.06	0.04	0.18	1.48	2171	100.0
Rietfontein	Lebowa Granite	75.78	0.21	12.19	1.54	0.01	0.05	0.38	3.88	5.62	0.02	0.29	0.39	2570	100.6
Pretoria Saltpan	Nebo Granite	73.99	0.22	12.05	3.58	0.05	0.13	0.78	3.56	5.3	0.03	0.11	0.48	437	100.3

3.2.2 Fluorine in rock and soil samples

Fluorine was determined in soil samples taken in the vicinity of the rock samples (see Chapter 2). Figure 3.5 shows a comparison of the concentrations found in the whole rock and whole soil samples. It is obvious that a soil fluorine concentration is generally lower than the corresponding rock fluorine concentration. Many of the soil concentrations are up to an order of magnitude less than that for the corresponding rock. One soil sample has a very high fluorine concentration compared to its paired rock sample: this sample comes from the Kwarriekraal fluorite mine and probably results from contamination of the soil by mine tailings.

The leaching of F from rock during the soil forming process is a well known and global phenomenon (Koritnig, 1974). F concentration would be expected to be at a minimum at the soil surface, increasing downwards towards the fresh rock boundary, as found by Koritnig (1951) in the weathering profile of a soil.

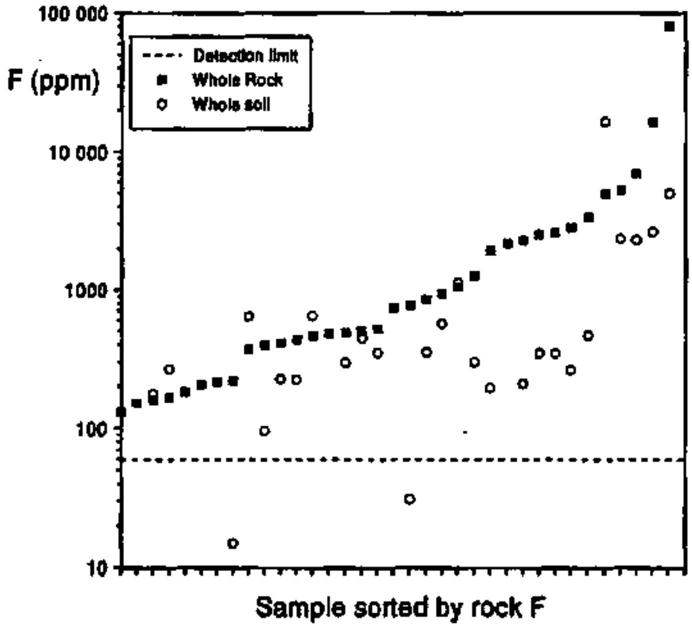


Figure 3.5. Fluorine concentration in paired rock and soil samples. Soil generally has a lower F concentration than the associated fresh rock, indicating that F has been leached away during soil formation.

3.2.3 Spatial distribution of F in rock and soil

Figure 3.6 shows the spatial distribution of F in rock and soil samples analysed for this study. The Pilanesberg and Lebowa Granites have high rock and high soil F contents, whilst the Nebo granite has scattered high values and the RLS values are uniformly low. F in soil has a similar relative distribution, but the absolute concentrations are lower. The distribution of F in rock and soil is very similar to the distribution of high F concentrations in groundwater (see Chapters 4 and 5).

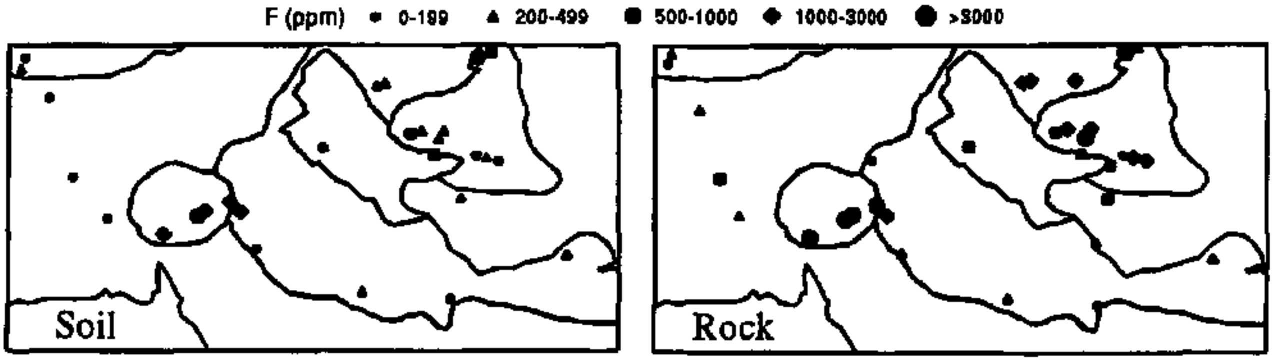


Figure 3.6. Distribution of F in soil and rock samples in the western Bushveld. Lines represent lithological boundaries (see Figure 3.1).

3.2.4 Leaching experiments

Leaching experiments (Section 2.3) were conducted on all soil and rock samples. The highest concentrations of fluoride in the leachate came from rocks and soils with the highest fluorine concentrations. Figure 3.7 shows the relationship of total F to leachable F in rock and soil samples. In the rock experiment, several of the samples had leachate with very high fluoride concentrations, and in general the leachate had a concentration approximately 2 orders of magnitude less than the whole rock concentration. In the soil experiment, very low absolute concentrations of F were produced, and leachable F is generally 3 orders of magnitude less than total F in these soils. Most of the fluoride concentrations in the leachate derived from soil samples were below ~4ppm, a figure which has relevance in the discussion of the source of the fluoride (see Chapter 5).

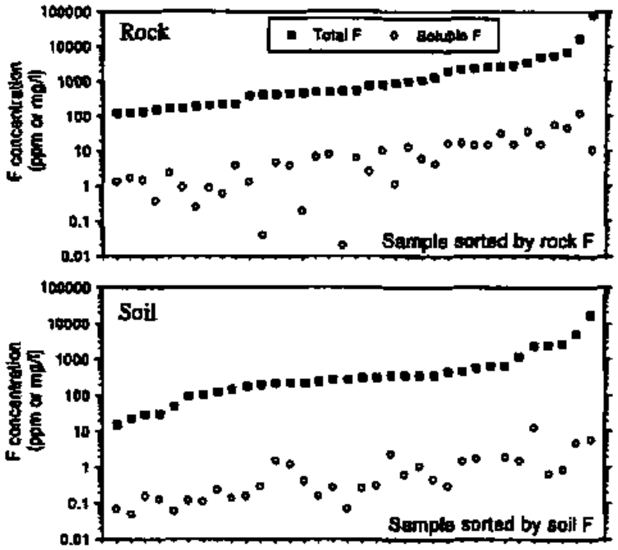


Figure 3.7. Results of leaching experiments on rock and soil samples. F concentrations in leachates are 2 or 3 orders of magnitude less than those in fresh rocks and soils, respectively.

3.3 Isotopic composition of rock samples

3.3.1 $^{87}Sr/^{86}Sr$

3.3.1.1 Previous work

Many rock and mineral samples from the area have been analysed by previous workers for the isotopes of Sr and Rb, almost exclusively to be used as a means of dating igneous rocks, but also as a method of gauging crustal contamination in ascending magmas (*e.g.* Schreiner (1958); Hunter and Hamilton (1978); Davies *et al.* (1970); Walraven *et al.* (1987); Harmer and Farrow (1995)). Many of the studies were summarised by Walraven and Hattingh (1993). Of importance to this study is the availability of whole rock Sr isotope ratios for all the major igneous rocks types in the study area, shown in Table 3.2. It can be seen that Bushveld Granite has by far the largest value and range of Sr isotope ratios of any of the rocks in the field area. The rocks of the RLS have a very small range, whilst diorites in the area have a range of ratios between that for the basic and acid rocks of the Bushveld.

Table 3.2 $^{87}Sr/^{86}Sr$ whole rock ratios for western Bushveld igneous rocks. ^{a}Initial $^{87}Sr/^{86}Sr$ ratio, but correction to present ratio is small because of low Rb/Sr ratio.

Rock type	Location	Reference	$^{87}Sr/^{86}Sr$
Granite	Veerkraal	Davies *et al.*, 1970	0.8176-1.8989
Carbonatite	Tweerivier	Harmer, 1985	0.7027^{a}
Norite	RLS	Davies *et al.*, 1970	0.7069-0.7070
Anorthosite	RLS	Davies *et al.*, 1970	0.7066-0.7076
Diorite	BIC	Davies *et al.*, 1970	0.7273-0.7308

3.3.1.2 This study

As shown in the previous section, Sr data exist for the igneous rocks of the field area, thus avoiding the necessity of analysing a large number of rock samples for background values. However, since the time of deposition of sedimentary rocks cannot be measured using the $^{87}Sr/^{86}Sr$ method, no such data for the Karoo sedimentary rocks were available. To provide a sample of the Sr isotope ratio for this potentially important aquifer, sample RO29 (a Karoo Sequence sandstone) was analysed. The rock was found to have a whole rock $^{87}Sr/^{86}Sr$ ratio of 0.7244 (±0.0008), just below the values for diorite. This value is compared later to the $^{87}Sr/^{86}Sr$ value of groundwater from the same formation.

3.4 Mineralogy

3.4.1 Mineralogy

A discussion of the detailed mineralogy of rocks in the area is beyond the scope of this report, but a discussion of minerals which may have a bearing on groundwater chemistry, especially of the halides, is pertinent. The rocks of the RLS and the Magaliesberg Quartzite generally contain no fluorine-bearing minerals. The granophyres, granites and alkaline complexes all contain fluorite (CaF_2), and the estimated volume percentages from this study are shown in Appendix A5. It will be noted that although the absolute volumes are small, fluorite can have a major effect on ground water at even very low volume percentages. Micas and amphiboles may contain F^-, substituting for OH^-.. Both mineral types occur in the rocks of the area. Fluorapatite should occur in the granitic rocks (Deer *et al*, 1977), but microscopic examination failed to reveal its presence (but see section 3.4.2). Of relevance to this report is the occurrence of carbonates in the igneous rocks, which has implications for ^{14}C dating of groundwater and for hydrogeochemistry. The BIC is essentially carbonate-free, but the alkaline complexes all have carbonate minerals to varying degrees (Verwoerd, 1993). A detailed study of carbonate minerals may be found at the end of this chapter.

3.4.2 Mineral chemistry

Isomorphous replacement of OH^- by F^- occurs in the major rock forming mineral groups of the micas and amphiboles. A knowledge of the F concentration in these minerals is significant in the understanding of the processes resulting in high fluoride groundwater in contact with these minerals. Mica, amphibole, apatite and carbonates were analysed from 10 rock samples by electron microprobe at UCT (Chapter 2) and the results are discussed in this and the following section. The full analyses are reproduced in Appendix A6.

3.4.2.1 Mica

Only one mica, a biotite from sample RO17, had detectable F, at 0.35 wt%. All other F concentrations in mica were below the detection limit (0.17 wt%), and so they are presumably hydroxy-micas. This is confirmed by the low elemental totals of approximately 95%. The low F concentrations in the micas is an unusual result, since mica should be an efficient trap for F in magmas (Koritnig, 1974; Nash, 1976) and the micas in the rock samples come from magmas rich in F. However, Nash (1976) also showed that F was lost by biotites during interaction with meteoric water in the Skaergaard intrusion, Greenland. He used oxygen isotope values in co-existing plagioclase to gauge exchange with groundwater in the intrusion and found an inverse correlation between the degree of exchange and the fluorine content of biotite. The F concentration of apatites from the same samples was unaffected. In contrast, Munoz and Ludington (1974) showed that biotite acts as an effective scavenger of F in F-bearing fluids. Nash (1976) calculated that meteoric fluids exchanging with the Skaergaard intrusion would have low F fugacities. The same conclusion is drawn for any groundwater system which may have exchanged with the BIC. Table 3.3 shows selected electron microprobe analyses of micas.

Table 3.3 Analyses of mica from miscellaneous rock types in the field area. Concentrations in weight percent. *n/d* is not detected, *n/r* is not reported. Electron microprobes can not differentiate between FeO and Fe_2O_3; all Fe is quoted for microprobe analyses in this table and those that follow as FeO. H_2O calculated on the basis of F+OH = 2.0 in the structural formula. Comparative samples: A) Phlogopite from magnetite gabbro, BIC (Boudreau, *et al.*, 1986); B) Biotite from quartz latite, Colorado; C) Biotite from granite, California (Deer *et al.*, 1977). All concentrations in wt%.

Element	RO4	RO11	RO17	RO25	RO30	RO42	A	B	C
F	*n/d*	*n/d*	0.35	*n/d*	*n/d*	*n/d*	0.42	1.11	0.85
Cl	*n/d*	*n/d*	0.16	*n/d*	*n/d*	*n/d*	0.35	*n/r*	*n/r*
Na_2O	12.97	0.07	0.08	0.12	*n/d*	0.10	0.22	0.70	0.15
K_2O	5.76	8.04	9.53	4.83	7.95	6.89	9.43	6.55	8.25
SiO_2	43.55	32.76	35.25	29.89	34.03	31.94	37.90	39.14	37.17
TiO_2	*n/d*	3.35	4.32	*n/d*	1.44	0.70	3.44	4.27	3.14
Al_2O_3	32.83	13.24	18.66	14.78	11.43	12.86	14.43	13.10	14.60
FeO	1.82	36.59	21.70	33.10	39.53	36.42	12.99	17.99	30.60
MnO	*n/d*	0.21	*n/d*	*n/d*	*n/d*	*n/d*	*n/r*	0.14	0.06
MgO	*n/d*	0.20	7.98	1.11	0.83	0.56	16.22	12.75	4.23
CaO	0.30	0.06	*n/d*	0.15	0	0.06	*n/r*	1.64	0.17
H_2O							3.74	2.99	1.35
subtotal							99.56	100.38	100.57
O=F,Cl							0.26	0.46	0.36
Total							99.30	99.92	100.21

3.4.2.2 *Amphibole*

F in amphibole ranged from below the detection limit of 0.17 wt% to 2.69 wt% in sample RO3 (Table 3.4). Pilanesberg amphiboles (n = 4) had a mean F concentration of 2.22 wt%, Nebo Granite amphiboles (n = 3) 0.61 wt% F and Lebowa Granite amphiboles (n = 2) 0.25 wt%. These results are somewhat unusual, since the whole rock concentration of the Lebowa Granite samples are at least double the mean F concentration of 500 ppm for the Nebo Granite samples. It is obvious, therefore, that total F concentration in the Lebowa granites is not dominated by the F concentration in the amphiboles. The abundance of fluorite is probably the controlling factor for the Lebowa granites. Table 3.4 shows selected amphibole analyses.

Table 3.4 Analyses of amphibole from miscellaneous rock types in the field area and comparative analyses. Concentrations in weight percent, *n/d* is not detected, *n/r* is not reported. Comparative samples: A) ferrohastingsite, nepheline syenite, Sweden: B) hornblende, latite, Colorado: C) arfedsonite, syenite, east Greenland. All from Deer *et al.* (1977). All concentrations in wt.%.

Element	RO3	RO4	RO11	A	B	C
F	2.69	*n/d*	0.65	*n/d*	0.35	2.95
Na_2O	4.11	3.92	2.01	2.06	1.35	7.37
K_2O	1.32	*n/d*	1.45	1.91	1.09	1.52
SiO_2	45.39	47.67	39.27	37.49	45.17	48.41
TiO_2	2.79	0.58	1.69	0.86	2.11	1.32
Al_2O_3	6.46	1.35	8.80	10.81	7.68	1.81
FeO	14.04	25.67	33.63	32.66	21.98	35.06
MnO	1.02	1.71	0.58	0.95	0.41	0.75
MgO	12.82	2.05	0.55	1.34	13.44	0.06
CaO	10.10	16.61	10.61	9.77	11.18	1.18
H_2O				2.01	0.25	1.07
Subtotal				99.86	100.14	101.50
O=F,Cl					0.14	1.24
Total	100.74	99.56	99.24	99.86	100.00	100.26

3.4.2.3 Apatite

Apatites from sample RO6 (a fluorite ore) were suspected to be fluorapatites because of the high F content of the rock (8 wt%), and they were analysed to confirm this. All contained appreciable F and no detectable Cl (Table 3.5). Of note is the high concentration of SrO, which reached 6.78 wt% in one analysis. Although the apatites are not saamitic (where SrO almost entirely replaces CaO and reaches 46 wt%; Elfimov *et al.*, 1962), the Sr content is higher than most igneous apatites (Edgar, 1989 and references contained therein). Edgar (1989) noted that high-Sr apatites had high F concentrations, and these analyses confirm that observation. He also noted that apatite composition closely reflects the composition of the magma from which it is derived. The analysis of the host rock (Appendices A4 and A6) shows that it has a high carbonate content, which suggests that the low analytical totals of these apatites may be due to the presence of CO_2 in the apatite structure. A high rare earth element content is also feasible.

Table 3.5 Typical analysis of apatite from sample RO6 (Pilanesberg), and comparative analyses: A) chlorapatite from the Merensky Reef, BIC (Boudreau *et al.*, 1986); B) fluorapatite from stilpnomelane-calcite vein, Wales (Deer *et al.*, 1977); C) from mica-apatite pyroxenite; and D) from carbonatite both from Phalaborwa, quoted in Dawson and Fuge (1980). *n/d* = not detected. *n/r* = not reported.

Element	RO6	A	B	C	D
CaO	51.99	53.34	55.88	*n/r*	*n/r*
P_2O_5	39.68	40.43	42.00	*n/r*	*n/r*
F	3.63	0.12	3.73	0.62	3.40
Cl	*n/d*	6.85	0.00	0.007	0.01
FeO	*n/d*	0.28	0.03	*n/r*	*n/r*
MnO	*n/d*	*n/r*	0.01	*n/r*	*n/r*
MgO	*n/d*	*n/r*	0.02	*n/r*	*n/r*
H_2O		0.00	0.05	-	-
Subtotal		101.02	101.80	-	-
$O=F_2Cl$		1.60	1.57	-	-
Total		99.42	100.23	-	-

3.4.3 Fluorine-bearing mineral abundances

3.4.3.1 Mineralogy

The detailed mineralogy of rocks in the area is beyond the scope of this report, but a discussion of minerals which may have a bearing on groundwater chemistry, especially the hydrogeochemistry of the halides, is pertinent. The rocks of the RLS and the Magaliesberg Quartzite generally contain no fluoride-bearing minerals. The granophyres, granites and alkaline complexes all contain fluorite (CaF_2). Although the absolute volumes can be small, fluorite can have a major effect on ground water at even very low volume percentages. Micas and amphiboles may contain F^-, substituting for OH^-. Fluorapatite should occur in the granitic rocks (Deer *et al*, 1977), but microscopic examination failed to reveal its presence (but see later).

Of relevance to this report is the occurrence of carbonates in the igneous rocks, which has implications for ^{14}C dating of groundwater and for hydrogeochemistry. The BIC is essentially carbonate-free, but the alkaline complexes all have carbonate minerals to varying degrees (Verwoerd, 1993; McCaffrey *et al*, 1996).

3.4.3.2 Quantitative estimation of F minerals

The abundance of common F-bearing minerals in each rock sample was estimated using thin sections and a Munsell (1992) area estimation chart. Appendix A5 details the results. If the mica and amphibole in these rocks are presumed to be biotite and hornblende respectively, and the maximum stoichiometric concentration of F in these minerals is calculated, an independent estimation of whole rock F content can be reached. If the average F concentration found from electron microprobe analysis is applied, a closer approximation should result.

Figure 3.8 shows that both methods provide estimates of total F far removed from that determined by XRFS. This could be due to several factors: 1) F-bearing mineral abundances have been underestimated, leading to an underestimate in total fluorine concentration; 2) maximum stoichiometric F is far in excess of the actual mineral F concentration, leading to an overestimation of whole rock F concentration; 3) the F content of both biotites and amphiboles is very variable, and therefore average values are meaningless. The truth probably lies somewhere between all three factors.

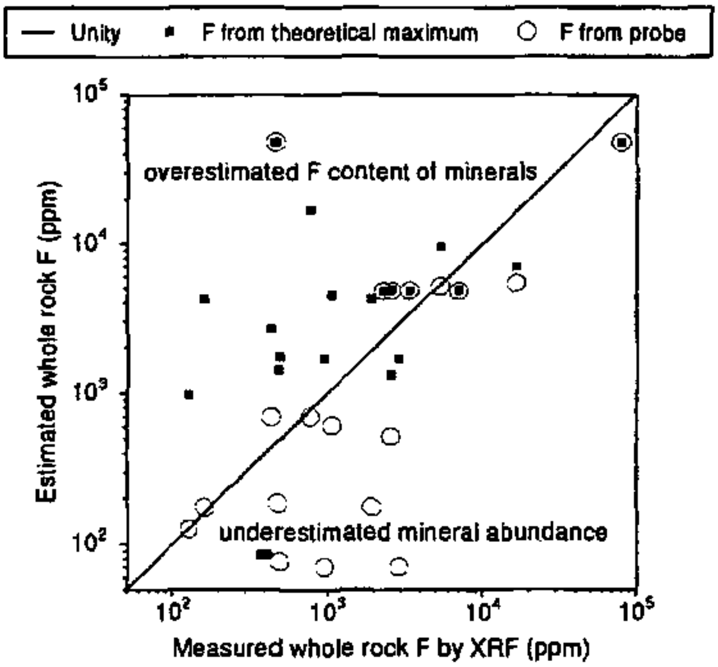


Figure 3.8. Whole rock F estimated from maximum theoretical F content of biotite, hornblende, fluorapatite and fluorite and from average electron microprobe analyses, plotted against F measured by XRF.

3.5 Composition, origin and significance of Pilanesberg fluorite ore

3.5.1 Introduction

During the analysis of other rock samples, sample RO6 was found to have an unusually high calcium content and loss on ignition (LOI) value compared to other rocks from the Pilanesberg. The rock sample itself was selected for the presence of visible fluorite and collected from an ore dump at the abandoned Moepo fluorite mine in the southwest of the Pilanesberg Complex (Figure 3.9). Further studies have been undertaken on this sample and the results presented here show for the first time the presence of carbonate-bearing rocks in the Pilanesberg (McCaffrey *et al.*, 1996). The methodology is described in Chapter 2.

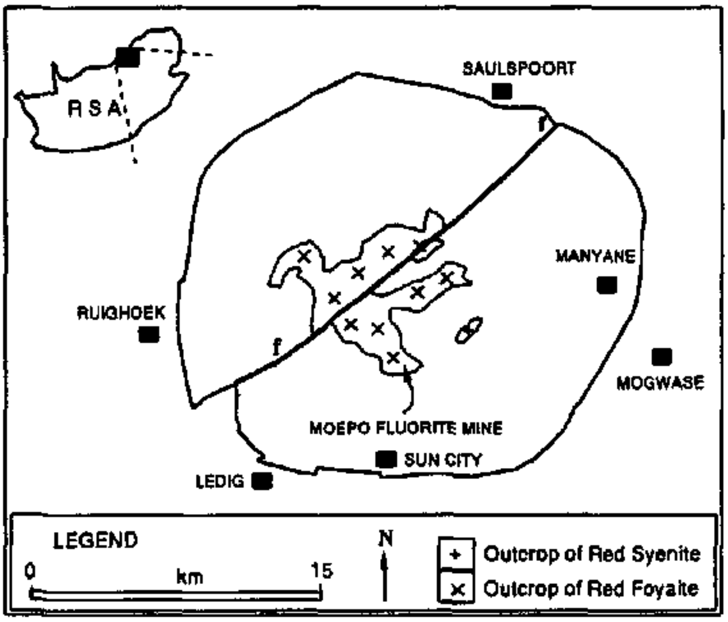


Figure 3.9. Location of the Moepo fluorite mine within the Pilanesberg Complex.

3.5.2 Results

Compared to the nepheline syenites which dominate the geology of the Pilanesberg (Lurie, 1974; Table 3.7), RO6 has a significantly greater content of calcium (31.6 wt% CaO) and strontium (6.22 wt% SrO). The sample has a Ba concentration of less than 10 ppm. A rock chip moistened with dilute hydrochloric acid and inserted into a bunsen flame produced a vivid red flame, indicative of strontianite (Deer et al., 1977). Initial X-Ray Diffraction (XRD) analysis on the whole-rock powder confirmed the presence of apatite, plagioclase and fluorite but failed to show the presence of calcite and produced a poor fit for dolomite. After heavy mineral enrichment, where plagioclase and calcite were separated from the denser phases, the powder was analysed again and strontianite was identified as the only carbonate phase, although the fit was poor.

Table 3.7. Major element analyses for sample RO6 and comparative samples. (a) From Kubu Drive Quarry, Pilanesberg. (b) From Harmer (1992). (c) From Woolley and Kempe (1989), as quoted in Kogarko (1993). (d) Total Fe as Fe_2O_3. *n/r* = not reported.

Comp. (wt%)	**RO6**	**Pilanesberg Syenite [a] (RO5)**	**Spitskop sövite [b]**	**ferro- carbonatite [c]**
SiO_2	10.62	57.31	2.51	4.70
TiO_2	1.29	0.22	0.04	0.42
Al_2O_3	2.57	16.72	0.07	1.46
Fe_2O_3[d]	13.55	10.38	2.47	7.44
MnO	1.09	0.47	0.69	1.65
MgO	1.00	0.10	2.29	6.05
CaO	31.60	1.15	50.94	32.77
Na_2O	1.28	6.08	0.63	0.39
K_2O	0.07	4.59	0.00	0.39
P_2O_5	6.94	0.04	1.76	1.97
CO_2	13.37	0.0	39.32	*n/r*
H_2O^-	0.52	0.64	0.01	*n/r*
LOI - CO_2	0.70	1.36	*n/r*	*n/r*
SrO	6.22	0.01	*n/r*	0.88
F	8.05	0.69	*n/r*	*n/r*
TOTAL	98.87	99.76	100.73	58.12

Carbon and oxygen isotope analyses of the total carbonate present in RO6 and data from the literature for comparative samples are presented in Table 3.8. Sample RO6 has a $\delta^{13}C$ value intermediate between the mean for sedimentary carbonates and the mean for fresh continental carbonatites. The $\delta^{18}O$ value of RO6 is much lower than those of the Transvaal sedimentary carbonates and quite close to the measured range for carbonatites.

Selected microprobe analyses of carbonate minerals in RO6 are presented in Table 3.9. Of 20 carbonate grains analysed, 14 were calcium carbonate, 3 were strontianite and 3 were manganoan ankerite. Calcium carbonate crystals contain as much as 11% $SrCO_3$ and occur either as inclusions in apatite or within the medium-grained carbonate groundmass. The strontium content of this calcite is much higher than that reported for other magmatic calcites. Strontianite is present both as a vein-filling mineral and in the carbonate groundmass, but was not observed as an inclusion in apatite.

Table 3.8. Bulk carbonate isotopic data for sample RO6, Moepo fluorite mine, Pilanesberg Complex. (a) Recalculated from Schidlowski *et al.* (1983). (b) Hudson (1977). (c) Taylor *et al.* (1967).

Sample(s)	$\delta^{13}C_{PDB}$‰	$\delta^{18}O_{SMOW}$‰
Pilanesberg RO6	-2.7	+12.1
Transvaal Supergroup (mean) and range[a]	(-0.8) -0.5 to -1.4	(+22.0) +20.0 to +24.9
Typical marine limestone[c] (mean) and range	(-0.79) -12.0 to +6.4	(+19.3) +10.6 to +24.9
Carbonatites (range)[b]	-4 to -8	+6 to +10

Table 3.9. Mean analyses of carbonate minerals in sample RO6 (Pilanesberg). All concentrations in wt%. LLD is lower limit of detection. *n/d* = not detected. n = no. of grains analysed.

Mineral	**$CaCO_3$**	**$FeCO_3$**	**$MgCO_3$**	**$MnCO_3$**	**SiO_2**	**$SrCO_3$**	**$BaCO_3$**	**Total**
LLD:	0.01	0.22	0.20	0.20	0.09	0.16	0.14	
Calcite (n=14)	93.14	0.52	*n/d*	0.66	*n/d*	4.69	*n/d*	99.01
Strontianite (n = 3)	12.09	*n/d*	*n/d*	*n/d*	*n/d*	89.99	*n/d*	102.08
Manganoan Ankerite (n=3)	54.33	21.29	14.32	8.17	0.61	0.62	*n/d*	99.35

3.5.3 Discussion

The lack of identification of calcite and the poor fit of strontianite in the XRD scans can be ascribed to the ubiquitous solid solution of strontium and calcium, which would alter the d-spacing of the minerals and result in poor peak matching from the JCPDS database. However, the analytical results leave no doubt that carbonate does exist as a mineral phase in the Pilanesberg Complex.

The high strontium content of the whole-rock and of the calcite indicate that the carbonate minerals in RO6 are magmatic in origin (Barker, 1993), although the negligible barium concentration is unusual (Barker, D.S., University of Texas, *pers. comm.*). The high strontium to calcium ratio of the minerals and high whole-rock strontium content of RO6 make the Transvaal Group dolomites an unlikely source. The mineral assemblage in RO6 is similar to that of late stage, low temperature and hydrothermally altered carbonatites (Barker, 1989). The $\delta^{13}C$ value of RO6, which is just outside the range for fresh continental carbonatites (Taylor *et al.*, 1967), may be interpreted as having a large mantle component (Figure 3.10), modified by late-stage fluids (Suwa *et al.*, 1975).

The $\delta^{18}O$ value of the carbonate in RO6 of 12.1‰ is consistent with precipitation from magmatic fluids at elevated temperatures. At 500°C the fractionation factor between calcite and water (Δ) is 1.8‰ (O'Neil *et al.*, 1969), which would be consistent with a fluid of $\delta^{18}O$ value of 10.3‰. However, ambient meteoric water in the Johannesburg area has a $\delta^{18}O$ of approximately -6‰ (NPRL, 1984) and calcite with a value of 12.1‰ would have precipitated from such a fluid at about 90°C (calculated from the equation for $\Delta_{calcite-water}$ (O'Neill *et al.*, 1969):

$$\Delta_{calcite-water} \approx 10^3 \ln\alpha = 2.78 . 10^6 T^{-2} - 2.89$$

As a temperature of 90°C seems too high for precipitation from groundwater, a late-stage magmatic origin modified by a hydrothermal system remains the most likely possibility.

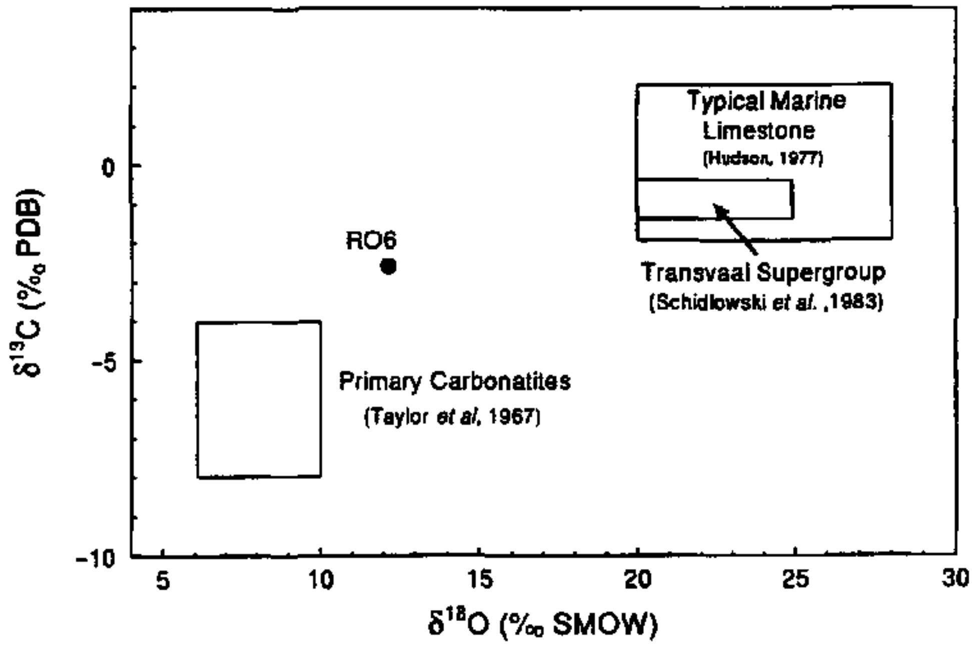
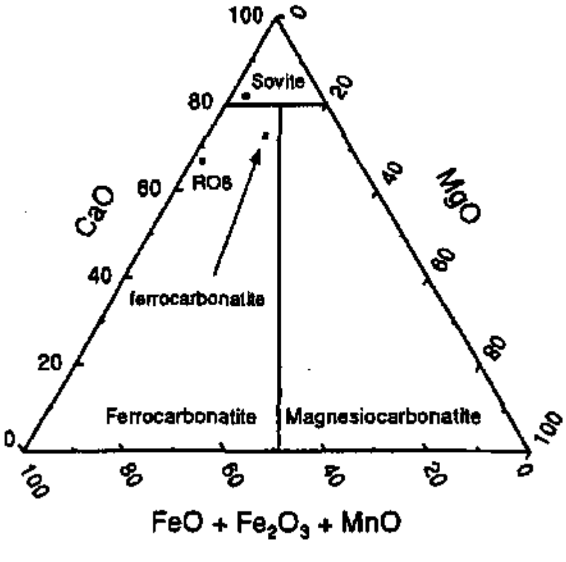


Figure 3.10. Oxygen and carbon isotope values of magmatic carbonate and marine limestone compared to that of sample RO6. Typical values for the Transvaal Supergroup, through which the Pilanesberg is intruded, are also shown.

Dawson and Fuge (1980) reported on halogen concentrations in primary, unweathered carbonatites from Africa. They reported a wide range of F and Cl concentrations and F/Cl ratios. The carbonatite with the closest halogen composition to RO6, from samples collected from all over Africa, interestingly comes from the Goudini carbonatite, located less than 100km to the west of the Pilanesberg. Only the carbonatitic lavas of Oldoinyo Lengai in Tanzania also have F above 1 wt%, but these lavas are extremely rich in Cl, up to 3.6 wt%.

Sample RO6 bears no chemical or petrographic resemblance to the nepheline syenite of the surrounding Pilanesberg Complex (c.f. sample RO5, Table 3.7). The CO_2 and electron microprobe analyses indicate that $CaCO_3$ and $SrCO_3$ are the dominant carbonate phases, making up 33.3% of the sample (assuming all Ca and Sr are as carbonate). The carbonate content of the rock is not sufficient (i.e. <50% carbonate) for it to be classified as a carbonatite (Le Maitre, 1989). However, the sample has a similar chemical composition to sövite and especially to ferrocarbonatite (Table 3.7; Figure 3.11). The high F and Sr contents further complicate classification of the rock.

The occurrence of RO6 at a fluorite rich location is of interest as several other fluorite prospects exist in the Pilanesberg (J. Lurie, *pers. comm.*, 1991) and it is possible that carbonate may also exist at these locations. Carbonatites are associated with fluorite deposits at other undersaturated igneous complexes in southern Africa, for instance Okorusu in Namibia (Prins, 1981). Large amounts of carbonate in the Pilanesberg would have important geohydrochemical and groundwater dating implications (McCaffrey, 1993), because the dissolution of essentially ^{14}C-free carbonate would dilute the ^{14}C content of modern groundwater and would result in an overestimate of residence time below ground. However, the abundance, and therefore importance, of carbonate in the Pilanesberg cannot be properly estimated until further investigations have taken place.



Carbonatite Classification Diagram

Figure 3.11. Analysis of sample RO6 plotted on the carbonatite classification diagram of Woolley (1982).

4 GROUNDWATER CHEMISTRY

4.1 Introduction

This chapter discusses the hydrogeochemistry of groundwater of the western Bushveld, with emphasis on fluoride. Although the distribution and concentration of fluoride is of primary significance in the study of fluorosis, the chemical characteristics of the groundwater are also of interest, and may provide valuable insight into the occurrence and remediation of fluorosis.

The discussion which follows will be based primarily on chemical and isotopic analyses performed on approximately 320 water samples taken from the primary field area. Although no borehole log is associated with these samples, they have been classified by host rock by digitising the relevant 1:250 000 geological maps and performing a spatial join using ARC/INFO. Sixteen host rocks were identified for initial groundwater classification purposes, namely, in age order, Archaean Granite, Chuniespoort and Pretoria Group sediments, Rustenburg Layered Suite basic rocks, Rashoop Granophyre, Nebo Granite, Lebowa Granite, Rooiberg Felsites, Pilanesberg Complex nepheline syenite, Carbonatite, Letaba basalt, Ecca, Irrigasie and Clarens formations of Karoo age, Waterberg sandstone and quaternary deposits. A large database of groundwater analyses exists for the Republic of South Africa, to which the authors were granted access. These analyses are also considered. Borehole locations are given in Figure 4.1.

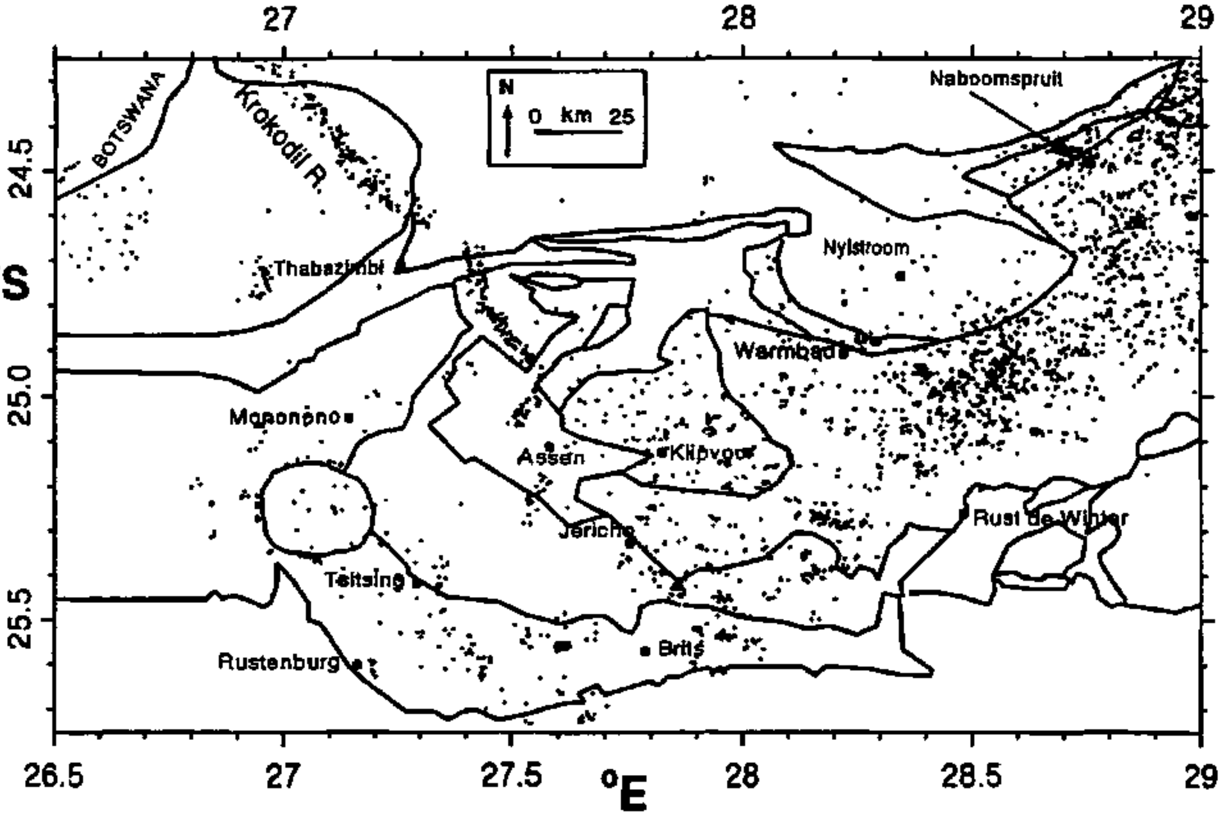


Figure 4.1 Sampling locations in the extended study area of 3244 groundwater samples discussed in this study. Lines represent lithological boundaries. See Figure 1.3.

4.2 Previous work

Bond (1947) undertook a major survey of groundwater chemistry in the Union of South Africa, and generally described groundwaters based on their host lithology. He noted that groundwaters from the Bushveld granites and felsites and from the Pilanesberg have similar chemical characteristics, although the granites and felsites have appreciably higher Cl concentrations than the Pilanesberg rocks. He presented 10 rock analyses and noted the high alkali content of the aforementioned lithologies. He asserted that high F is present in Pilanesberg groundwater as NaF. He conjectured that the water from the Warmbaths spring is magmatic in origin. He also compared the water of the Pretoria Saltpan (PSP) crater with that in the surrounding rocks. The PSP water has similar ionic proportions to that of the country rocks, apart from the readily precipitated Ca, Mg and Si, but has a greatly increased concentration overall, which he ascribed to evaporation of inflowing groundwater from the Nebo Granite. Bond could find no fluorite in his rock samples and so ascribed F in groundwater to the dissolution of apatite.

McCaffrey (1993) studied the hydrochemistry of major, trace, lanthanide and actinide elements, as well as stable and radioactive environmental isotopes in the Pilanesberg Complex. It was postulated that two different water types exist in the complex, one with a long residence time and very high fluoride concentrations, the other with a shorter residence time and moderately elevated fluoride values.

4.3 This work

The results of the analyses obtained in this work are described element by element, with reference to the host lithology where features of significance exist. The analyses have been divided into major anions and cations, trace elements and isotopes. The results are discussed also in relation to the latest recommended health guidelines for drinking water in South Africa (Table 4.1).

4.4 Physico-chemical parameters

A key to the abbreviations of the sixteen lithologies used in many of the following diagrams is given in Figure 4.2.

4.4.1 Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

EC and TDS are highly correlated (Figure 4.3), as is to be expected from electrochemical theory. Groundwater from the carbonatites has the highest mean EC, whilst the Archaean Granite, Nebo Granite, Chuniespoort Group and Irrigasie formation have very high maximum EC. No lithology has a mean value above the low risk limit, but most have maximum EC values well above the high risk limit (Figure 4.4). Apart from a sample from the Pretoria Saltpan, no brines (TDS > 10g/l) were sampled.

Table 4.1 Recommended quality (health) guidelines for drinking water for elements and ions in RSA waters (DWAF, 1999). All values in mg/ℓ except pH and EC.

Parameter	Maximum limit of no risk Ideal - Good	Low risk range Marginal	Medium-high risk range Poor - Unacceptable
EC (mS/m, 25°C)	150	150 - 370	>370
pH low	4.5	4.5 - 4.0	<4.0
pH high	10	10.0 - 10.5	>10.5
Ca	150	150 - 300	>300
Mg	100	100 - 200	>200
Na	200	200 - 400	>400
K	50	50 - 100	>100
Cl	200	200 - 600	>600
SO_4	400	400 - 600	>600
F	1.0	1.0 - 1.5	>1.5
$NO_3 + NO_2$ (as N)	10	10 - 20	>20

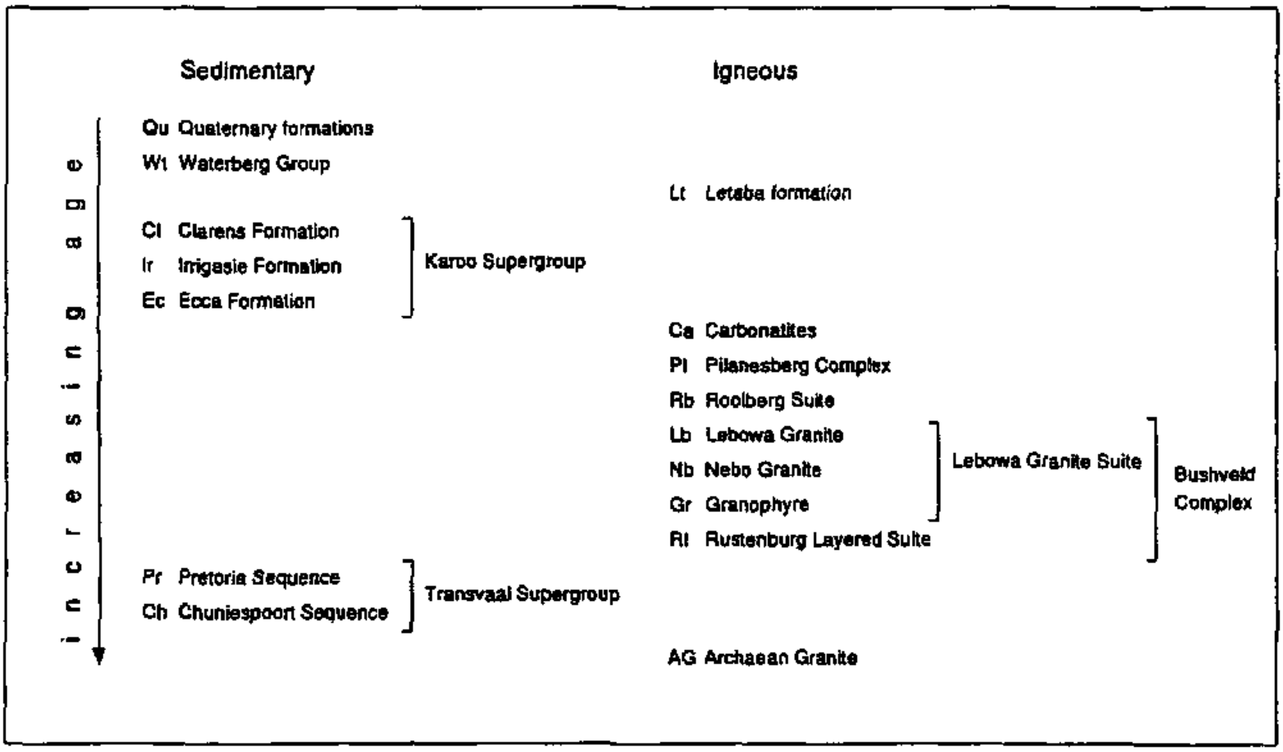


Figure 4.2. Key to abbreviations used in many of the following figures.

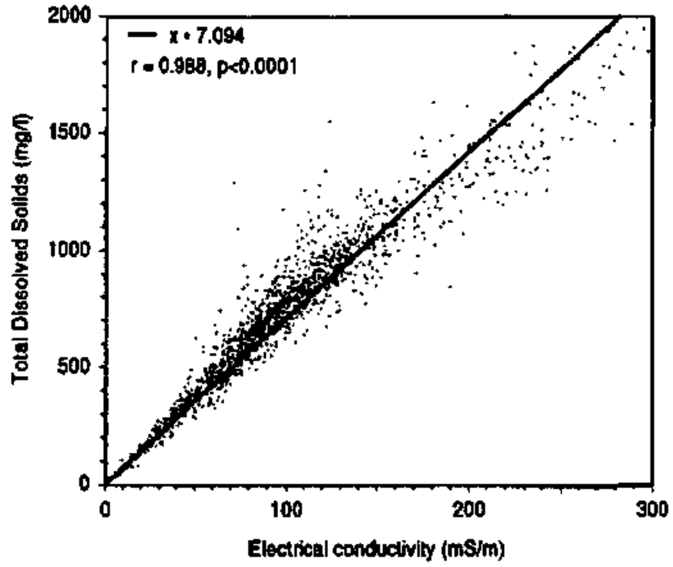


Figure 4.3. EC *vs.* TDS for RSA and Bophuthatswana groundwater analyses. An excellent correlation is evident.

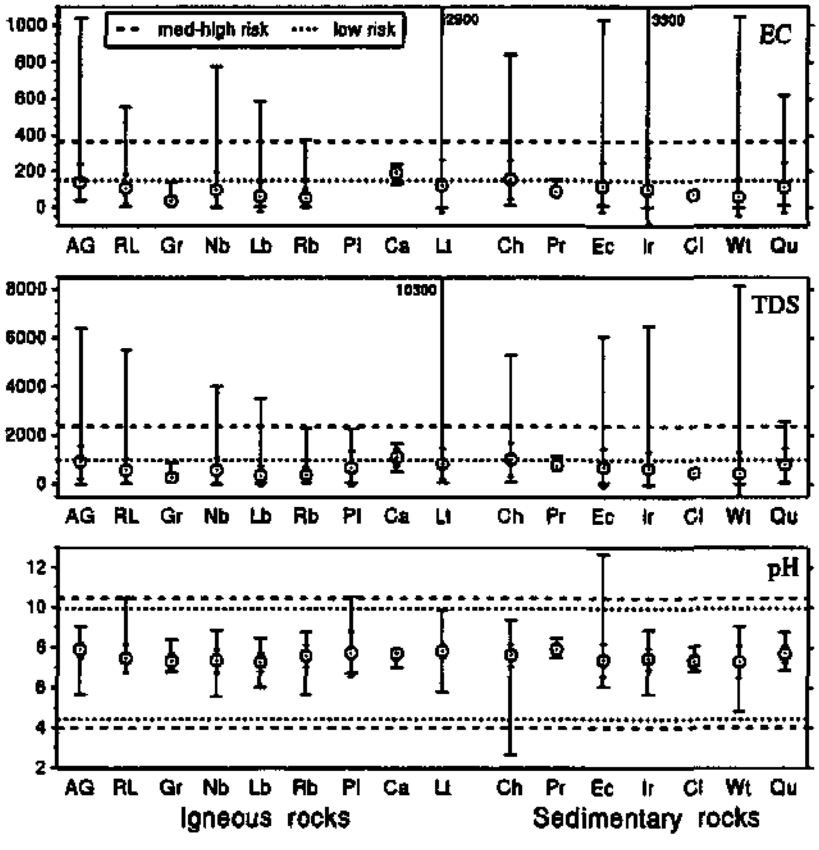


Figure 4.4. Summary statistics for EC, TDS and pH in groundwater from 16 lithologies. Circles mark the mean, small tick marks represent ± 1 s.d., large tick marks minimum and maximum values. Also indicated are the Department of Health's recommended health limits.

4.4.2 pH

Only the Pilanesberg waters deviate significantly from the normal distribution expected for pH, and are conspicuous for high pH outliers (see Appendix A8). The mean values for all water samples are similar, between pH 7-8. The highest pH value, pH = ~12.5, was measured in Karoo Ecca sediments, and the lowest, pH = ~3, in the Chuniespoort Group rocks from the RSA database (Figure 4.4).

4.5 Major elements - Anions

4.5.1 Fluoride

Figure 4.5 shows F^- concentrations in groundwater in the study area as a whole, plotted as a histogram.

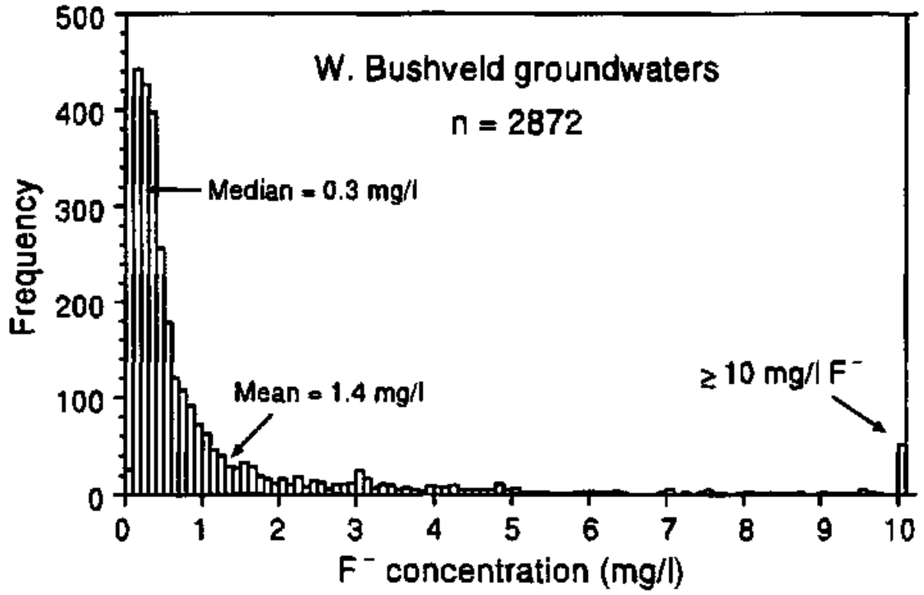


Figure 4.5. Groundwater fluoride histogram for the study area as a whole.

The median concentration is 0.3 mg/ℓ, whilst the mean is 1.43 mg/ℓ; the population is highly skewed towards high fluoride concentrations. Although the tail of the histogram is irregular, there is an increased frequency of fluoride values at ~3 mg/ℓ. Figure 4.6 shows summary statistics and Figure 4.7 shows histograms of fluoride concentration in the 16 major lithologies of the study area.

Fluoride is found at low concentrations in most samples from the Rustenburg Layered Suite, with a mean of 0.4 mg/ℓ fluoride. High values occur in isolation and these may be due to Pilanesberg dykes. Of interest are the histograms for the Lebowa Granite and the Pilanesberg. Fluoride concentrations are high in the acid parts of the BIC, with the two granites showing very different levels of groundwater fluoride. Nebo Granite groundwater has a mean concentration of 2.0 mg/ℓ F (Figure 4.7). Much higher values were determined for samples from the Lebowa Granite, with the mode at over 10 mg/ℓ and a higher mean value of 3.7 mg/ℓ. The Lebowa groundwater fluoride histogram has a normal Gaussian distribution, whilst the Nebo does not.

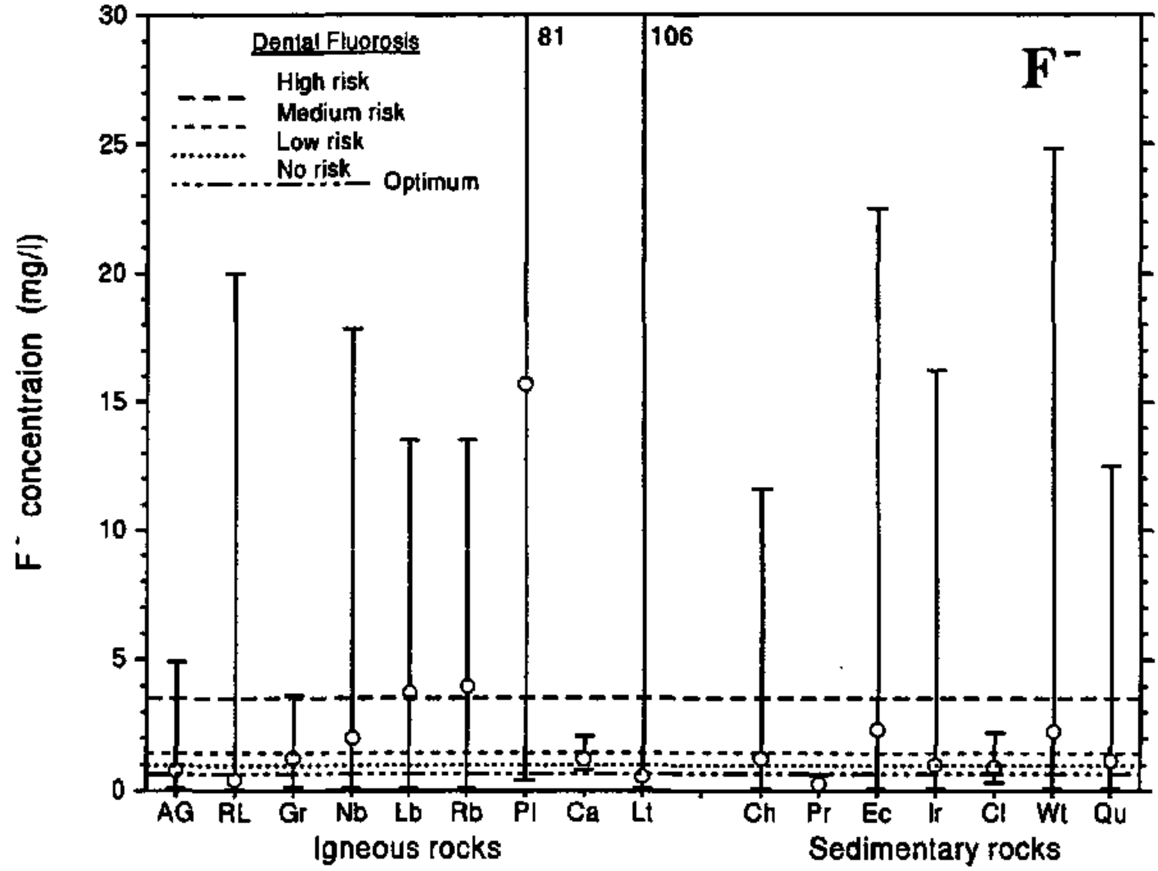


Figure 4.6. Summary statistics of F in 16 lithologies from the western Bushveld. ⊙ = mean. Large ticks = minimum, maximum.

Groundwater around the Pretoria Salt Pan, which is hosted in Nebo granite, had fluoride concentrations up to 20 mg/ℓ, and the brine in the pan had a fluoride value of 195 mg/ℓ. This is in direct contradiction to the findings of Ashton and Schoemann (1983), who found that fluoride occurred generally below their detection limit. Although they did not specify a detection limit, they report a concentration of 0.14 mg/ℓ F, and it is assumed that their detection limit was below this value. The Rooiberg Group has a number of elevated fluoride concentrations as well as a group of low concentrations. The two populations may reflect the heterogenous nature of the Rooiberg Group (see section 1.3.3).

The Pilanesberg has two types of fluoride enriched groundwater, namely the Shand and Bond groundwater facies (McCaffrey, 1993). Shand-type groundwater has comparatively low F^-, a short residence time and pH=~7. Bond-type groundwater has F^- concentrations > 30 mg/ℓ, a long residence time and pH > 9. The complex as a whole has the highest mean groundwater fluoride concentration (15.0 mg/ℓ) of any of the rock types in the study area. Concentrations are highest in Bond type groundwater, which occurs on the perimeter of the Complex. Concentrations reach 80 mg/ℓ at the Quarantine Camp borehole, although values for the perimeter are generally in the range of 40 to 80 mg/ℓ. Fluoride concentrations of Shand type groundwater, which occurs within the geographic boundaries of the Complex, range from 2 to 7 mg/ℓ and have a normal or Gaussian distribution. No systematic variation in fluoride values with the various foyaite bodies has been discerned.

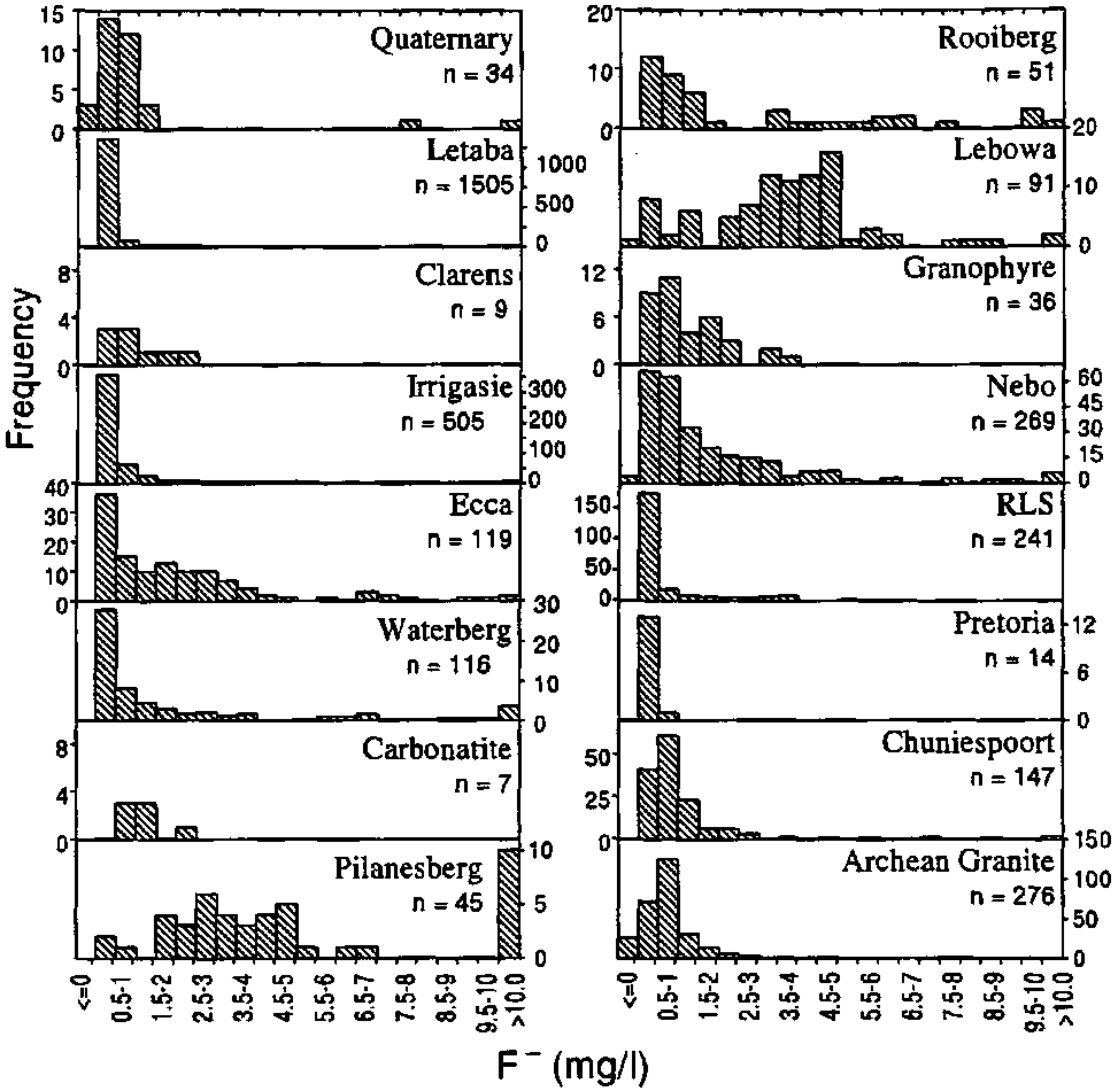


Figure 4.7. Groundwater fluoride histograms for 16 lithologies of the western Bushveld.

Groundwater taken from boreholes in the outcrop area of the Ecca shales have a mean value of 2.3 mg/ℓ F^-. The majority of samples have less than 3 mg/ℓ F^-, but outliers occur at much higher values. The groundwater from boreholes in the outcrop areas of the Irrigasie and Clarens Formations, in the central part of the basin, have lower mean fluoride concentrations, at 1.0 and 0.9 mg/ℓ F^-, respectively, (Figure 4.6), and there are fewer high fluoride outliers than in the Ecca (Figure 4.7).

4.5.2 Chloride

It is striking that the carbonatites have a very high mean concentration of Cl in the groundwater which exceeds the low risk limit (Figure 4.8), but because of the small number of samples (n=6),

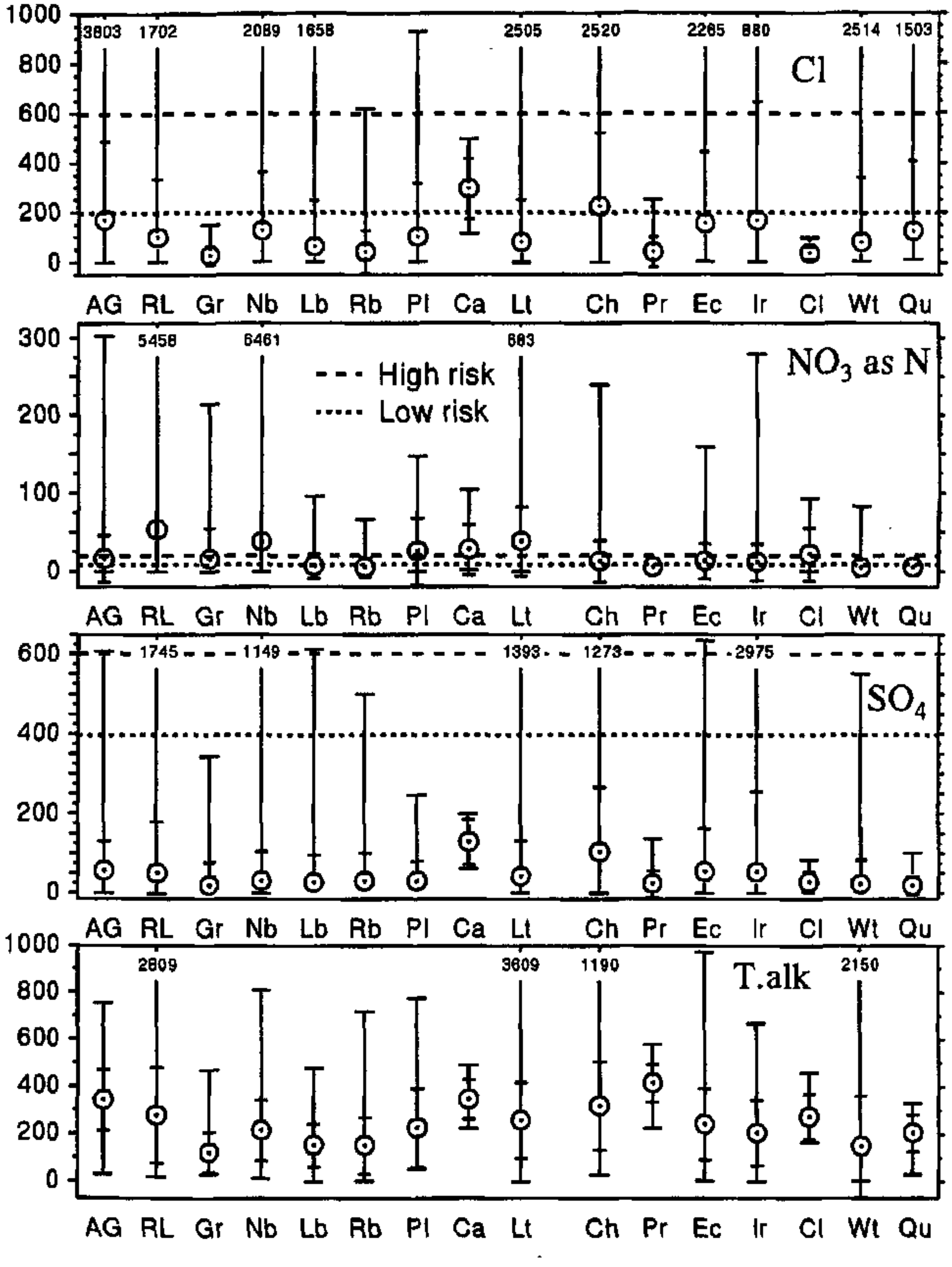


Figure 4.8. Summary statistics for anion analyses from 16 major lithologies from the western Bushveld. Symbols as in Figure 4.6.

this may not be significant. No clear trend is apparent for either the igneous or the sedimentary rocks. Four of the lithologies (Archaean granite, Chuniespoort Sequence, Ecca and Irrigasie Formations) have a mean concentration slightly above or slightly below the low risk limit, but, as with EC and TDS, most have maximum values well above the high risk limit.

4.5.3 Nitrate

Only five lithologies (Lebowa granite, Rooiberg Suite, Pretoria Sequence, Waterberg group and Quaternary Formations) have mean nitrate concentrations below the low risk limit (10 mg/ℓ) in the groundwaters of the field area (Figure 4.8). The Archaean granites, granophyres, Chuniespoort Sequence, Ecca and Irrigasie Formations have nitrate values between the low and high risk levels. The RLS, Nebo Granite and Letaba formation have mean values well above the high risk limit (20 mg/ℓ) and also have very high maximum values. None of these lithologies contain significant amounts of N-bearing minerals, and so the high values are almost certainly anthropogenic. McCaffrey (1993) showed that high NO_3 values to the west of the Pilanesberg in the RLS were spatially associated with villages.

4.5.4 Sulphate

All mean concentrations of sulphate are well below the low risk limit (400 mg/ℓ). Groundwaters from five lithological groups (Chuniespoort Sequence, RLS, Nebo granites, Letaba and Irrigasie Formations) have maximum levels well in excess of the high risk limits. These levels are probably related to weathering of sulphide minerals which are known to occur in these rock types.

4.6 Major elements - cations

Summary statistics for cations are presented in Figure 4.9.

4.6.1 Sodium

Of the igneous rocks, the Pilanesberg has the highest mean concentration of Na, which is just below the low risk level of 200 mg/ℓ, whilst the concentration is similar in all the BIC lithologies. The relative concentrations of Na are very similar to those of Cl, apart from the Pilanesberg. Most of the lithologies, notably the Letaba and Irrigasie Formations and the Witteberg Group, have groundwater with maximum Na concentrations very much greater than the high risk health limit.

4.6.2 Calcium

The highest mean Ca concentration in groundwater occurs in the carbonatite, but all mean values are well below the low risk limit (Figure 4.9). The Letaba basalt and Chuniespoort Group also have elevated concentrations. The Granophyre and Pilanesberg have low mean Ca concentrations in groundwater. No clear trend is seen in the BIC, the rocks of the Karoo sedimentary sequence host groundwater with a decreasing Ca concentration with higher stratigraphic height. The maximum Ca concentrations in groundwaters from the RLS, Letaba and Irrigasie Formations, and the Nebo and Archaean granites greatly exceed the high risk level.

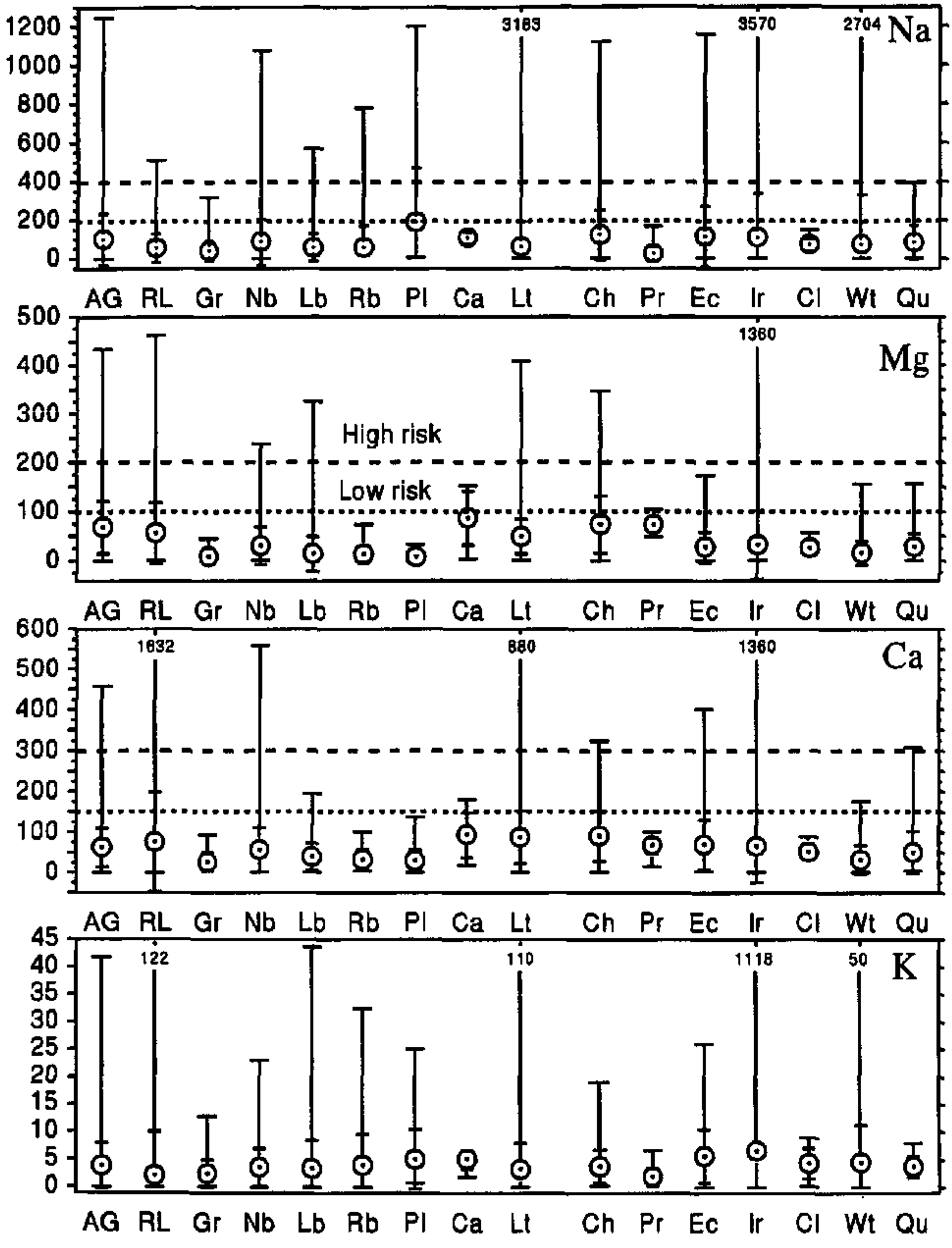


Figure 4.9. Summary statistics for cation analyses from 16 lithologies from the western Bushveld. Symbols as in Figure 4.6. Y-axis units are mg/ℓ. For K, low risk = 50-100 mg/l and high risk is > 100 mg/l.

4.6.3 Magnesium

All mean Mg concentrations in groundwater are less than the low risk limit. High mean concentrations are present in the RLS (composed of mafic minerals), Pretoria Sequence, the carbonatites, the Chuniespoort Group (predominantly dolomite), and the Archaean Granite.

4.6.4 Potassium

All lithologies have mean K values well below the low risk level. There is a clear trend of increasing mean K concentration in groundwaters from the BIC rocks, RLS to Pilanesberg. The Pilanesberg and carbonatites both have groundwater with high K concentrations, and the highest mean concentrations are found in the Ecca and Irrigasie groundwaters. Only the RLS, Letaba and Irrigasie Formations host groundwaters with maximum K values exceeding the high risk level (100 mg/ℓ).

4.7 Trace elements

Groundwater samples from 8 lithologies were analysed for trace elements (see Chapter 2). The results are discussed in descending order of mean concentration, apart from Sr, Al and I, which are discussed in more detail at the end of the section. Summary statistics are shown graphically in Figures 4.10 and 4.11 (means ± 1 s.d) and 4.12 (mean, minimum and maximum). In these figures the lithologies, plotted on the horizontal axis, have been ordered thus: age decreases to the right, and degree of rock fractionation increases to the right; igneous rocks on the left (RL to Pl), sedimentary rocks on the right (Ec to Cl). This allows the identification of age, fractionation and genetic trends.

4.7.1 Zinc

Zinc occurs in appreciable quantities, especially in the Pilanesberg. Although no mean values are above the low risk level for drinking water (20 mg/ℓ), the granophyres and the Pilanesberg lithologies have values above the low risk level (aesthetic) of 5 mg/ℓ Zn No trend is seen in the BIC groundwaters, but Zn concentration increases upwards in Karoo sediment groundwaters.

4.7.2 Molybdenum

Little variation is seen in Mo concentration, which is generally at very low levels, close to the detection limit. However, Lebowa Granite groundwater has a mean concentration above the maximum safe limit of 0.2 mg/ℓ (CSIR, 1991). Molybdenum is an element frequently enriched in pegmatites and other highly fractionated rocks.

4.7.3 Barium

Interesting and very clear trends appear in the Ba concentration of groundwater. Ba concentrations are much lower in the groundwater of the BIC than in that of the Karoo rocks, and decreases with increasing fractionation of the host rock. This is the opposite trend from that expected from a fractionating magma. Mean Ba concentrations in groundwater from the Karoo sediments clearly decrease in higher stratigraphic units.

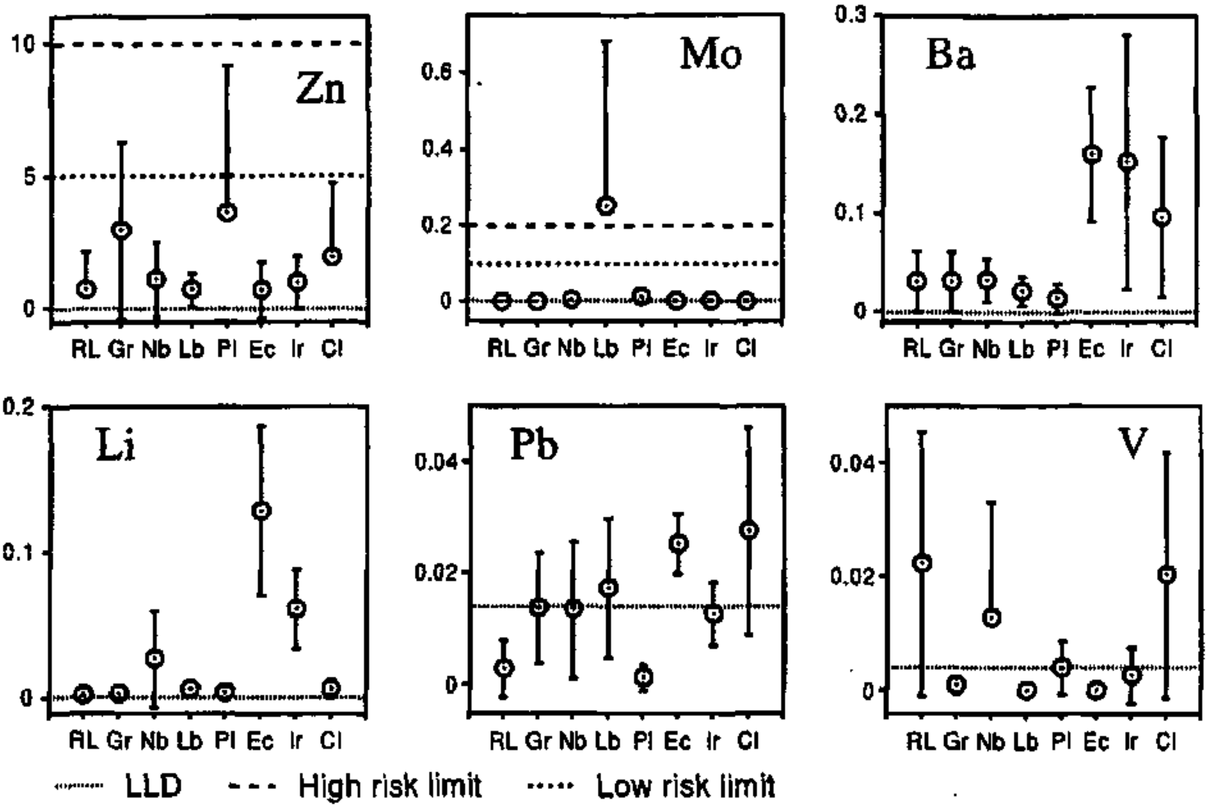


Figure 4.10. Mean concentrations of Zn, Mo, Ba, Li, Pb and V in groundwater from 8 major lithologies in the western Bushveld. ⊙ = mean, small ticks ±1 s.d.. Y-axis units are mg/ℓ.

4.7.4 Lithium

There is no clear trend for Li concentrations in BIC groundwaters, but the Li concentration in the Karoo groundwaters decreases markedly in higher stratigraphic units. The trend is more pronounced than that for Ba.

4.7.5 Lead

Only the Lebowa Granite, Ecca and Clarens Formations host groundwaters with a mean Pb concentration above the detection limit. Lead concentration in groundwater increases sporadically towards the more fractionated lithologies of the BIC, but is very low in the Pilanesberg. No clear trend is seen in the Karoo groundwaters, but the concentrations are generally higher than in BIC groundwater.

4.7.6 Vanadium

Most of the analyses for vanadium are below the detection limit, but of the groundwaters in the BIC the RLS and Nebo Granite both have high V concentrations (Figure 4.10). In the Karoo Formation only the Clarens groundwaters have detectable V concentrations.

4.7.7 Copper

No trend in Cu concentrations can be identified in groundwater from the BIC, but in the groundwater of the Karoo sediments Cu decreases from the Ecca shales (older) to the Clarens sandstone (younger) (Figures 4.11 and 4.12).

4.7.8 Arsenic

Only the mean As concentration in groundwater from the Nebo granite exceeds the detection limit, and the maximum concentration is well below the low risk safe limit of 0.3 mg/ℓ. Arsenic concentrations in the other groundwaters are uniformly low and below the detection limit.

4.7.9 Chromium

Chromium "apparently" shows the clearest trends of any of the trace elements. Unfortunately most of the results are below the detection limit, and the trends are spurious. Only the groundwaters from the mafic Cr-rich rocks of the RLS have a mean Cr concentration above the detection limit.

4.7.10 Cobalt, Cadmium and Nickel

These three elements have concentrations generally below the detection limit and the identification of trends is meaningless.

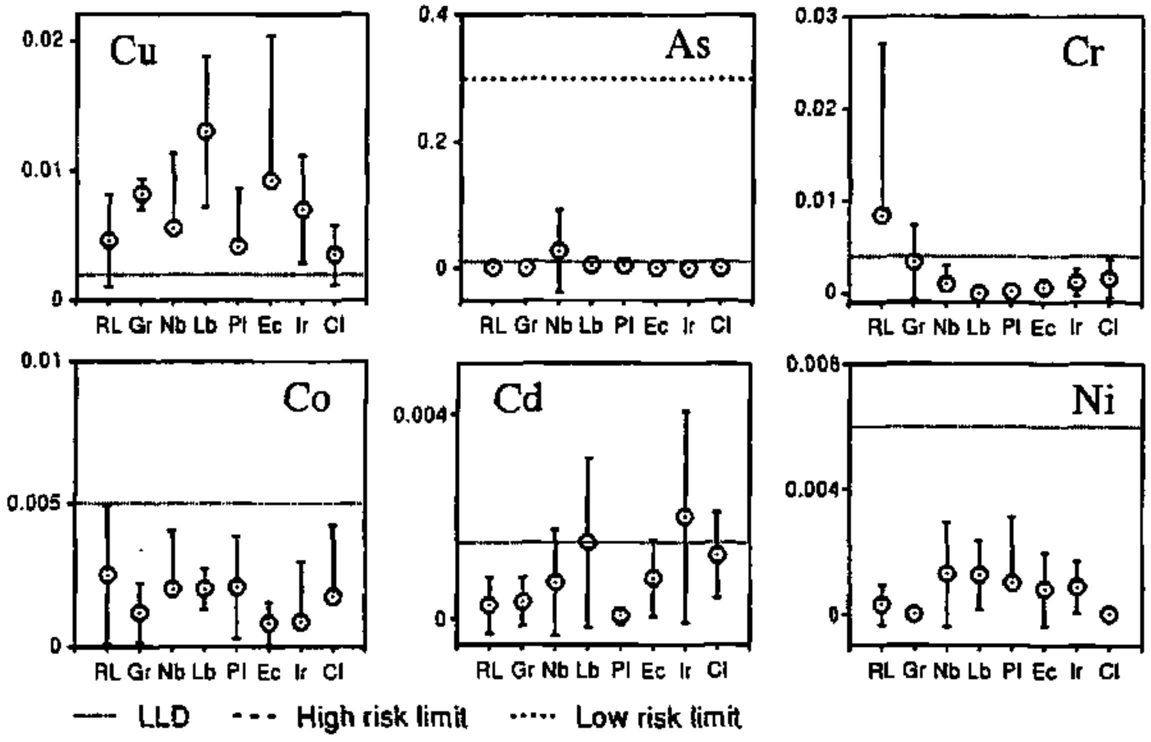


Figure 4.11. Mean concentrations of Cu, As, Cr, Co, Cd and Ni in groundwater from 8 major lithologies from the western Bushveld. Symbols as in Figure 4.9. Y-axis units are mg/ℓ.

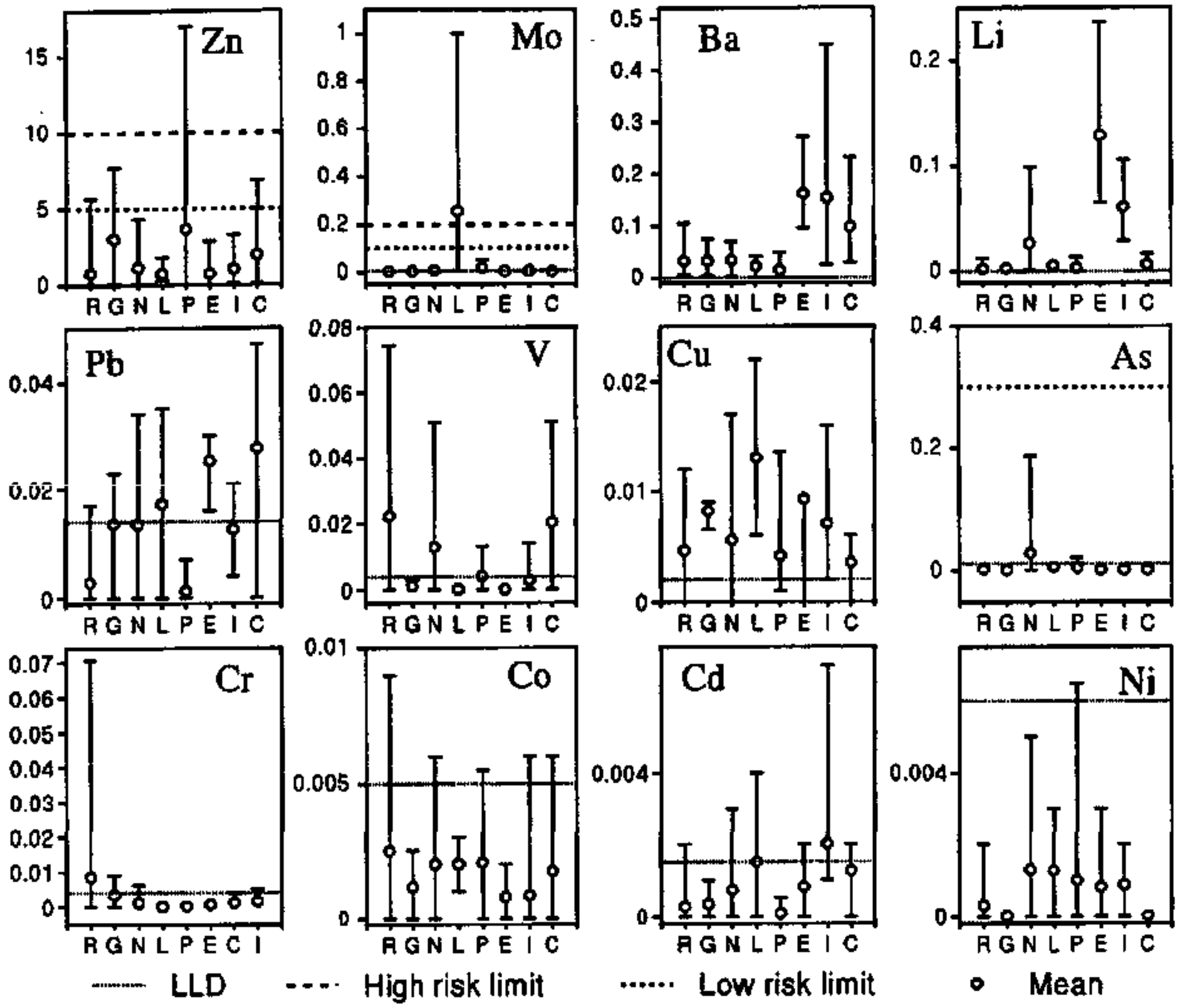


Figure 4.12. Mean (○), maximum and minimum (tick marks) concentrations of trace elements in groundwater. Y-axis units are mg/ℓ.

4.7.11 Iodide

The iodide data, shown in full in Appendix A10, is for a sub-set of the acidified samples. The detection limit, calculated as 3 times the baseline noise, was 1 µg/l I^- (SAIMR, *pers. comm.*). Twenty-one of the samples had no detectable iodide, eleven had between 0 and 20 µg/l, sixteen had between 20 and 100 µg/l and four had over 100 µg/l. Notably, water from the Pretoria Saltpan lake had a very high iodide concentration of 641 µg/l.

The World Health Organisation recommends an intake of 100 µg/l per day (W.J. Kalk, Department of Medicine, Division of Endocrinology, University of the Witwatersrand, *pers. comm.*). Matthess (1982) stated that "the iodine content in most fresh waters should lie below the detection limit", but did not detail the analytical method.

Given that I^- is present in rainwater at concentrations generally less than 5 μg/l (Fuge, 1988), and that the field area is over 1000 km from the nearest source of marine-derived I^- aerosol, the results indicate that I^- in the groundwaters is derived from the weathering of rocks. The very large variations in I^- concentration also suggest that atmospheric deposition is not a factor. The discussion of I^- levels in groundwaters around the world in Fuge (1989) indicates that those groundwaters of the western Bushveld with >20 μg/l I^- are anomalously enriched.

Table 4.2 gives summary statistics for I^- concentrations from 8 lithologies, and the statistics are shown graphically in Figure 4.13. It is apparent that very high concentrations occur in the Irrigasie formation, which is predominantly shaley (Section 1.2.3). The Ecca formation also shows elevated concentrations. The Pilanesberg has the highest I^- concentration in groundwater contained in the igneous rocks, and this is in accordance with the fact that I^- becomes enriched in a fractionating magma. No clear trend is apparent from the BIC rocks, although the RLS rocks have a wide concentration range, with a few very high values. This may reflect the chalcophylic nature of I.

Table 4.2. Summary statistics of iodine concentrations in groundwater from the BIC, Pilanesberg and the Karoo sediments. Concentrations in μg/l. See Appendix A10 for original analyses.

Lithology	Mean	Std. dev.	Number
RLS	21	49	17
Granophyre	3	3	3
Nebo Granite	15	25	5
Lebowa Granite	3	2	3
Pilanesberg	32	42	7
Ecca	65	38	5
Irrigasie	122	65	6
Clarens	4	2	4

4.7.12 Strontium

Although present at very low concentrations, Sr is of importance when using Sr isotopes in the study of groundwater provenance. Sr should act similarly to Ca in the geochemical environment (Section 1.4.1.2), but Figure 4.14 shows that in the more fractionated (Ca- and Sr-poor) rock types of the BIC, *e.g.* Nebo and Lebowa granites, the groundwater becomes increasingly impoverished in Sr. The Pilanesberg, known for its high Sr content (and which contains the mineral strontianite, section 3.5.2) has a mean groundwater Sr concentration similar to that of the RLS. The Karoo sediments show a decreasing trend with increasing stratigraphic height. The Ecca and Irrigasie formations both have groundwater with moderately high (>1 mg/ℓ) Sr concentrations.

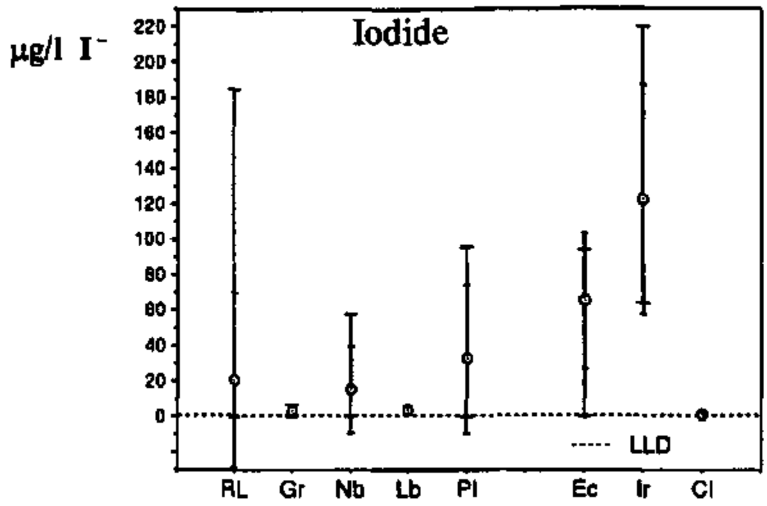


Figure 4.13. Summary statistics for iodide in groundwater from the field area. Abbreviations and symbols as in Figure 4.6.

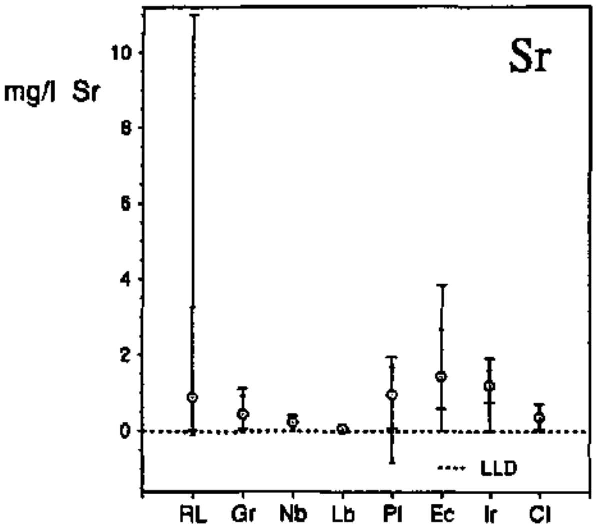


Figure 4.14. Summary statistics for Sr concentration in groundwater from the western Bushveld.

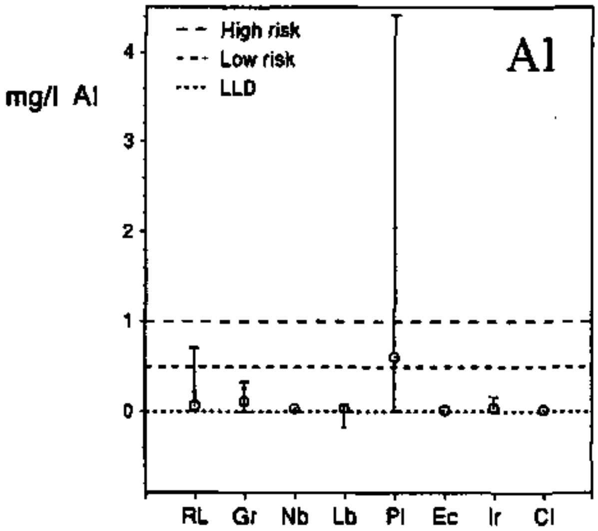


Figure 4.15. Summary statistics for Al concentration in groundwater from the western Bushveld.

4.7.13 Aluminium

Generally an element with low solubility at normal pH levels of groundwater ($5 < \text{pH} < 9$), Al concentration is at its maximum in Pilanesberg groundwater (Figure 4.15), where water with a pH greater than 10 is known to occur (Section 4.4.2). Many values are well above the acceptable high risk limit. BIC and Karoo groundwaters show no clear trend in Al concentration.

4.8 Temporal variation

A number of boreholes were resampled to determine possible temporal variation in chemical composition. Sites 298 and 299 were resampled with an interval of approximately 1 year, whilst the other sites were sampled after an interval closer to two years. The results are shown in Figure 4.16. There is a great deal of variation, especially in NO_3 and SO_4. To a lesser but still significant extent, the measured concentration of the other major ions also vary with time at specific sites. The anion concentrations vary most at site 34, just outside the Pilanesberg, where Cl^- has replaced NO_3^- and SO_4^-, and where Ca^{2+} shows a marked increase over time. Site 298 shows a significant decrease in Ca and Mg concentration, whilst the Na and K concentrations in the groundwater at site 233 have also decreased over the sampling time. F^- shows the least temporal variation (Figure 4.17). This may be due either to the fact that the determination is the simplest and probably the most accurate of the analytical methods used in this study (Chapter 2), or that F^- is buffered by dissolution-precipitation reactions. Temporal variation in groundwater is not well documented in South Africa; the inauguration of a national groundwater chemistry monitoring network should rectify the problem.

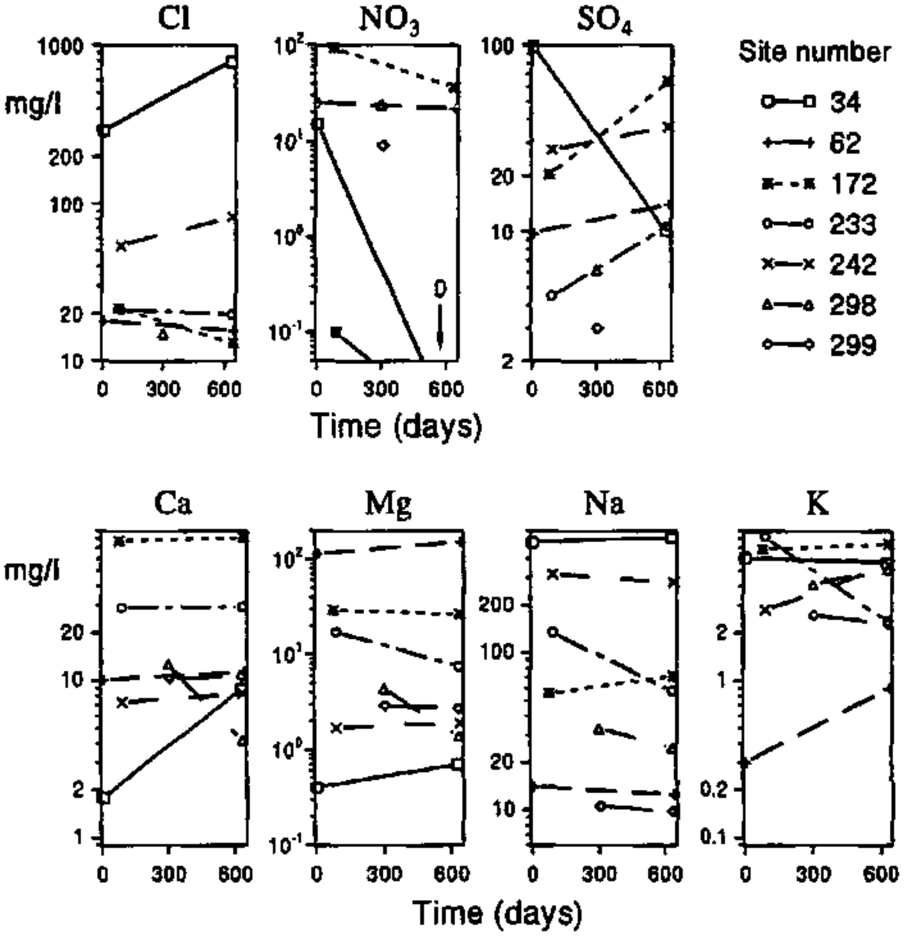


Figure 4.16. Variation in groundwater ionic concentrations with time from re-sampled boreholes. Concentrations are expressed in mg/ℓ.

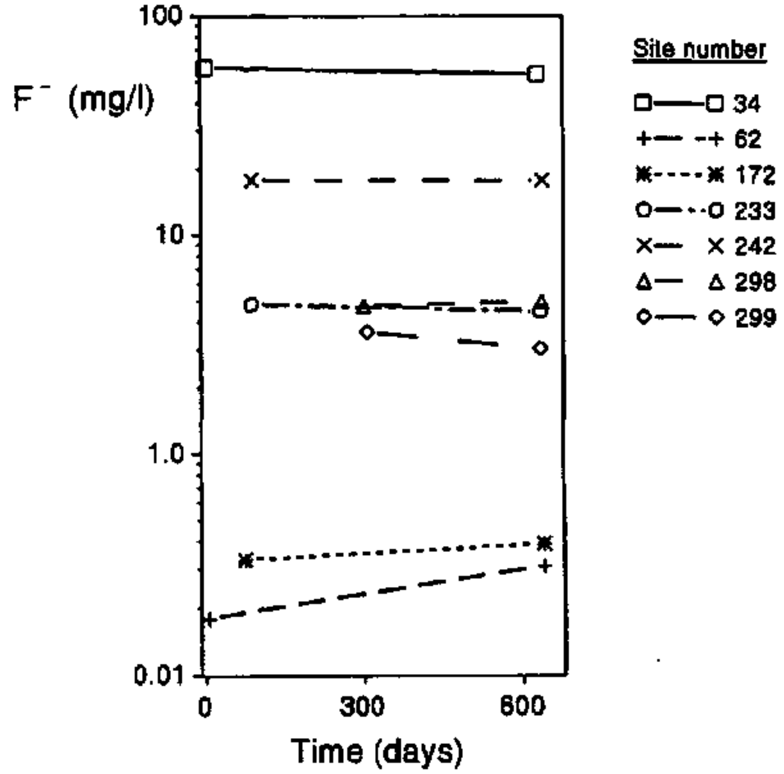


Figure 4.17. Temporal variation of fluoride concentration in groundwater from resampled boreholes.

4.9 Results of isotopic analyses

Naturally occurring and anthropogenic isotopes have been studied in hydrological systems around the world and provide valuable insights into geohydrological processes (*e.g.* Verhagen *et al*, 1991, 1974; Blavoux and Letolle, 1995). Determinations of ^{18}O and ^{2}H have been used in conjunction with hydrological modelling and radiogenic isotopes to estimate palaeoclimates (Heaton *et al*, 1986), for the location of recharge areas and for modelling both terrestrial (McCaffrey *et al.*, 1996) and extraterrestrial water-rock interactions (Jakosky and Jones, 1994). Other radiogenic isotopes studies, principally using ^{3}H, ^{14}C and ^{36}Cl, have concentrated on the estimation of recharge rates in sedimentary basins (*e.g.* Verhagen *et al.*, 1974) and continental scale groundwater flow. $^{87}Sr/^{86}Sr$ ratios have been used for several purposes in the earth sciences, chiefly in dating rocks. Increasing use is being made of Sr isotopes for environmental geological purposes, such as dating glacial influences on landscapes (Blum *et al.*, 1994), investigation of water/rock interaction (Collerson *et al.*, 1988; Dia *et al.*, 1995), nuclear waste safety studies (Stuckless *et al.*, 1991) and for groundwater provenance studies (Verdoux *et al*, 1995; Banner *et al*, 1994).

The use of ^{3}H as a recharge rate indicator is now limited, due to the radioactive decay of ^{3}H to concentrations below natural background levels. ^{3}H was introduced into the atmosphere as a result of thermonuclear weapons testing in the 1960s. Blavoux and Letolle (1995) predict that anthropogenic ^{36}Cl, produced during thermonuclear tests in atolls of the Pacific Ocean between

1952-1958, will supersede tritium as the tracer of choice. This will be due mainly to the large amounts of ^{36}Cl produced in these tests and its long half life (~300 kyrs). Although the analysis of ^{36}Cl may have proved useful, no arrangements exist for its determination in South Africa at present.

Use has been made of ^{14}C and the ratio of the isotopes δ^{18}O/^{16}O, δ^{2}H/^{1}H and ^{87}Sr/^{86}Sr for this study; the results are presented in Tables 4.3 and 4.4 and discussed in the following sections. Sampling locations are given in Figure 4-18.

Table 4.3. Isotope analyses for groundwater, precipitation and pan water from the study area. See text for details of notation and analysis. Sample types are 'G', groundwater and 'B', brine from the surface of the Pretoria Salt Pan. 'P' is Pilanesberg, 'N' is Nebo Granite, 'L' is Lebowa Granite, 'RLS' is Rustenburg Layered Suite. 'PSP' is Pretoria Saltpan. 'n/d' is not determined.

Sample No.	**LOCATION**	**Type**	**Lithology**	**^{14}C (pmC)**	**δ^{2}H**	**δ^{18}O**	**±1 s.d.**
n/a	Hail, Pilanesberg		-	*n/d*	-43.17	-7.31	0.07
n/a	Rain, Pilanesberg		-	*n/d*	-14.18	-3.03	0.02
287	Quarantine Camp	G	P	4.0	-33.56	-5.69	*n/d*
288	Letswaaneng	G	P	55.0	-32.27	-5.46	0.01
242	Theledi's Farm	G	N	3.2	-22.49	-4.62	0.01
243	Stinkwater	G	N	63.3	-27.31	-4.16	*n/d*
292	Makoropeja	G	L	9.0	-33.06	-3.31	0.04
299	Klipvoor	G	L	87.5	-26.62	-3.72	0.02
300	Slipfontein	G	L	51.9	-21.08	-3.59	0.03
301	Northam Plat	G	RLS	*n/a*	-28.16	-3.75	0.02
230	PSP Surface	B	-	*n/a*	+9.68	+1.89	0.01
335	PSP, Old artesian	G	N	*n/a*	-27.34	-4.35	0.01
337	PSP, Strat	G	N	*n/a*	-28.00	-4.54	0.02
336	PSP, Museum	G	N	*n/a*	-29.52	-4.63	0.03
338	PSP, Mr Mon's store	G	N	*n/a*	-10.48	-2.03	0.02

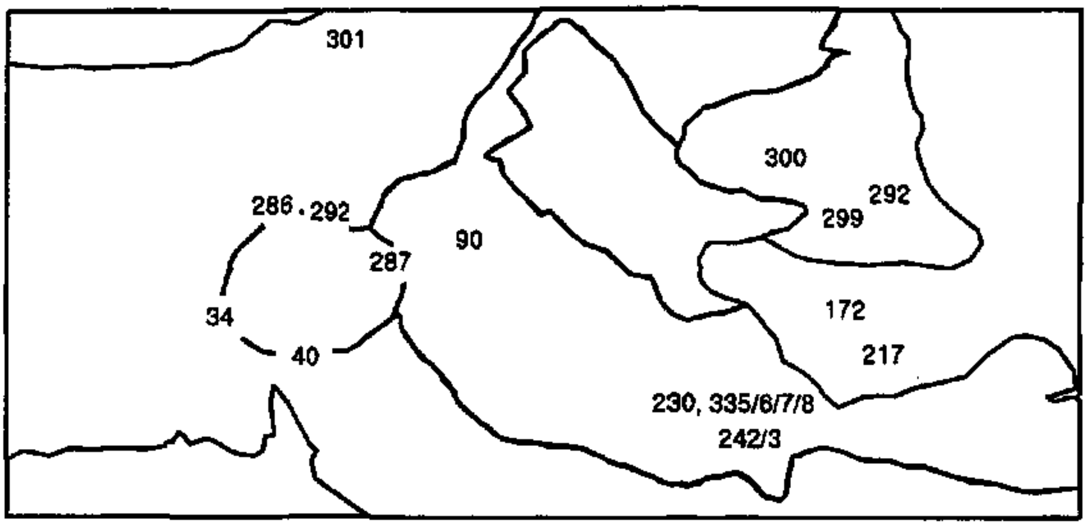


Figure 4.18. Locations of groundwater samples in which environmental and radiogenic Sr isotope ratios were determined.

4.9.1 Environmental Isotopes

4.9.1.1 Oxygen ($\delta^{18}O$)

The results for $\delta^{18}O$ in groundwater range from -5.69 from the Quarantine Camp borehole to -2.03 from a borehole in the Yard of Mr Mon's Trading store, 1 km from the Pretoria Saltpan. It is apparent that the $\delta^{18}O$ values of the groundwater samples vary according to the host lithology (Table 4.3); Pilanesberg groundwater has a $\delta^{18}O$ of between -5.5 and -5.7, the Nebo Granite samples have around -4.5, except for the sample from Mr. Mon's store, and the Lebowa Granite groundwaters have values around -3.5. Groundwater becomes enriched in ^{18}O the further east the sample is taken. Notably, the $\delta^{18}O$ values for samples from the perimeter of the Pilanesberg are low, as predicted by McCaffrey (1993). The analysis of a groundwater sample from the Quarantine Camp borehole yielded a value of -5.69 in this study. Water from the same borehole was analysed and reported in McCaffrey (1993) as having a $\delta^{18}O$ of -6.4.

Other samples of water of relevance to this study were analysed. Water from the first 5 cm of the surface of the Pretoria Saltpan had a $\delta^{18}O$ of +1.89, a very 'heavy' sample of potentially great significance to the regional geohydrology (see Chapter 5). Also sampled were rain and hail from the same thunderstorm, on the night of the 7th May 1995, which occurred over the Pilanesberg. Rain water was collected in a saucepan, whilst the hail was collected from the centre of "hail drifts" up to 50 cm thick found the next day. The difference between the two samples is large and may be influenced by several processes which are discussed in Chapter 5.

4.9.1.2 Hydrogen (δ^2H)

Marked differences in hydrogen isotope ratio occur in the groundwater of the field area (Figure 4.19). The δ^2H values, when plotted against δ^{18}O, show that most of the groundwaters plot close to the meteoric water line of Craig (1961). Deviations from this line towards heavier ratios for δ^2H and δ^{18}O indicate that evaporation is taking place. Some of the Pilanesberg central groundwaters show a marked evaporation trend, as noted and discussed in McCaffrey (1993). Lebowa Granite groundwater has a range of δ^2H values, with little variation in δ^{18}O. Such variation is difficult to explain.

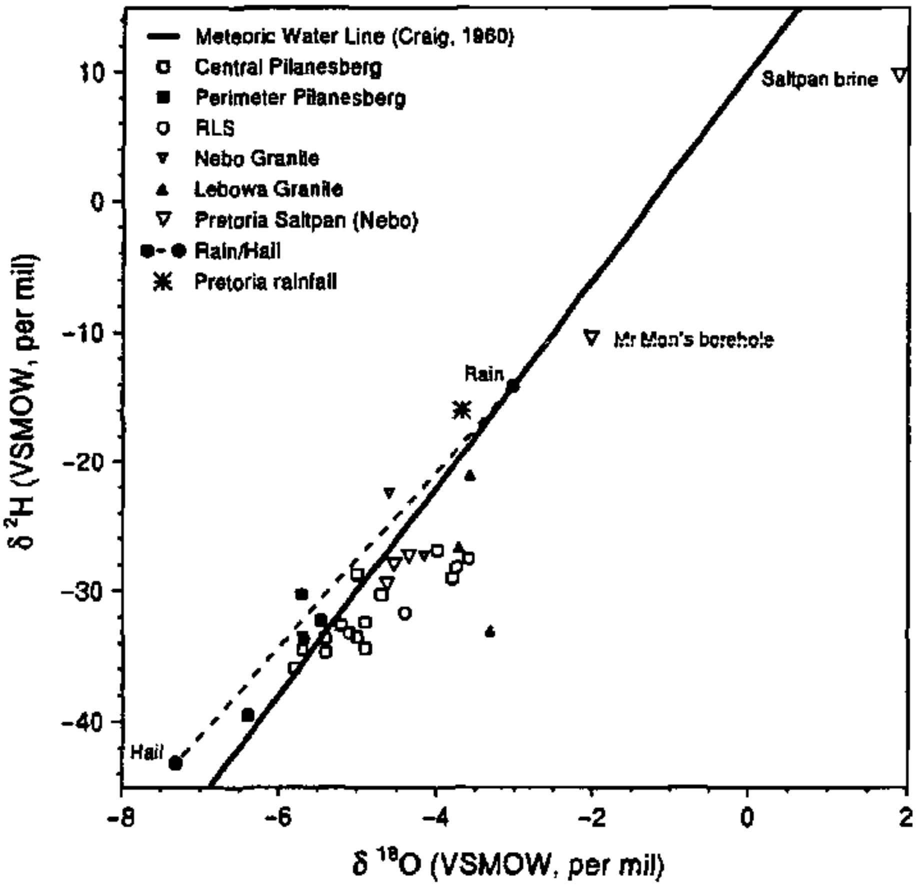


Figure 4.19. δ^{18}O and δ^2H isotope analyses for groundwaters from the field area.

4.9.2 Radiogenic Isotopes

4.9.2.1 Carbon (^{14}C)

A wide range of radiocarbon contents has been shown to occur in the groundwater of the field area, from just 2 pmC ^{14}C from a Pilanesberg sample (at the Quarantine Camp) to 98.5 pmC ^{14}C at Mankwe Camp inside the Pilanesberg (McCaffrey, 1993). The radiocarbon contents on the perimeter of the Pilanesberg are not as uniformly low as reported in McCaffrey (1993).

Samples from the granites also have a wide range of radiocarbon contents, from 3.2 pmC ^{14}C at Theledi's Farm to 87.5 pmC ^{14}C at Klipvoor Dam. The radiocarbon content of these samples has a marked correlation with fluoride content (Figure 4.20), although this may be a function of the small data set. The small sample size notwithstanding, this trend may indicate that F is being incongruently leached at a very slow rate from amphibole and mica to eventually reach very high concentrations.

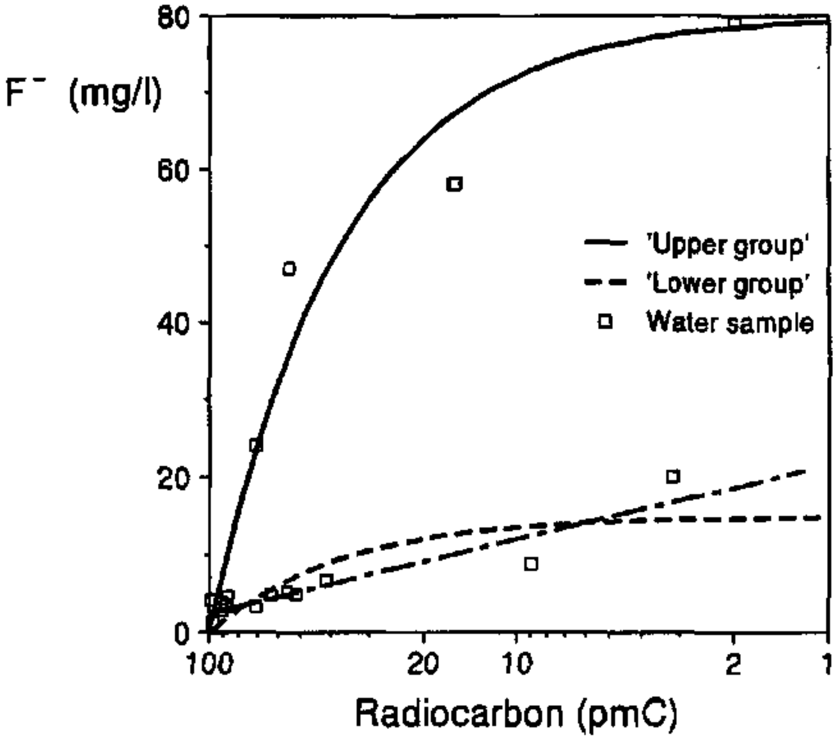


Figure 4.20. Plot showing correlations between ^{14}C and F^-. See text for discussion.

4.9.2.2 Strontium ($^{87}Sr/^{86}Sr$)

The $^{87}Sr/^{86}Sr$ ratio of groundwater from the lithologies of the field area show a wide range of values, from 0.7038 in the Pilanesberg to 0.8028 in the Lebowa granite. Where more than one sample has been taken from the same lithology at different locations, the $^{87}Sr/^{86}Sr$ value is generally similar (within ± 0.02). The results are given in Table 4.4, where samples have been grouped by lithology. The results are shown graphically in Figure 4.21. It can be seen that good discrimination is achieved between groundwaters hosted in different formations. Lebowa Granite groundwater has a significantly different Sr ratio to the other formations. Figure 4.21 also shows the range of Sr ratios for the host rocks. There is general similarity between groundwater and host rock, *i.e.* groundwater plots within or near the rock ratios, and there is no systematic shift.

Table 4.4. $^{87}Sr/^{86}Sr$ values for groundwater in various lithologies.

Sample No.	Site Name	Lithology	$^{87}Sr/^{86}Sr$
40	Ledig	Pilanesberg	0.70382
287	Quarantine Camp	Pilanesberg/ Nebo Granite	0.71183
90	Rietspruit	Nebo Granite	0.72728
242	Theledi's Farm	Nebo Granite	0.73732
292	Makoropeja	Lebowa Granite	0.78148
300	Slipfontein	Lebowa Granite	0.80284
172	Sephai	Karoo, Clarens	0.72290
217	Botshabelo	Karoo, Irrigasie	0.71637
301	Northam Mine	Rustenburg Layered Suite	0.71436

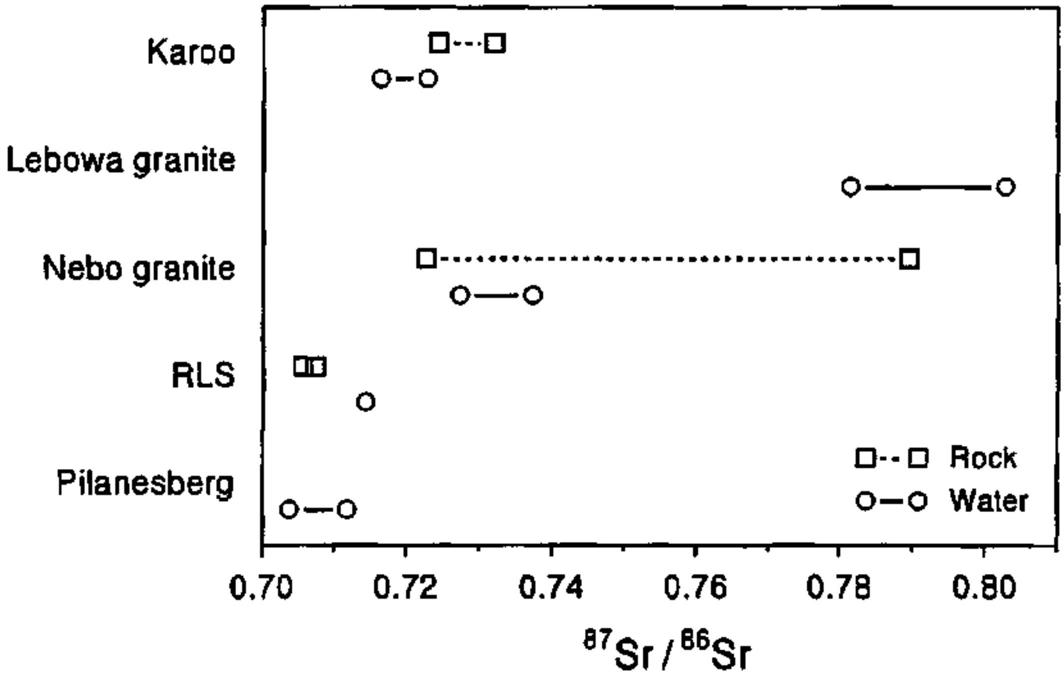


Figure 4.21. Sr isotope data for groundwater and host rocks from the Bushveld. All groundwater and Karoo rock Sr ratios from the RIF, University of Cape Town. RLS values from Hamilton (1977), Nebo values from Harmer (1992).

5 DISCUSSION

5.1 Introduction

In this chapter the results presented in Chapters 3 and 4 will be discussed in relation to their significance from several aspects:

1) the health related aspects of groundwater fluoride concentration and speciation;
2) geochemical controls of fluoride concentration and speciation;
3) the hydrochemical systems present in the western Bushveld.

Ions which have an affect on fluoride in groundwater are also discussed here.

5.2 Fluorine Geochemistry And Health

This section will review previous work on the geochemical behaviour of fluoride, the distribution and causes of high fluoride groundwater, fluorosis, and some aspects of hydrochemistry. These topics are of relevance to arguments advanced later in the report.

5.2.1 Geochemical behaviour of Fluorine

Fluorine is the lightest element in the Halogen group and is the 14th most abundant element in the lithosphere. It is the most electronegative and reactive element known. Fluorine is rarely found in the elemental state; usually it forms ionic bonds. Bonding with anions of groups VA, VIA and VIIA (apart from P, As, Sb and Bi) does not occur because of the high electronegativity of F.

5.2.1.1 Natural Waters

Most simple compounds of F are readily soluble in water. The Eh and pH conditions of F speciation are shown in Figure 5.1. It is noted that under conditions in which water is stable, F usually exists as the monovalent anion, F^-. At a pH below 3.5, F in solution may occur in the HF° form. The close similarity in size and the equivalence of charge of hydroxide and fluoride ions causes interference when a fluoride ion selective electrode is used for water analysis. F can also occur as a complex, such as $(AlF_6)^{3-}$ or AlF^{2+}. Formation of these complexes takes place rapidly (in the order of minutes) at the pH and temperature of typical temperate groundwaters, and their formation can be regarded in the hydrogeological context as an equilibrium process (Plankey and Patterson, 1986).

5.2.1.2 Fluorine in minerals

Fluorine is not an essential element in any of the common rock-forming minerals. Topaz ($Al_2[SiO_4](OH,F)_2$) and fluorite (CaF_2) are the only two common accessory minerals in which F is an essential element. Just under 150 fluorine-bearing accessory minerals are known, and many others contain small amounts of F^- replacing OH^- and O^{2-} (Koritnig, 1974). Table 5.1 shows a comparison of the ionic radius of F^-, with the other members of the halide group and the geochemical analogues of F^-, OH^- and O^{2-}. It is apparent that the F^-, OH^- and O^{2-} ions have similar ionic radii, with OH^-

having the same charge as F^-; Cl^-, Br^- and I^- have the same charge but much larger ionic radii. This leads to very different partitioning behaviour between F^- and the rest of the halides in silicate melts.

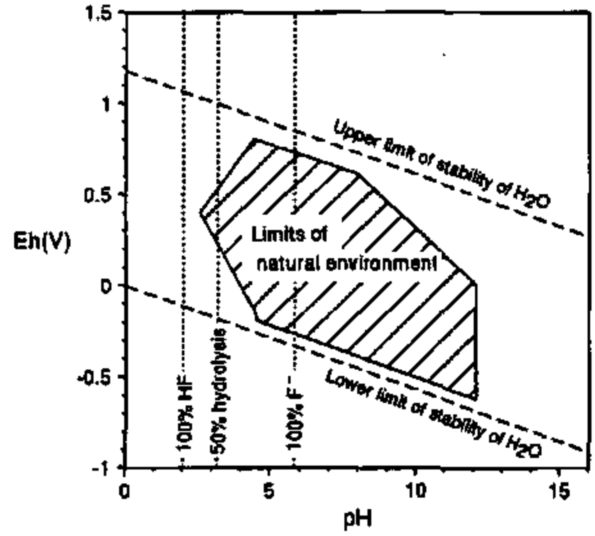


Figure 5.1. Eh-pH equilibrium diagram for the system F-H_2O at 25°C, and for total F concentration less than 2000 mg/ℓ. After Boyle (1976).

Table 5.1 Relative atomic mass (RAM) and ionic radius of halogen group ions and geochemical analogues. Ionic radii are in picometres and are for coordination number VI. *Source:* Ahrens (1952), quoted in Henderson (1986).

Ion	**Symbol**	**RAM**	**Ionic Radius**	**Ion**	**Symbol**	**RAM**	**Ionic Radius**
FLUORIDE	**F^-**	**19**	**133**	Chloride	Cl^-	35.5	181
Hydroxide	OH^-	17	140-160	Bromide	Br^-	79.9	196
Oxide	O^{2-}	16	132	Iodide	I^-	126.9	220

Because of the similarity in ionic radius to OH^-, F^- can isomorphously replace OH^- in minerals such as topaz, micas, [e.g. muscovite, $K_2Al_6Si_6O_{20}(F,OH)_4$], and amphiboles, [e.g. tremolite-ferroactinolites, $Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(F,OH)_2$] (Deer *et al.*, 1977). A higher thermal stability has been reported for pure fluormica (phlogopite) compared to hydroxy phlogopite, and this is the case with many minerals with solid solutions of F and OH. The ability of F^- to substitute for OH^- or O^{2-} depends mainly on the coordination and kind of ligand that the OH^- or O^{2-} ions form within the lattice of a given mineral (Boyle, 1976). The amount of F in a magmatic system is the primary control of F concentration in minerals, but O fugacity affects the F concentration of micas and amphiboles (Koritnig, 1974). According to Koritnig coexisting amphibole and biotite have F contents of about the same magnitude.

5.2.1.3 Magmatic systems

Koritnig (1974) summarised the geochemical behaviour of F in igneous rocks in general, whilst Bailey (1977) reviewed the geochemistry of F in granitic rocks and melts. Boyle (1976) discussed the F concentrations for many rock types and his values are shown here in Tables 5.2, 5.3 and 5.4. Fluorine concentrations within similar lithologies are subject to large variations, for instance in granites ranging from tens of ppm to several percent (Bailey, 1977). However, in general the concentration trend in igneous rocks follows ultramafic < intermediate < granitic < alkaline. The mean concentrations are approximately 100, 400, 800 and 1000 ppm, respectively (Koritnig, 1974; Bailey, 1977), although Boyle (1976) gives slightly different mean values (Table 5.2).

Table 5.2 Fluorine in intrusive and extrusive igneous rocks. After the compilation by Boyle (1976). 'Tr.' is trace. All concentrations in ppm.

Rock Type	Range		Mean	Number
	Minimum	Maximum		
Intrusive				
Ultramafic	Tr.	2000	130	37
Gabbros	50	11000	430	47
Diorites	300	1300	665	20
Granites and Granodiorites	20	30000	810	182
Syenite and monzonite	200	4000	1360	26
Alkaline ultramafic	Tr.	3800	1400	41
Alkali syenite	100	25800	1800	249
Alkali granite	670	12400	5500	20
Carbonatites	200	24000	8100	96
Kimberlites	520	2500	1310	42
Dolerites	198	500	420	14
Pegmatites	800	9000	4320	6
Extrusive				
Basalts	20	2400	375	317
Andesites	Tr.	1200	250	97
Rhyolites	Tr.	6850	610	151
Trachyte and Latite	200	2250	750	9

In granitic melts F^- replaces O^{2-}, breaking the Si-O chains and forming Si-F bonds instead, in effect depolymerizing the melt. With decreasing SiO_2/alkali ratios F becomes linked to Na and Ca, although the exact proportions are not clear (Kogarko *et al.*, 1968). Fluorine has been found to depress the temperature of the liquidus by up to 110°C, delays the onset of crystallization, and promotes quartz, topaz and feldspar above biotite in the order of crystallization in granitic magmas (Bailey, 1977). The main rock forming minerals are unable to accept F into their structure and so F is enriched in fractionating magmatic systems. Boyle (1976) stated that F is enriched in the residual, aqueous and vapour phases of a magma, and is often associated with pegmatites and hydrothermal alteration.

F-rich melts may immiscibly separate into a fluoridic alkaline melt and a polymerized silicate melt. It has been found that large amounts of F (8%) are needed to maintain carbonatite magmas in the liquid state at the low eruption temperatures (500-590°C) seen at the carbonatite volcano Oldoinyo Lengai in Tanzania (Jago and Gittins, 1991). In alkaline magmas the separation of F into a separate gaseous phase is suppressed, F is trapped by NaF and F therefore becomes enriched in the magma.

Between 30 and 90% of F in calc-alkaline granites is found in biotite, with the remainder in hornblende, muscovite and accessory minerals such as fluorite. The concentration of F in these biotites is a function of the H_2O-HF composition and temperature of the fluid which last re-equilibrated with the mica, and the composition of the mica (Mg rich biotites can contain much more F than those rich in Fe) (Speer, 1984).

In F-rich granites and metasomatic roof zones, accessory minerals such as fluorite, apatite, sphene, microlite, pyrochlore, topaz, tourmaline and bastnasite can host more than 50% of the total F. Fluorine is also found in solid and fluid inclusions (e.g. micas in feldspar and fluid inclusions in quartz), and as glasses (Bailey, 1977; Correns, 1956). Fluorine concentrations in granitic fluid inclusions are usually less than those of H_2O, CO_2 and Cl (Roedder, 1972). Near-surface degassing causes the F content of extrusive rocks to be generally lower than that for the equivalent intrusive rock (although it should be noted that the inclusion of some alkali basalts in the mean for basalts in Table 5.2 has increased the basalt mean beyond that for andesites). The HF content of volcanic gases is generally below 0.03 vol% (White and Waring, 1963).

After solidification of silicic magmas (between 600 and 450°C), F probably forms highly soluble complexes with a variety of elements, e.g. $[AlF_2(H_2O)_4]^+$, $(SiF_6)^{2-}$ and $NaAlF_4$. These early complexes decompose with decreasing temperature and pressure, releasing F as a true gas phase. Greisenization takes place in these conditions. Between 400 and 200°C F combines with Al and Ca to form topaz and fluorite in hydrothermal quartz veins (Shcherba, 1970). Fluorine-metasomatism during greisenization is associated with deposition of W, Sn, Be and Li.

5.2.1.4 Metamorphic rocks

Fluorine concentration in metamorphic rocks is highly variable (Table 5.3), as the F content is related to the amount present in the pre-metamorphic protolith. Fluorine is remobilised during regional metamorphism to zones of low pressure, temperature or F concentration or to reactive rocks such as limestone. Regional metamorphic rocks are generally low in F, as shown, for instance, by the mean values for schists (250 ppm) and shales (790 ppm, Table 5.4). Fluorine substitutions for O^{2-} tend to occur at high temperatures and pressures, resulting in the minerals sphene and pyrochlore. Fluorine is lost from biotite at low temperatures but gained at higher grades. Biotite has 0.65% F in granulite facies compared to 0.24-0.38% F in amphibolite facies and <0.2% F in low grade rocks (Filippov *et al.*, 1974; Guidotti, 1984). Muscovite has F up to 0.25%, but usually around 0.1%. Guidotti (1984) proposed that as metamorphic grade increases, hydrous minerals are lost and F becomes enriched in the remaining hydrous phases.

Metasomatised rocks may have high F contents because, along with CO_2, HCl and H_2O, HF can be a major component of metasomatising fluids. Skarns can contain a wide range of F-bearing minerals such as fluorite, apatite, hornblende, mica, topaz and sphene.

Table 5.3 Fluorine in metamorphic rocks. After the compilation by Boyle (1976). 'Tr.' is trace. All concentrations in ppm.

Rock Type	Range		Mean	Number
	Minimum	Maximum		
Regional				
Metagabbro	99	140	120	2
Schists	60	580	250	48
Amphibolite	140	1400	740	10
Gneiss	240	2800	1030	14
Metasomatic				
Hornfels	26	7800	1630	57
Contact Skarns	700	43500	9780	28
Greisens	1600	20400	9800	26
Kaolinized Granite	800	7400	2800	26
Fenite	Tr.	600	400	3

5.2.1.5 Sedimentary rocks

Fluorine becomes a component of sedimentary rocks through several processes. Fluorine may be present in resistant minerals such as topaz, tourmaline and apatite, and to a lesser extent fluorite and the micas. It may be absorbed onto an anion receptor such as a clay particle, or it may be transported into the sediment as an aqueous ion or complex. In marine sediments it may co-precipitate from seawater with $CaCO_3$ and phosphate. In clastic sediments F is highest in clay-bearing rocks such as shales and mudstones (Table 5.4), although some sandstones have become cemented by fluorite. In limestones some CaF_2 and MgF_2 coprecipitate with $CaCO_3$, but most F is found as fluorapatite in the skeletal remains of marine organisms. In anhydrite and gypsum, F co-precipitates with $CaSO_4$ as CaF_2, but the inability of F to precipitate as Na or K compounds is reflected in the very low concentrations in rock salt.

Table 5.4 Fluorine in sedimentary rocks. After the compilation by Boyle (1976). 'Tr.' is trace. All concentrations in ppm.

Rock Type	Range		Mean	Number
	Minimum	Maximum		
Clastic				
Shales, siltstones and mudstones	10	11660	790	141
Sandstones and Greywackes	10	880	180	49
Oceanic sediments	100	1600	640	151
Biogenic/Chemical				
Limestone	Tr.	1210	220	98
Dolomite	110	400	260	14
Phosphate Rock	10400	42000	30500	74
Anhydrite and Gypsum	130	890	600	6
Rock salt	2	6	5	4

5.2.1.6 *Fluorine in Soils*

Fluorine is richest in soils with high contents of phosphates, clay minerals and colloids and at its lowest concentration in light, sandy soils (Boyle, 1976; Robinson, 1978), and is generally depleted in soils relative to the parent fresh rock (Koritnig, 1974). Micas and amphiboles have F leached from them without dissolution of the mineral. The process presumably takes place more efficiently at tropical temperatures, low F concentration of the leaching water and high water-mineral ratios. In general, F^- can be absorbed onto mineral surfaces in place of hydroxide, but the element is displaced by the hydroxide ion with increasing pH (Matthess, 1982; Hübner (1969) quoted in Koritnig, 1974). Fluorine is boosted artificially by the addition of superphosphate fertilisers.

5.2.1.6.1 Mobility in soils

Soils adsorb F^- from dilute and concentrated solutions (Fluhler *et al.*, 1982; Gupta *et al.*, 1982) and this process is being used industrially (e.g. Ginster and Fey, 1995). Pickering (1985) noted that F^- mobility depends on soil type, the pH of the system and F^- concentrations. Retention of F^- in the soil system was favoured in acidic sediments containing clays and poorly ordered hydrous oxides of aluminium. Jinadasa *et al.* (1993) investigated F^- adsorption onto the surface of goethite (FeO.OH). They found that adsorption was minimal above pH 7, and increased with decreasing pH, being greatest at pH 4. Meeussen *et al.* (1994) assumed that the behaviour of F^- in a soil profile was mainly determined by adsorption onto metal oxide and hydroxide surfaces, specifically goethite and gibbsite.

5.2.1.7 Biosphere

In plants fluorine is mostly stored in the leaves, after translocation from the root system or directly from absorption from the atmosphere. The availability of F to the root system is decreased by increases in the pH, phosphate, Ca, clay and organic matter content of the soil. Typical F concentrations in non-accumulator plants are below 20 ppm dry weight. Notable amongst plants which accumulate F is *camellia sinensis*, the tea bush. In Chinese varieties the concentrations in dried leaves reach 178 ppm, and in Indian varieties up to 115 ppm (Robinson, 1978). Fluorine usually accumulates as microscopic crystals of fluorapatite, but some plants accumulate it as fluoracetate, fluor-oleic acid or fluor-palmitic acid. These compounds are extremely toxic to mammals. In F intolerant plants increased F concentration disturbs photosynthesis, carbohydrate metabolism and water management causing intense respiration, growth retardation, inhibition of pigment synthesis, chlorosis, wilting, plasmolysis and collapse of cells followed by necrosis. Susceptibility varies greatly between species, and even between varieties (Robinson, 1978).

5.2.1.8 Mineral - aqueous fluoride interaction

Ionic compounds of F dissolve congruently and can be modelled using simple equations. Those compounds where F is adsorbed onto the surface or where F replaces OH are more complex, as they often dissolve incongruently.

5.2.1.8.1 Ionic compounds of F

The congruent dissolution of ionic compounds of F^- is well known and behaves according to the equation

$$cCnF \rightarrow cB + nF^- \tag{5.1}$$

where C is a cation such as sodium or calcium, B is the aqueous species of that cation and c and n are the molar proportions. The equilibrium dissolution of the compound then follows the equation

$$K_{cCnF} = \frac{(a_C)^c \, . \, (a_F)^n}{a_{cCnF}} \tag{5.2}$$

where K is the equilibrium constant (also known as the solubility product) for that reaction and a is the activity (at low ionic strength equivalent to concentration). For instance, simple dissolution of CaF_2 produces activities of Ca^{2+} and F^- in solution according to the equation

$$K_{CaF_2} = \frac{a_{Ca^{2+}} \, . \, (a_{F^-})^2}{X_{CaF_2}} \tag{5.3}$$

The mole fraction (X) of pure CaF_2 is one, and so the equation is simplified to

$$K_{CaF_2} = a_{Ca^{2+}} \, . \, (a_{F^-})^2 \tag{5.4}$$

The value of K_{CaF_2} is 4.26×10^{-11} (Gill, 1996), or in logarithmic form,

$$\log_{10} K_{CaF_2} = -10.4 \qquad (5.5)$$

By analogy with pH, $pK_{CaF_2} = 10.4$. Table 5.5 shows the solubility products of fluoride minerals.

Table 5.5 Solubility products of fluoride minerals, expressed as *p*K (-log *K*) at 25°C. First two values from Gill (1996). Final four values recalculated from solubility data in Handbook of Chemistry and Physics (Weast, 1975).

Compound	***p*K**
CaF_2	10.4
BaF_2	5.8
SrF_2	8.57
KF	-2.4
MgF_2	8.14
NaF	0.0044

5.2.1.8.2 Dissolution of F-bearing alumino-silicates

The dissolution of F-bearing alumino-silicate minerals has been little researched, and few references to the leaching of F from alumino-silicates are found in the literature. Nagy (1995) reviewed the dissolution kinetics of sheet silicates, and summarised that most sheet silicates have a dissolution rate of approximately 10^{-17} mol/cm^2/sec at 25°C and a pH of 5. The rate for biotite dissolution under these conditions is 6×10^{-17} mol/cm^2/sec (Stumm *et al.*, 1987), and for muscovite 10^{-17} mol/cm^2/sec (Acker and Bricker, 1992). Trotignon and Turpault (1992) studied the dissolution of biotite, using F-free specimens. They showed that dissolution of biotite is strongly dependant on the pH of the solution. Acker and Bricker noted that biotite dissolved incongruently between pH 3 and 7, with preferential release of Mg and Fe over Si. Most dissolution takes place on the edge of biotite crystals, which are altered to vermiculite. Fanning and Keramidas (1977) stated that high F concentrations in micas retard the release of cations and thus the weathering process.

Sverdrup (1990) was of the opinion that "weathering rates and mechanisms of dissolution of inosilicates [pyroxenes and amphiboles] are poorly understood, and that for augite and hornblende are particularly deficient". Inosilicates often weather non-stoichiometrically (incongruently), with rapid release of Ca and Mg (Brantley and Chen, 1995). However, they found that hornblende approached stoichiometric dissolution after experimental weathering of longer than 115 days duration. For hornblende in a solution at 25°C and ph 4.0, Zhang *et al.* (1993) calculated a dissolution rate of 1.3×10^{-8} mol/cm^2/sec, whilst Sverdrup (1990) calculated a rate of 3×10^{-8} mol/cm^2/sec under the same conditions. These rates are remarkably fast. Sverdrup stated that solution chemistry made little difference to dissolution rates, apart from high Al and P_{CO_2}. To summarise, alumino-silicates dissolve incongruently and slowly in near surface conditions, and little is known of the behaviour of F during dissolution of these minerals. No solubility constants were found for these minerals.

5.2.1.9 *Review of the base exchange process*

It will become evident that ion exchange processes may be important in influencing several groundwater compositions, and so a review of this process is provided (Freeze and Cherry, 1979; Lloyd and Heathcote, 1985). Aqueous cations are preferentially absorbed onto exchange media in the following order:

$$Cs^+ > K^+ > Na^+ > Li^+$$
$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

In other words, in order of increasing hydrated ionic radius, but with divalent ions more strongly adsorbed than monovalent ions. The exchange of cations can be described by equilibrium reactions, e.g.

$$2NaR + Ca^{2+} \rightleftharpoons CaR_2 + 2Na^+ \tag{5.6}$$

where R is the exchange medium. The equilibrium is described by

$$Q_{(Na-Ca)} = \frac{X_{Ca}}{X^2_{Na}} . \frac{(Na^+)^2}{(Ca^{2+})} \tag{5.7}$$

where X is the equivalent fraction of the ion on the exchanger R, e.g.

$$X_{Ca} = \frac{2[CaR_2]}{2[CaR_2] + [NaR]} \tag{5.8}$$

Q is the selectivity coefficient which, as it varies with the ionic strength of the solution, is only semiquantitative. Q decreases with increasing ionic strength, as shown by the values in Table 5.6. Cation exchange capacity varies with pH (Freeze and Cherry, 1979).

5.2.2 Distribution and causes of high F^- concentration in groundwater

5.2.2.1 *Global*

Many countries of the world have significant areas where groundwater contains elevated concentrations of F^-. The United States of America, Canada, China and India are amongst countries in the northern hemisphere that experience high F^- groundwater (e.g. Corbett and Manner, 1984; Yong and Hua, 1991; Gupta and Sharma, 1995; Boyle and Chagnon, 1995; Hitchon, 1995). Yong and Hua (1991) attributed high F^- groundwater to several separate causes: high F content of aquifers;

low groundwater flow rates; arid and semi-arid climate increasing potential evaporation; and water with high pH.

Table 5.6 Ion exchange on clays with solutions containing Ca^{2+} and K^+ at equivalent concentrations.

Clay	Exchange capacity (meq/g)	Variation of Ca^{2+}/K^+ ratio (Q) on clay, with concentration of solution (meq/ℓ)			
		100	10	1	0.1
Kaolinite	0.023	-	1.8	5.0	11.1
Illite	0.162	1.1	3.4	8.1	12.3
Montmorillonite	0.810	1.5	-	22.1	38.8

In a detailed study in the Alberta basin of Canada, Hitchon (1995) found formation waters with up to 22 mg/ℓ F^-. He noted a trend of increasing fluorite saturation from shallow, cool, low Ca, fresher waters to deeper, hotter (73°C), more saline and Ca-rich water. He noted the importance of the MgF^+ complex, and that the complexes NaF^0, VO_2F^0 and AlF_2^+ were of minor importance. He stated that the F concentration in groundwater is controlled by an intricate relation between saturation with respect to fluorite and the concentration of ions which form F complexes, all of which are controlled by ionic strength and temperature. It was calculated that many possible F complexes were not in fact of quantitative importance, e.g. aluminium complexes from AlF^{2+} to AlF_6^{3-}, vanadium complexes VOF^+ and VOF_2, FeF^{2+} and SiF_6^{2-}.

Kraynov *et al.* (1969) found that waters with up to 15 g/ℓ F^- had been in contact with villiaumite (NaF), an abundant accessory mineral in the deep zones of the Lovozero Massif. The massif is composed of alkalic rocks, similar to those of the Pilanesberg Complex. The author noted that evaporation had increased the F^- concentration in the groundwaters. The waters are highly alkaline ($pH > 12$) and are characterised by very high concentrations of Na (up to 26 g/ℓ), Si (up to 13 g/ℓ) and virtual absence of Ca.

5.2.2.2 Africa

In Africa, high F^- groundwaters have been studied in some detail in Kenya (Gaciri and Davies, 1993; Davies, 1994), Ethiopia (Ashley and Burley, 1994; Gizaw, 1996) and Tanzania (Smet, 1992). The abundance of F^- in Rift Valley groundwater has been attributed to weathering of alkaline volcanic rocks rich in F and the interaction of groundwater with volcanic HF exhalations (Gaciri and Davies, 1993); outgassing of CO_2, geothermal heating and low groundwater Ca and salinity (Gizaw, 1996) and ion exchange processes (Ashley and Burley, 1994). Botchway *et al.* (1996) attributed high F^- concentrations in the groundwater of Accra in Ghana to the decay of plant material. Other countries which have F^- enriched groundwaters include Sudan (Ibrahim *et al.*, 1995), Nigeria, Senegal, Algeria, Egypt, Zimbabwe, Morocco, Uganda and Somalia (Smet, 1992).

5.2.2.3 South Africa

Several researchers have noted the high F^- content of certain groundwaters in South Africa, especially in the Pilanesberg and Bushveld Complexes. Shand (1928) gave a description of the hydrology of the Pilanesberg Complex and commented on spring water composition: 'high level' springs being pure, 'low level' springs being 'high in soda'. Ockerse (1943) measured rock, soil and groundwater concentrations of F^- in an attempt to understand the causes of endemic dental fluorosis. His study covered the whole of South Africa but unfortunately gave the western Bushveld only superficial attention. He did, however, single out the Pilanesberg, Warmbaths and Pretoria Saltpan as areas with endemic dental fluorosis deserving greater investigation. He suggested F^- in groundwater of the Springbok flats came from the Ecca formation, and suggested detrital fluorapatite as the source. Fayazi (1995) suggested that the Karoo sedimentary strata contained fluorite derived from the surrounding Bushveld Granites during episodes of arid erosion. He suggested that F^- concentrations in groundwater hosted by the Karoo formations is strongly controlled by the geochemistry of the rock.

Grobler and Dreyer (1988) determined F^- concentrations in drinking water from surface waters and groundwaters for 162 towns and cities across South Africa. Forty percent of the groundwaters had F^- below 0.1 mg/ℓ, and less than 7% had F^- greater than 1.0 mg/ℓ. Of the groundwaters, 84% had significantly lower concentrations of F^- when water levels increased, which Grobler and Dreyer ascribed to dilution. They also showed that groundwaters had significantly higher F^- concentrations that surface waters.

Raubenheimer *et al.* (1990) determined F^- concentrations in rivers flowing through the Kruger National Park. Their main conclusion was that all 5 rivers (the Olifants, Luvuhu, Letaba, Sabie and Crocodile Rivers) had higher concentrations of F^- during the latter part of the dry winter season. The Olifants River had differences of up to 2 mg/ℓ F^- between wet and dry season flows. Changes in mean F^- concentration in each of the 5 rivers over 5 years was very slight, and not significant.

McKenzie *et al.* (1966) published a map of groundwater with a F^- concentration above 1.5 mg/ℓ, prepared by the Soil Research Institute. The map was based on unspecified data sources and is at variance with the current known distribution, as presented in Figures 5.2 and 5.3. These figures are based on unpublished distribution maps calculated from the SA National Groundwater Database. It can be seen that large areas of the country are subject to F^- concentrations in groundwater greater than 1.5 mg/ℓ, especially in the arid western and south-western Cape.

5.2.2.3.1 Bushveld area

Bond (1947) was the first worker to extensively discuss chemical analyses of ground water from the Pilanesberg Complex. He noted the 'high soda alkalinity and the consistently high fluoride content'. He stated that the highest recorded concentration of fluorides in ground water 'so far discovered in the Union' of South Africa was 67.2 ppm in spring water from the farm Doornhoek, although the exact location was not given. Retief (1963) published 9 analyses of ground water, which were only analyzed for F^- and Cl^-. Fluoride was consistently high in his analyses. Lurie (1974) gave a full chemical analysis of water from an artesian borehole in tuffs, which showed a F^- concentration of 2.4 mg/ℓ. Bond (1947) described groundwaters occurring in other lithologies in the field area, based

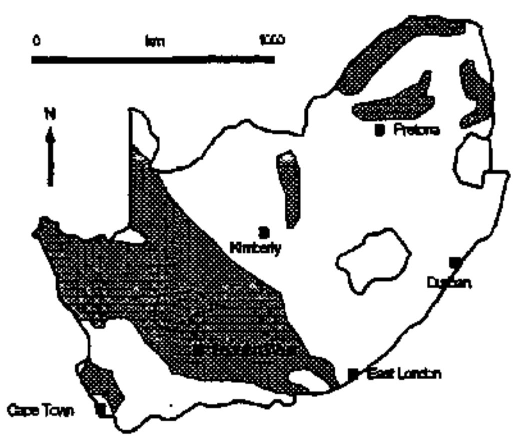


Figure 5.2. South African groundwater with F⁻ concentration greater than 1.5 mg/l.

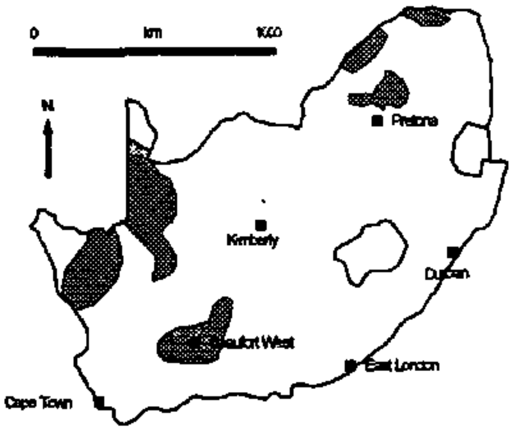


Figure 5.3. South African groundwater with F⁻ concentration greater than 3.0 mg/l.

on a fairly limited sample set. He stated that Pilanesberg groundwater was similar in chemical composition to those of the 'Red Granites' (Lebowa Granite Suite) which are also characterised by high F^- concentrations. The 'Old Granite' (Archaean Granite) occasionally has 'an appreciable F^- content', whilst in some samples it is absent. Both Bond (1947) and Ockerse (1943) stated that fluoride was present in solution as "sodium fluoride".

5.2.3 Fluorine and Health

As Paracelsus, a philosopher from Ancient Greece put it,*'All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy.'* Fluorine is an excellent example of this principle. It is one of a group of trace elements which are beneficial at low dosages, but which at higher doses are harmful and even fatal. Fluorine not only affects humans. The first recorded outbreak of recognisable fluorosis in farm animals took place after the eruption of the volcano Hekla in the eighteenth century. Mass mortality of livestock due to acute F^- poisoning caused starvation and a 25% reduction in the human population of Iceland (Fridriksson, 1983). Chronic fluorosis in animals is manifested by severe dental lesions, lameness and exostoses. Fluorosis in animals has been recorded from just north of the field area (Botha *et al.*, 1993). Also affected are wildlife (Fourie *et al.*, 1996) and plants (see earlier in this chapter). However, this section addresses the affect of F^- on human health only.

5.2.3.1 Metabolism of fluoride

Fluoride passes into the blood plasma by absorption through the lungs or gastrointestinal tract. In contrast to the other halogens, F^- is rapidly absorbed from the stomach; plasma F^- concentrations peak approximately 1 hour after ingestion. The free F^- ion is converted to HF in the stomach (Jenkins, 1990). In the blood three quarters of the total F^- is found in the blood plasma, with the balance taken up by red blood cells. Fluorine in plasma exists primarily as the free F^- ion, whilst the rest is present as lipid-soluble organic fluorocompounds. The kidneys rapidly remove F^- from the blood, so that a typical background level is only 0.02 mg/ℓ (Jenkins, 1990). Approximately 50% of absorbed F is eliminated from the body within 24 hours, primarily in urine. The residue becomes associated with calcified tissue, where 99% of the total F in the body is found. Whilst Jenkins (1990) states that F is firmly bound to the bone, Whitford (1996) states that F is not irreversibly bound to the surface bone crystallites, so that F concentration in bone can eventually reflect changes in the amounts of F ingested chronically. The fluoride half life in bone is approximately 8 years (Schlatter, 1978). Fluoride is not accumulated in the thyroid gland and is eliminated many times faster than the other halogens. Urinary pH affects the efficiency with which the kidneys remove F^- from the body, so chronic acid-base disturbances are important in F metabolism. Acid-base status is influenced primarily by diet, as well as certain drugs, metabolic and respiratory disorders, physical activity and altitude (Whitford, 1996). Fluoride freely passes through the placenta, so that foetal F^- plasma levels are directly proportional to those of the mother.

The cariostatic effect of F^- is probably due to its ability to promote enamel remineralisation and to inhibit acid production by plaque bacteria - F is a potent inhibitor of many enzymes. Fluoride has the ability at low levels to *inhibit* soft tissue calcification and may decrease the chances of death due to cardiovascular disease, particularly ischemic heart disease.

5.2.3.2 Dental Fluorosis

Human beings throughout history have suffered from dental fluorosis, but until this century the aetiology of the condition was unknown. Given the common incidence of high F^- groundwaters in the East African Rift Valley (Gaciri and Davies, 1993; Smet, 1992), it is quite possible that ancient ancestors of humanity could have had dental fluorosis. The victims of the volcanic eruption at Pompeii in *AD* 79 suffered from dental fluorosis, probably due to high F^- concentrations in their drinking water (Torino *et al.*, 1995). The eruption of the Icelandic volcano Hekla in the eighteenth century produced severe fluorosis in the surrounding human populations (Fridriksson, 1983) and recent eruptions continue to release F^- into the hydrosphere (Gíslason *et al.*, 1992). Early studies of stained tooth enamel in communities in Colorado showed that such staining did not render the tooth more susceptible to dental caries (McKay and Black, 1916). However, the inverse relationship between dental caries and mottled enamel was established by Bunting and co-workers in 1928 and by McKay in 1929 (Dean, 1954). This led to the search for the causative agent of mottled enamel, which was found to be the high F^- concentrations in drinking water supplies of the affected communities. Since then it has been widely shown that high concentrations of F^- in drinking water can cause deleterious effects in human dentition (e.g. Senewiratne *et al.*, 1973; Driscoll *et al.*, 1983; Dissanayake, 1996). It has also been shown that a moderate intake of F^-, often facilitated by fluoridation of drinking water, is beneficial to dental health by causing a reduction in dental caries (Arnold *et al.*, 1953; Newbrun, 1989). Fluoride deficiency is marked by an increased incidence of dental caries.

The incidence and severity of dental and skeletal fluorosis are influenced by other factors apart from the concentration of F^- in drinking water. A diet deficient in vegetables and fruit has been suggested as a factor (Dodd *et al.*, 1960). The increase in the availability of fluoridated toothpaste and fluoride supplements has caused an upsurge in dental fluorosis in communities with optimally fluoridated water (Pendrys, 1995). The increases in dental fluorosis with increasing altitude (observed by Shortt *et al.*, 1937) and average temperature (Galagan and Lamson, 1953; Brouwer *et al.*, 1988) are due to increased water consumption, thus increasing total F^- intake. However, Whitford (1996) attributes increasing fluorosis at higher altitudes to the alteration of kidney function, which affects the excretion of F^-. Unusual causes of fluorosis have been described from Spain (Franke *et al.*, 1978), where NaF was added to wine to avoid abnormal fermentation, resulting in a form of skeletal fluorosis ("wine fluorosis"), and China, where high F in tea has caused skeletal fluorosis in immigrant Tibetans (Cao *et al.*, 1996). Other effects of F^- are discussed in section 5.2.3.3.

5.2.3.2.1 Symptoms

Mottled tooth enamel is a common sight in many rural parts of the world. Until 1931 the term 'mottled tooth enamel' was common, but since the source of the condition has been traced to excess ingestion of F^-, the term 'dental fluorosis' has been adopted. The following descriptions of the clinical manifestations of dental fluorosis are summarised from Fejerskov *et al.* (1988). Normal tooth enamel is a microporous solid comprised of highly ordered, tightly packed hydroxyapatite crystals. The surface of the enamel in normal teeth is translucent, smooth and glossy even when dry, with a pale creamy white colour. Dental fluorosis is a developmental disturbance which increases with time. Therefore primary teeth are less severely affected than the permanent teeth, and those teeth which erupt first (the incisors and first permanent molars) are less affected than those erupting later (the premolars and other permanent molars).

The first signs of dental fluorosis (*moderate dental fluorosis*) are thin white lines running across the entire enamel surface and which can only be seen after drying of the tooth surface. This phenomenon is caused by air replacing saliva in enamel porosities, increasing opacity in the more porous areas. The porosity occurs at crystal boundaries and is caused by impairment of the final growth of the hydroxyapatite crystals. With more fluorosis these thin lines become broader, merge and may be clear without the need for drying. At slightly greater severity the tooth surface shows distinct, irregular, opaque or cloudy white areas, caused by increasing porosity of the tooth enamel. The patches may take up brown stains from food particles. Rarely, minute pits may occur in the cloudy areas. *Moderate dental fluorosis* is characterised by the entire tooth surface becoming chalky white. Such teeth can be damaged by mechanical wear in the mouth and by the probing of dentists.

In *severe dental fluorosis* pits occur in the now completely opaque enamel. The pits, of varying diameter, are scattered over the tooth surface to begin with, but merge to form a band across the tooth, often coincidental with the position of the top or bottom lip. The pits are caused by hypomineralized enamel breaking off, revealing normal enamel underneath. At no time is dentine exposed. Severely fluorotic teeth have an almost total loss of surface enamel, and become misshapen and are often stained brown or black. The staining, although common, depends entirely on the post-eruptive oral environment and is not an intrinsic feature of dental fluorosis.

Dental clinicians originally used the classification of dental fluorosis proposed by Dean *et al.* (1942), which used the descriptions *normal, questionable, very mild, mild, moderate* and *severe*. More recently, dentists have turned to the TF index, proposed by Thylstrup and Fejerskov (1978) which arranged the severity of dental fluorosis into 10 classes, from 0 (equivalent to *normal*) to 9 (*severe*). Unfortunately, the precise levels of F^- dietary intake at which each level of fluorosis becomes apparent are not well established (Brouwer *et al.*, 1988; Leung, 1988; White, 1988; Du Plessis, 1995).

5.2.3.2.2 Dental fluorosis in the field area

Investigations of dental fluorosis in the field area are confined to village-based studies only. No full scale census or survey has been carried out. Ockerse (1941 and 1943) and Ockerse and Meyer (1941) were the first workers to report on the occurrence of endemic dental and skeletal fluorosis in South Africa. In the field area Ockerse (1943) found evidence of the condition in the Pilanesberg, Warmbaths, Kalkheuvel and Pretoria Saltpan areas. Not all occurrences were large; only 3 cases were located around the Saltpan, and the cases at Kalkheuvel were found only in the workers of a certain quarry. However, he stated that the Pilanesberg was '*one of the worst affected endemic fluorosis areas in the Transvaal*', and that '*some of the worst cases of mottled enamel are found among school children who were born and grew up in Warmbaths*'. He stated that 144 endemic areas had been identified in the Transvaal, mostly in areas underlain by the Bushveld Igneous Complex.

The studies of Zietsman (1985, 1989 and 1991) have been methodical and illuminating, with surprising and controversial conclusions. Her small study area encompassed several villages, in the centre of the current author's field area. Most of the villages were situated on Nebo Granite and granophyre, whilst one was situated on the edge of the Ecca Formation outcrop. Zietsman (1989) discussed the spatial variation of dental fluorosis in 7 villages, and attempted to correlate the variation to underlying geological causes and to the variation of F^- concentrations in groundwaters. She sampled 120 boreholes, and found much spatial variation of F^- concentrations, ranging from 0.1 to 5.5 mg/ℓ. Importantly, she found that 33% of children drinking groundwater with a F^- content of <0.5 mg/ℓ had dental fluorosis. Furthermore, she found the occurrence of different rock types did not *fully* explain the spatial variation in groundwaters F^- concentration. Her conclusions are somewhat compromised in that, in her discussion of the geological setting of the village of Rietgat, whilst correctly stating that the village is within the outcrop area of the Ecca Formation, she ignores the fact that the village is on the very edge of the Karoo basin. Boreholes in the village in all likelihood penetrate through the Ecca formation, into the underlying Nebo Granite. Geological logs of the boreholes would be needed to confirm this contention.

Zietsman (1991) further developed her ideas on spatial variation and fluorosis in the same study area. Each of the 3103 school pupils which were examined for dental fluorosis were linked to individual drinking water sources, usually boreholes. The history of each source was known for up to 30 years before the study, and from this Zietsman based her conclusions. The positive correlation between F^- concentration in the drinking water and the *severity* of dental fluorosis was statistically significant at 95% confidence limits, but the spatial variation in fluorosis was not fully explained by the variation in F^- concentration. She could recommend no safe 'threshold level', as the severity of fluorosis formed a continuum at any F^- concentration. She also found only 4% of the groundwaters exhibited variation in the F^- concentration from dry to wet season, and that this variation was always less than 30% of the mean value. If any criticism had to be levelled at this excellent paper, it would be that children (with an ungauged and questionable sense of direction) were responsible for pointing out the location of their principal source of water.

Rudolph *et al.* (1995) have investigated dental fluorosis in four villages near the Pilanesberg Complex. Two of the villages had high F^- groundwater, whilst the two control villages had low F^- groundwater. They found that severe dental fluorosis occurred in 28% of subjects drinking groundwater with a F^- concentration of 7 to 8 mg/ℓ, whilst 41% had moderate dental fluorosis. Every person in the two villages with high F^- groundwaters showed some evidence of dental fluorosis.

Only three people from the two villages with low F^- had dental fluorosis. In 1991, 95% of the inhabitants of Bophuthatswana received their drinking water from groundwater (Pelpola *et al.*, 1992).

Dental fluorosis has been studied in several other parts of South Africa. The study by Lewis and Chikte (1995) of school children in KwaNdebele showed that even at a drinking water F^- concentration of between 0.6 - 1.6 mg/ℓ, 90% of the subjects had some sign of dental fluorosis, bringing into question the recommendations of the WHO (1984). Furthermore, Carstens *et al.* (1995) showed that children in the North Western Cape who drank water with a F^- concentration below the WHO recommendations still had a high incidence of dental fluorosis. They recommended a drinking water F^- concentration of only 0.4 mg/ℓ. According to du Plessis *et al.* (1995), race was found to be a factor in the severity of dental fluorosis. They found that 39% of white school children in the Bloemfontein area had evidence of dental fluorosis on the maxillary central incisors, compared to 16% of black schoolchildren drinking water of the same F^- concentration (0.54 mg/ℓ). Retief *et al.* (1979) showed that a positive association existed between F^- concentration in tooth enamel and the degree of fluorosis in the individuals of the town of Kenhardt in the northern Cape, supplied with high F^- drinking water (3.2 mg/ℓ). The study of van der Merwe *et al.* (1977) reached similar conclusions.

5.2.3.3 Other effects of F^- on the human body

5.2.3.3.1 Skeletal fluorosis

Fluorapatite is an order of magnitude less soluble than hydroxyapatite, the principal mineral constituent of bone. The F^- ion aggressively substitutes for the OH^- ion, leading to a build up of F in bone tissue with increasing age. A typical 55 year old human is expected to have between 2000 and 2500 ppm F in their bones, although up to 6000 ppm F has been recorded with no pathological change (Jenkins, 1990). Skeletal fluorosis often occurs in endemic dental fluorosis areas; generally, only villages with higher than average F^- groundwater will also have cases of skeletal fluorosis. Asymptomatic skeletal fluorosis can be diagnosed most securely with X-Rays. This is due to the increased bone density, especially in vertebrae (Meunier *et al.*, 1989). Several studies, such as Riggs *et al.* (1990) on women with postmenopausal osteoporosis, showed that with very high F^- consumption, bone mass increases but skeletal fragility also increases.

The first symptoms of skeletal fluorosis are aching joints and muscles. Increasing severity produces stiffness of the lumbar, thoracic and cervical regions of the spine and restriction of head movement, caused by thickening of the joints and mineralisation of the tendons. In extreme cases the vertebrae of the back become rigid, giving rise to a condition known as 'poker back' or 'bamboo spine'. The patient is unable to stand erect, the rib-cage becomes rigid and all breathing is performed abdominally, whilst bony outgrowths form at the end of ribs and along the long bones (Shortt *et al.*, 1937; Ockerse, 1941). Paraplegia, quadriplegia, wasting of the muscles and neurological disorder (radiculomyopathy) may finally ensue (Boyle and Chagnon, 1995; Goldman *et al.*, 1971).

Artificial skeletal fluorosis was first described in Danish workers, who ingested large amounts of F by accidental inhalation of cryolite dust (Na_3AlF_6; Moller and Gudjonsson, 1932). In parts of India, notably Madras, where ingestion of water with a F^- concentration greater than 8 mg/ℓ has occurred for more than 40 years, skeletal fluorosis is endemic (Shortt *et al.*, 1937). Endemic skeletal fluorosis has been reported in many countries (Lyth, 1946; Kilborn *et al.*, 1950; Hamamoto, 1957; Zipkin *et al.*, 1958; Odenthal and Wieneke, 1959; Felsenfeld and Roberts, 1991; Boyle and Chagnon, 1995).

Skeletal fluorosis has been reported from several areas of South Africa. Ockerse (1941) reported 6 cases of confirmed skeletal fluorosis in workers at a cement factory north of Pretoria. The occurrence in Kenhardt in the Northern Cape Province (Dodd *et al.*, 1960) is unusual in that children have been affected; in other parts of the world skeletal fluorosis usually manifests itself after 20 to 40 years. The groundwater of the area is only moderately enriched in F^-, at 4.8 mg/ℓ. The symptoms are also unusual in that softening of the long bones occurred, causing bending. Fluoride in this case is probably only one of several aetiological factors in the condition, another being malnutrition. Pettifor *et al.* (1989) suggested that low dietary calcium intakes may exacerbate the severity of bone lesions in children living in areas of endemic fluorosis.

5.2.3.3.2 Goitre

It has been noted that endemic goitre is often found in the same area as high F^- concentrations in groundwaters, although it is unlikely that F^- is directly goitrogenic (Day and Powell-Jackson, 1972). Yang *et al.* (1994) investigated the effects of high iodine and F on children's intelligence. Although they found the intelligence quotient was lowered in children with high F and iodine intakes, Yang *et al.* did not investigate which element was responsible. Parts of the current field area are iodine deficient (Kalk *et al.*, 1997).

5.2.3.3.3 Cancer

Childhood osteosarcomas occur most frequently in the knees, ankles, shoulders and wrists, areas showing a high response (osteoblast proliferation and bone formation) to F^- (Schulz *et al.*, 1984). High F^- drinking water was initially implicated in higher rates of osteosarcoma (Kinlen, 1975). However, more recent research (Oldham and Newell, 1977; Hrudey *et al.*, 1990; Anderson, 1991; Mahoney *et al.*, 1991; US Dept of Health and Human Services, 1991; Freni and Gaylor, 1992; Gelberg *et al.*, 1995) has shown that F^- is not osteocarcinogenic in humans.

5.2.3.3.4 Acute fluoride poisoning

Gessner *et al.* (1994) reported acute F^- poisoning in a small community in Alaska. The incident followed an accidental NaF overdose at a water treatment works. Initial symptoms include nausea, epigastric distress and vomiting. Excessive salivation, mucous discharge from the nose and mouth, headaches, sweating, diarrhoea and general weakness are sometimes present. Spasm of the extremities, tetany and convulsions develop in lethal doses, as well as failure of the cardiovascular system indicated by a weak pulse and cardiac arrhythmias. Renal function and respiration is depressed causing respiratory and metabolic acidosis. Extreme disorientation is followed by unconsciousness and death.

Large amounts of F^- must be ingested to induce acute F^- poisoning, far more than is possible from the ingestion of almost all naturally fluoridated drinking water. Gessner *et al.* (1994) reported death after ingestion of 18 mg/kg body weight, although other workers have quoted an LD_{100} (the dose which is 100% lethal to a specified group of subject, in this case human males of 70kg mass) of a quarter of this value.

5.2.3.3.5 Risk levels and optimal fluoride concentration in drinking water

There is uncertainty as to the precise concentrations of F^- in drinking water which are optimal for human health. Table 5.7 shows that the F^- concentration limits for drinking water suggested by national and international bodies vary considerably. It is apparent that the upper limit for avoiding widespread dental fluorosis is approximately 2.0 mg/ℓ, although this value is lowered in tropical climates because of increased water ingestion (see below). The upper limits for skeletal fluorosis and crippling skeletal fluorosis show no such agreement between countries. This may be because of the smaller amount of epidemiological evidence on which to base guidelines. The high guideline value for Tanzania is a result of widespread very high F^- concentrations in that country, and the resulting economic and humanitarian consequences of imposing a more realistic value. Similar arguments have resulted in the double standard in Argentina.

Table 5.7 Guidelines for F^- concentration in drinking water, based on the affects of drinking such water. After Smet (1992).

	Proposed effects/mg/ℓ F^- in drinking water		
	Objectionable dental fluorosis	**Skeletal fluorosis**	**Crippling skeletal fluorosis**
WHO (1984)	> 1.5	3.0 - 6.0	> 10.0
US EPA	> 2.0		> 4.0
Tanzania		>8.0	
Argentina - urban - rural	> 1.5 > 2.2		
Brouwer *et al.* (1988) - tropics	> 0.6		> 7.0
South African Drinking Water Guidelines (DWAF, 1996)	>1.5	>3.5	

It has been noted that as water ingestion is proportional to air temperature, the optimal F^- concentration in groundwater used for drinking purposes should be dependant on the mean maximum temperatures experienced in any particular area. This led Foss and Pittman (1986) to propose an empirical equation for optimal F^- concentration, equivalent to:

$$optimal\,F^- = \frac{0.34}{0.2364 + \frac{9T}{5}\,0.0062} \tag{5.9}$$

where T is temperature in °C. The resulting calculated optimal F^- concentration in drinking water for large towns in the field area is shown in Table 5.8. There is a small variation of 0.07 mg/ℓ F^- about the mean of 0.65 mg/ℓ F^-, over the range of mean maximum temperatures experienced in the study area. All of the values are similar to the maximum safe concentration of 0.7 mg/ℓ F^- calculated by Du Plessis (1995) for the Orange Free State gold fields.

Table 5.8 Optimal F^- concentration in groundwater, calculated using the equation of Foss and Pittman (1986). Raw data obtained from the Weather Bureau, Pretoria. Latitude and longitude are in decimal degrees. 'mamsl' = metres above mean sea level.

Location	Lat. S.	long. E.	Elevation (mamsl)	Mean Maximum temp. (°C)	Optimum F^- level (mg/ℓ)
Rustenburg	25.72	27.30	1157	26.5	0.64
Buffelspoort	25.75	27.48	1230	26.2	0.64
Brits	25.58	27.77	1107	26.9	0.63
Pretoria	25.73	28.18	1330	24.8	0.66
Waterkloof	25.83	28.22	1498	23.3	0.68
Irene	25.92	28.27	1524	23.7	0.68
Lindleyspoort	25.48	26.70	1175	26.0	0.65
Pilanesberg	25.33	27.17	1043	27.9	0.62
Funda Muni	25.42	28.87	1407	23.9	0.68
Thabazimbi	24.58	27.42	970	27.9	0.62
Warmbaths	24.90	28.33	1143	26.7	0.64
Sentrum	24.27	27.35	1005	28.5	0.61
Potgietersrus	24.18	29.02	1116	26.3	0.64
			Mean:	26.0	0.65

5.2.4 Fluoride concentration and fluorosis risk

5.2.4.1 Magnitude of the problem

The results presented in Chapter 4 showed that much of the study area is underlain by groundwater having a F^- concentration above the optimum (~0.7 mg/ℓ) and also above recommended maximum concentrations (1.5 mg/ℓ). Spatial analysis by GIS shows that groundwater underlying approximately 17 000 km^2 of the western Bushveld has a F^- concentration >0.7 mg/ℓ. Just over 540 of the 3 000 groundwater samples have a F^- concentration > 1.5 mg/ℓ. Since between 150 and 200 people are supplied by each borehole (BDWA, 1992), between 82 000 and 109 000 people are drinking groundwater which may induce fluorosis in the long term. 145 500 to 194 000 are drinking water with F^- concentrations higher than optimal.

5.2.4.2 Distribution of risk areas

It is essential to have a map of areas in the western Bushveld where F^- concentrations in groundwater are above optimum levels. Possible methods of representation include marker size (Figure 5.4) and colour variation, contours and pseudo topographic perspective. Given the variability of fluoride concentrations in some areas, such as the groundwater of the Nebo Granite and the Karoo basin, marker size, colour plots and contouring are visually confusing. Figure 5.5 shows the preferred method of representing areas of fluorosis risk. The F^- concentration of the groundwater was classified into **no risk** (<0.7 mg/ℓ), **low risk** (0.7-1.5 mg/ℓ), **medium risk** (>1.5-3.0 mg/ℓ) and **high risk** (>3.0 mg/ℓ). Theissen polygons were constructed around each sampling point (*i.e.* borehole) and classified into risk groups according to groundwater F^- concentration. Adjoining polygons with the same classification were merged. The resulting areas accurately reflect the distribution of groundwaters of different degrees of fluorosis risk. Even in areas of low borehole density this statement is valid. However, the size of the Theissen polygons increases with decreasing borehole density, giving them a disproportionate visual impact. A perspective view (Figure 5.6) gives a general impression of the distribution of high values, but is not a useful analytical or planning tool.

5.2.5 Bioavailability and speciation

It was shown in Chapter 2 that the FISE method using TISAB determines the *total* concentration of fluoride in solution. However, F^- can be complexed by Al, Ca, Mg and H in solution. These complexes may not be as bioavailable as the free F^- ion, and so thermodynamic modelling of several samples was conducted to estimate the degree of complexation of F^-. The computer programme MINTEQA2 (Allison *et al.*, 1991) was used to predict the speciation of elements in solution, based upon the measured concentration of ions. The same programme also provides estimations of the saturation index, and these values are used later in the discussion.

MINTEQA2 is a public domain software package notable for its relative ease of use. However, the thermodynamic database upon which its calculations are based is not internally consistent (Dr P Wade, CSIR, *pers. comm.*, 1995), and therefore the conclusions reached must be treated with some caution. The copy of MINTEQA2 used in this study was implemented on an IBM compatible 386 personal computer running at 40 MHz, and was obtained from the Computing Centre for Water Research at the University of Natal (Pietermaritzburg). Calculations for each water analysis generally took less than 60 seconds.

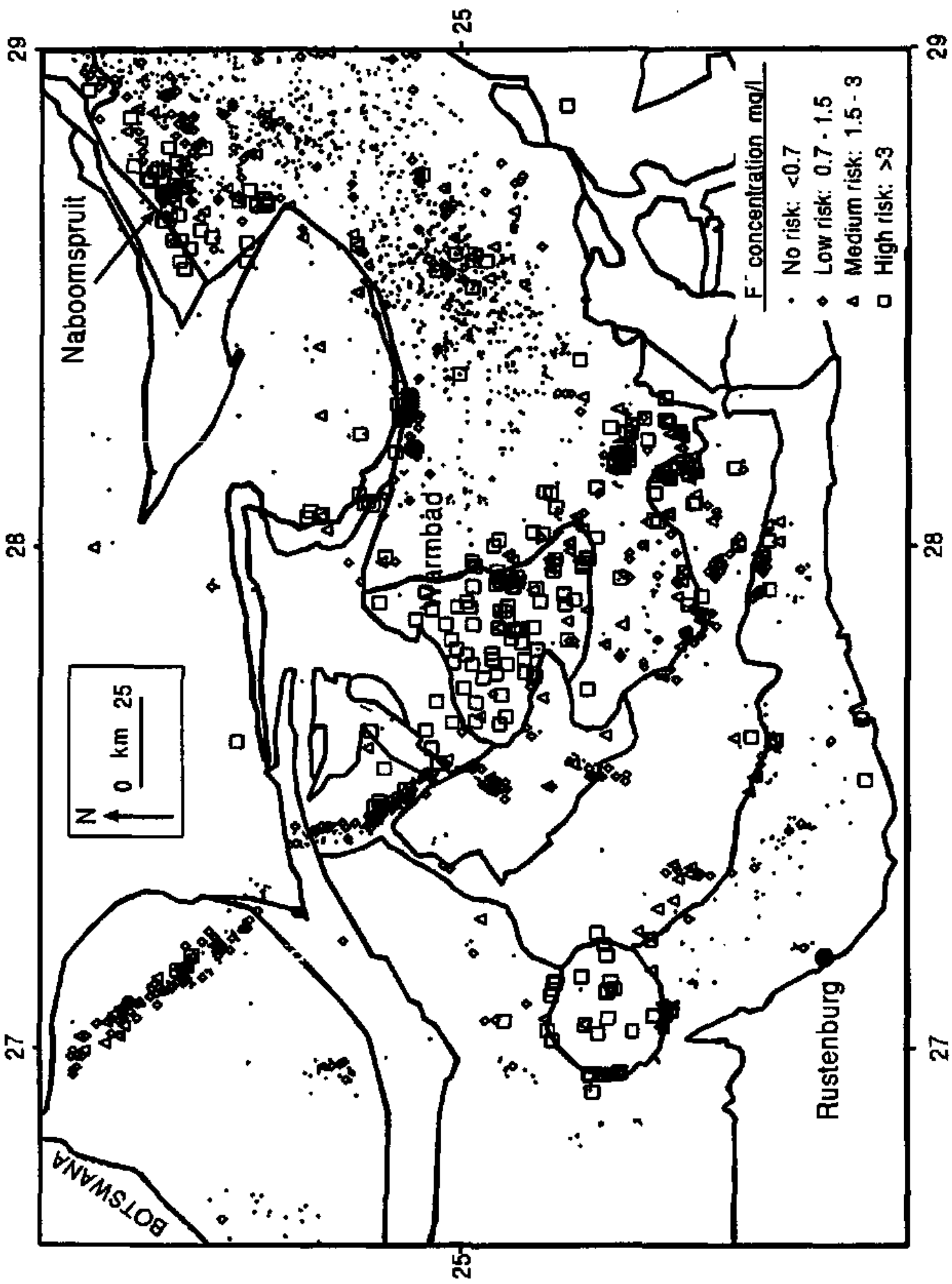


Figure 5.4. Plot of F⁻ concentrations in 3244 groundwater samples from the study area. Samples are divided into four risk levels. Lines are lithological boundaries and details of sample sites are given in Appendix A1.

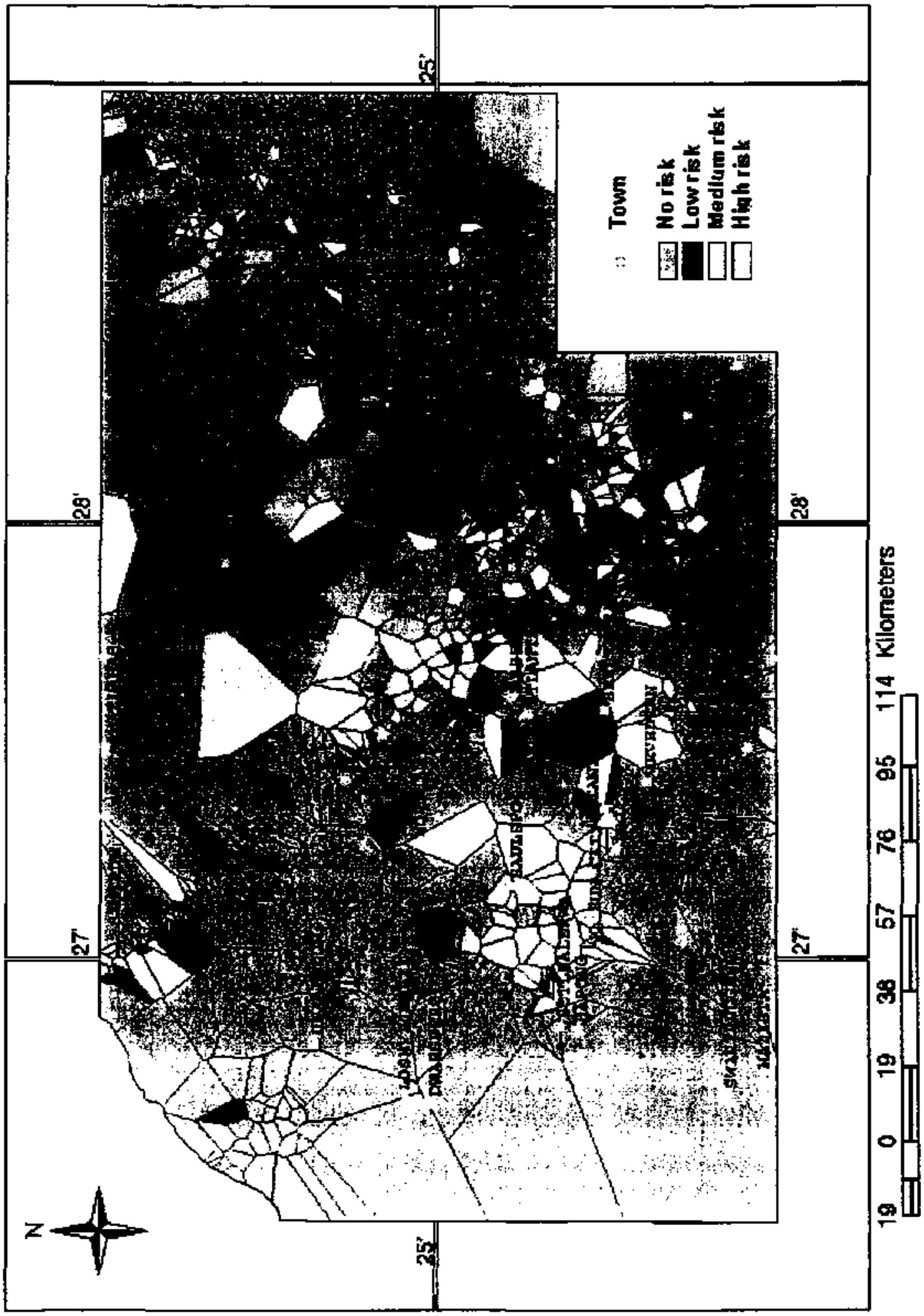


Figure 5.5. Fluorosis risk zones in the field area. Sampling site locations are given in Figure 4.1 and details of sampling sites are given in Appendix A1.

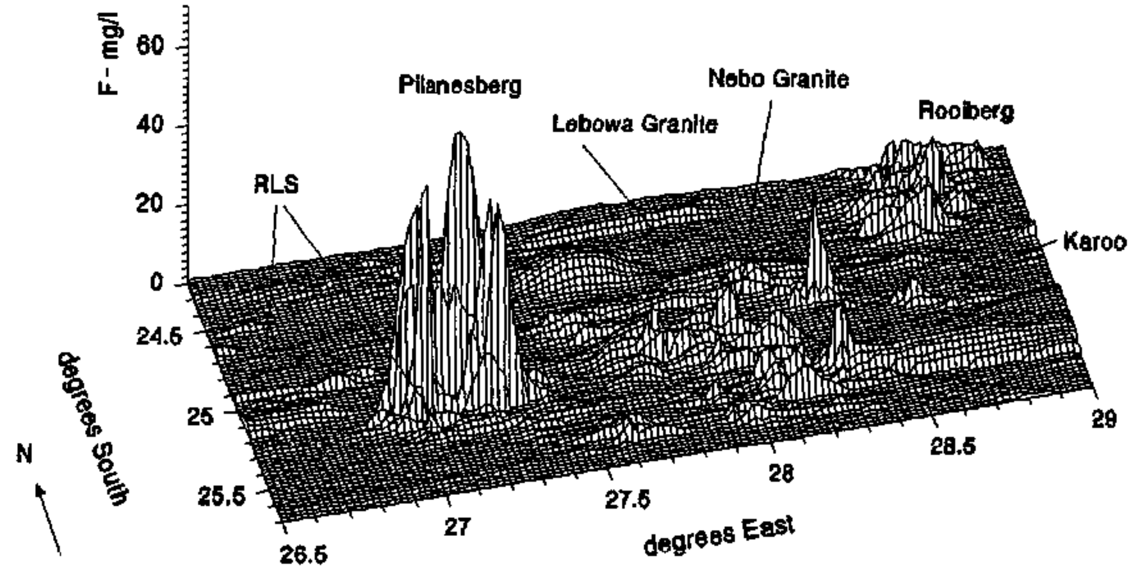


Figure 5.6. Fluoride levels in groundwater in the western Bushveld, presented as a perspective topographic view from the SSW.

Table 5.9 shows the results of speciation calculations made by the programme MINTEQA2, based upon all water analyses with Al concentration >0.050 mg/ℓ. It is apparent in five out of the eight examples that less than 5% of the F^- is complexed by Mg, Al or Ca, and that Mg is the most important complexing ion, which came as a considerable surprise. The majority of F exists in the form of the free fluoride ion, F^-. Only at site 109 does the groundwater have a high percentage of complexed F^-, and the groundwater has low F^- and high Al and Mg concentrations. In such cases because the amount of F^- is very low, the complexation of F^- by Al is of little biological significance. The biological importance of the MgF^+ ion is at present unknown to us. Complexation of F^- by other aqueous species is discussed in the next section.

5.2.5.1 Speciation of F inside the human body

The speciation results reported above were calculated at the temperature and pH values which were measured at the well head. It is of interest to determine the speciation of ions within a biological system, since such speciation may be significantly different from that found in groundwaters.

In order to model the speciation of ions in a typical groundwater under the conditions of the human stomach, the pH must be reduced to ~3, and the temperature increased to 37°C. Although the water would be mixed with the other stomach contents, and thus the ionic composition would change, for the purposes of this simulation the stomach is assumed to contain only stomach acid (HCl). It can be seen from Figure 5.7 that complexation of F^- by aluminium is only slightly affected by changing pH, the percentage of AlF_3° increasing at the expense of AlF_2^+ and MgF^+ with decreasing pH. This effect is swamped by the conversion of free F^- to HF°. The concentration of total F in groundwater, even at concentrations likely to cause fluorosis, are too low to cause HF° (hydrofluoric acid) to be dangerous, especially in relation to the high concentration of HCl normally present. The residence time of F in an empty stomach is in any case very short, approximately 30 minutes (Backer Dirks, 1992).

Table 5.9. Speciation calculations of F^- complexation in groundwaters with >0.050 mg/ℓ Al. Species which contribute less than 1 % of the total are ignored.

Site	**Analysed (mg/ℓ)**				**Speciation calculated by MINTEQA2 (% of total F)**					
	Al	**Ca^{2+}**	**Mg^{2+}**	**F^-**	**F^-**	**MgF^+**	**CaF^+**	**AlF_3°**	**AlF^{2+}**	**AlF_2^+**
27	0.12	49.7	12.1	3.54	94.3	2.0	-	2.2	-	-
37	4.42	11.2	2.8	2.05	97.2	-	-	1.4	-	-
74	0.16	14.9	4.5	69.4	99.1	-	-	-	-	-
103	0.15	101	59.1	0.08	91.2	7.7	1.0	-	-	-
108	0.064	6.35	1.73	0.12	93.6	5.7	-	-	-	-
109	0.71	1630	460	0.09	69.5	22.1	6.1	-	1.0	1.1
155	0.17	61.6	9.4	0.95	97.8	1.3	-	-	-	-
201	0.091	3.5	1.6	5.51	96.2	-	-	2.6	-	-

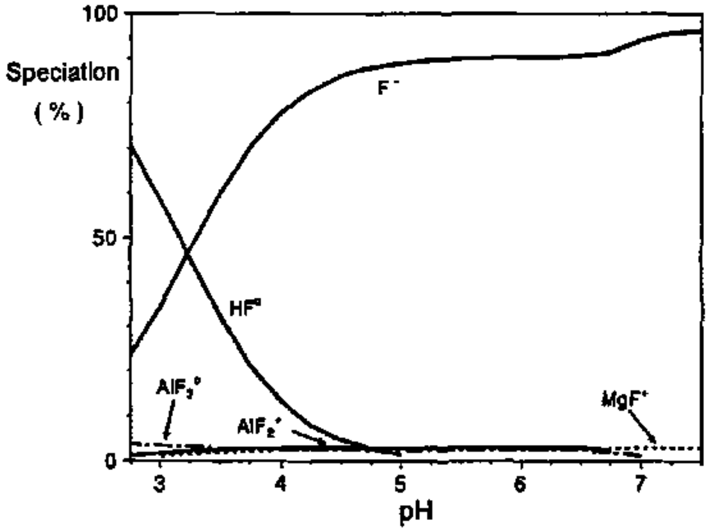


Figure 5.7. Speciation of F^- in water from site 27, down to a pH found in the human stomach and at 37°C, calculated using MINTEQA2 and assuming a stomach empty of food and containing only stomach acid (HCl).

5.2.6 Other elements

Groundwaters of the field area frequently have concentrations of several trace elements in excess of South African guidelines. These will be discussed briefly.

5.2.6.1 Aluminium

The solubility of Al^{3+} is very low at pH values usually found in groundwater, whilst it increases at very high and very low pH. A plot of pH against aluminium concentrations determined in this study confirms the low solubility of Al between pH = 6.3 and 10, and shows that no clear trend exists (Figure 5.8). Only a single very high concentration of aluminium (analytical error?) was found at near neutral pH, from site 37.

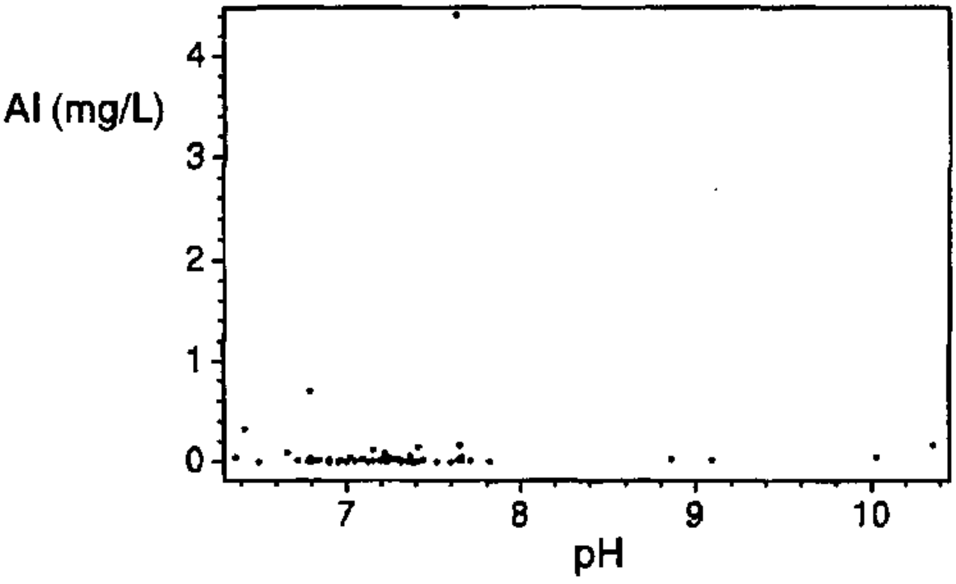


Figure 5.8. Aluminium concentration plotted against pH for groundwaters from the study area.

Speciation calculations performed using MINTEQA2 show that at high pH, Al is present in solution as $Al(OH)_4^-$, consistent with the findings of Pokrovskii and Helgeson (1995). The results of speciation modelling (shown graphically in Figure 5.9) also show that at pH < 7, $Al(OH)_3^\circ$ and AlF° can be more abundant than $Al(OH)_4^-$. The low pH, low Al and high concentration of fluoride in groundwater from site 201 results in all the aluminium being complexed by F^-, and none is associated with OH^-. Also of interest is the speciation of Al in groundwater from site 74. Even though the fluoride concentration is 69 mg/ℓ, the highly alkaline pH of 10.03 results in all Al occurring as a single species, $Al(OH)_4^-$.

5.2.6.2 Molybdenum

One sample, site 192 from Doornfontein grazing camp situated on the Lebowa Granite, had an anomalously high Mo concentration of 1.0 mg/ℓ. Molybdenite, MoS_2, is sparingly soluble in water. Late stage granites are often enriched in Mo, and this may be the source of the high Mo in this

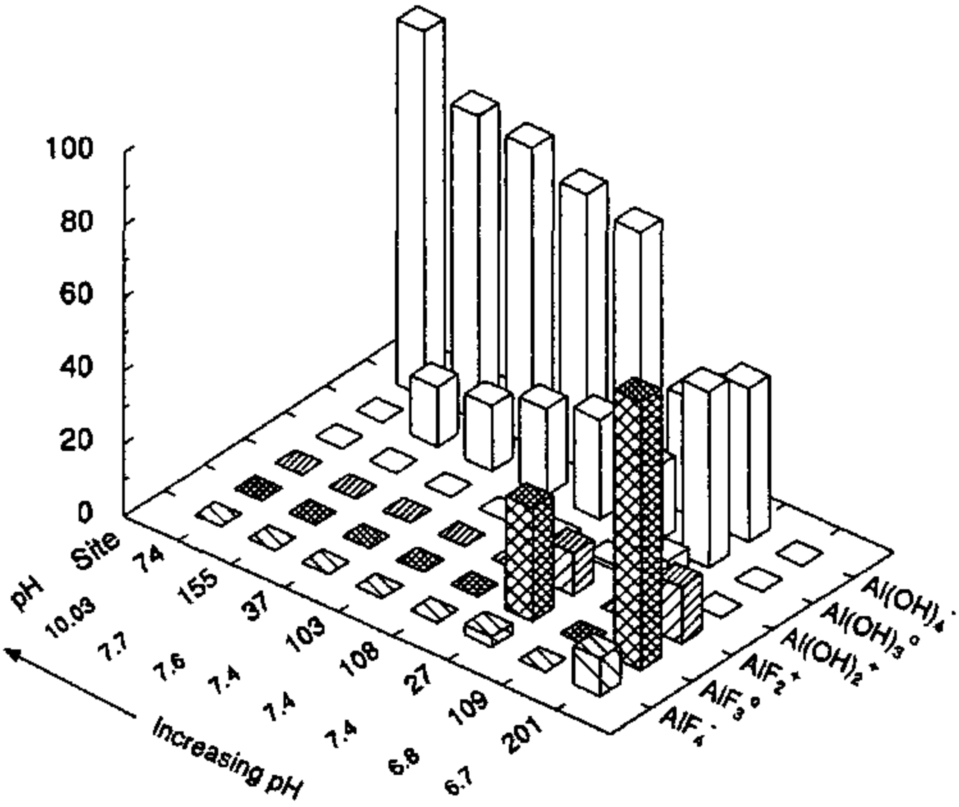


Figure 5.9. Aluminium speciation in groundwater samples, modelled using MINTEQA2.

sample. Mo concentrations in natural waters are usually less than 0.05 mg/ℓ Mo, but can increase to 0.20 mg/ℓ around mining operations (Galvin, 1996). The high risk limit for South African drinking water is currently 0.2 mg/ℓ Mo (Watertek, 1991).

5.2.6.3 Zinc

Zinc occurs in surprisingly high concentrations in the groundwater of the area. The highest concentrations are found in groundwater from the Pilanesberg Complex. No systematic variation of Zn concentration with pH is seen in this sample set (Figure 5.10). Zn speciation was modelled in a similar manner to that for Al, and the results are presented in Figure 5.11.

Compared with Al, a greater variety of Zn species are present. Much of the Zn is present either as Zn^{2+} or as a carbonate complex, the exact form of which is determined by pH. At higher pH values, $ZnCO_3^{\circ}$ and $Zn(CO_3)_2^{2-}$ are dominant. $ZnHCO_3^+$ is more abundant at a pH close to 7, whilst Zn^{2+} dominates in acidic samples. Where appreciable concentrations of other anions are present, such as SO_4^{2-} and Cl^-, these also form complexes with Zn but to a limited degree. Of interest is the predicted absence of Zn-F complexes, such as ZnF^+. At pH 3.0 and 37°C, all Zn is likely to be in the form of Zn^{2+}, which can be readily metabolised.

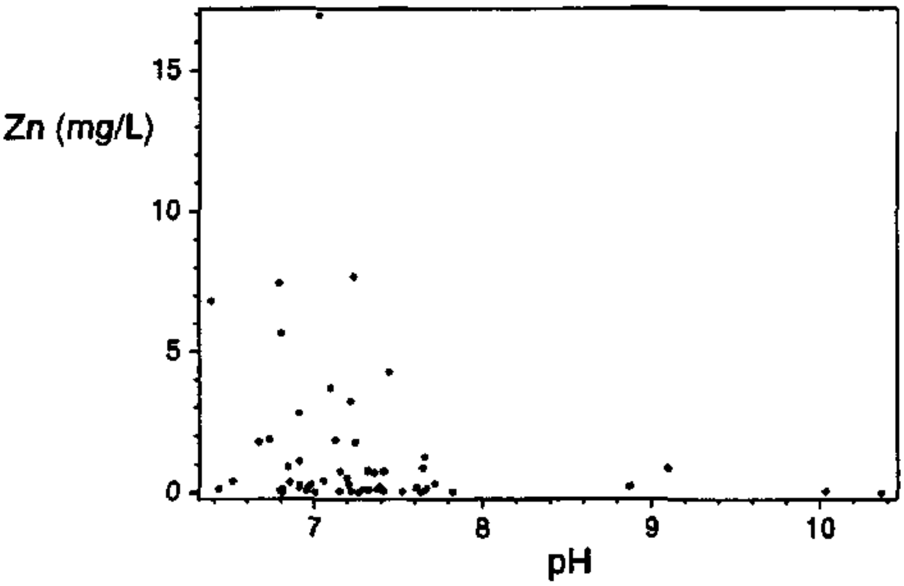


Figure 5.10. Zn plotted against pH for groundwaters from the study area.

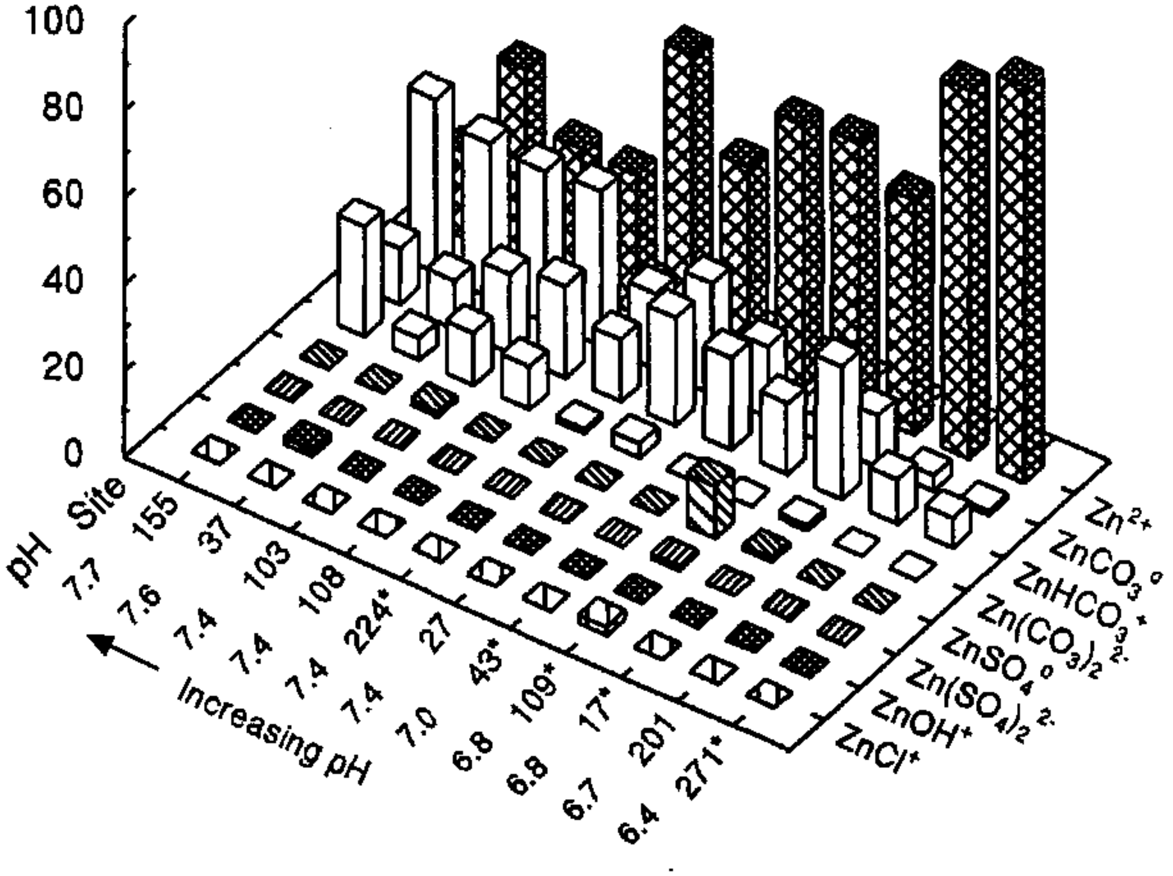


Figure 5.11. Speciation of Zn in several samples from the field area, calculated using MINTEQA2.

5.3 Geochemical controls of groundwater fluoride concentration

5.3.1 Whole Rock composition

For most chemical elements in a rock, the single most important factor controlling their interaction with water is not the total percentage of the element in the rock, but rather the minerals in which the element is located. For instance, Na in NaCl passes more readily into the hydrosphere than Na in nepheline ($NaAlSiO_4$). This is simply a function of the solubility constant of the mineral. That rock sample RO6 has 8% total fluorine is less important to this study than the mineral forms in which the fluorine is present. There are exceptions to this rule, however, *e.g.* iodine. Since I (and to a lesser extent, Br) is not readily accepted into crystal lattices of common rock-forming minerals, it tends to be adsorbed onto crystal surfaces, as well as occurring in fluid inclusions (Fuge, 1988). However, iodine presumably binds more readily to some mineral surfaces than others, and so for iodine the mineralogy of the rock still exerts a certain control on elemental availability. For this reason the mineralogy, and not the bulk chemical composition, is stressed in the following discussion.

5.3.2 Mineral solubility

Solubility products (*pK*, or pK_{25}, if specifically at 25°C) are available for most rock forming minerals, but there is often considerable uncertainty associated with these values. A discussion of the solubility of various minerals is warranted, especially of the main F-hosting minerals, fluorite, fluorapatite, micas and amphiboles.

5.3.2.1 Fluorite (CaF_2)

The solubility of fluorite has been investigated by many workers including Guntz (1884), Petersen (1889), Treadwell and Koch (1904), Seemann (1905), Kohlrausch (1908), Launay (1913), Auméras (1927), Charter (1928), Mougnard (1931), Kazakov and Sokolova (1950), Smyshlyaev and Edeleva (1962), Strübel (1965) and Nordstrom and Jenne (1977). The solubility of fluorite, expressed as the concentration of F^- in solution in mg/ℓ, calculated by some of these workers is shown in Figure 5.12. A great deal of variation exists in the calculated solubility of fluorite. Strübel (1965) reviewed the work of all previous workers and revised the solubility for fluorite at ambient and elevated temperatures and pressures, as well as in NaCl solution of varying molality. He found that fluorite exhibits retrograde solubility at temperatures above 100°C. Supporting evidence for retrograde solubility in natural systems was found by Nordstrom and Jenne (1977). The solubility of fluorite (160 mg/ℓ) reported by Freeze and Cherry (1979) is seen to be incorrect.

Qi and Knaebel (1989) showed that, since natural fluorite is rarely pure and usually contains calcite and quartz inclusions, the solubility of fluorite in a system in equilibrium with the atmosphere, fluorite and calcite is controlled predominantly by the activities of F^-, HCO_3^- and Ca^{2+}. Fluorite is regarded as the mineral which most frequently controls F^- concentration in natural waters (e.g. Alberta (Hitchon, 1995), Yellowstone (Stauffer, 1982), Kenya (Gaciri and Davies, 1993), Ethiopia (Ashley and Burley, 1994) and New Zealand (Ellis and Mahon, 1977)). There are three main reasons for implicating fluorite as a major control of F^- distributions in natural waters: fluorite is the most ubiquitous and abundant F containing mineral; it is sparingly soluble; and Ca is generally always present in natural waters. These three factors also show why fluorapatite is less frequently cited as

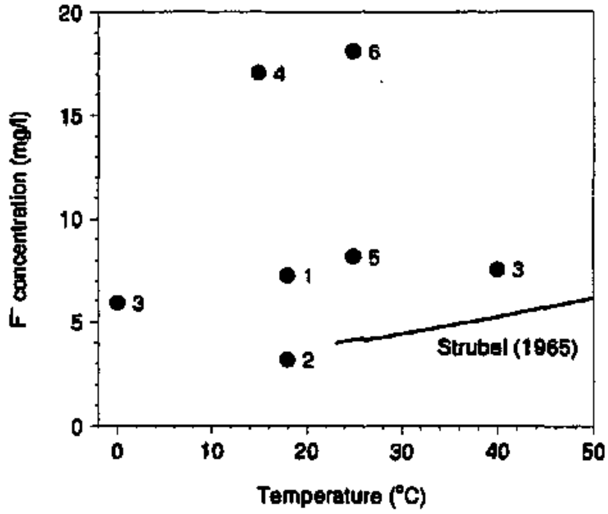


Figure 5.12. CaF_2 solubility, as the concentration of F^- in aqueous solution. Sources: 1: Treadwell & Koch (1904); 2: Seemann (1905); 3: Kohlrausch (1908); 4: Launay (1913); 5: Auméras (1927); 6: Charter (1928).

a controlling factor in F^- concentration: fluorapatites are relatively uncommon, they are markedly less soluble than fluorite, and phosphate is found at very low concentrations in natural waters.

Figure 5.13 shows the solubility of fluorite in the presence of Ca and F ions, plotted against the Ca and F analyses for groundwaters from the field area. It can be seen that most of the groundwaters fall in the field below the solubility of fluorite, suggesting simple dissolution. However, several of the groundwaters sampled from the Pilanesberg Complex, Lebowa Granite and Karoo rocks have Ca and F above that which would be expected if Ca and F were controlled solely by fluorite solubility and several of the Pilanesberg groundwaters have large amounts of F^- and very little Ca (<5mg/ℓ): these groundwaters may have been subjected to base exchange softening (see following sections).

5.3.2.2 *Fluorapatite and hydroxyapatite*

Stauffer (1982) thoroughly reviewed the thermodynamic data pertaining to hydroxyapatite and fluorapatite. He found that the pK_{25° of hydroxyapatite ranged from -57.0 to -59.4, the wide variation resulting from ion substitutions in the natural crystals used in experiments. The pK_{25° of fluorapatite is even less well known, but is accepted to be less than that for hydroxyapatite. The values accepted by Stauffer (1982) range from -59.8 to -62.3. In relation to dental health, fluorapatite is much less soluble than hydroxyapatite, and F^- aggressively substitutes for OH^- in hydroxyapatite, thereby hardening tooth enamel and reducing caries.

5.3.2.3 *Micas and Amphiboles*

Rates of dissolution and precipitation of micas and amphiboles are described in Section 5.2.1.8.2. No reference to solubility constants could be found for mica or hornblende in the literature, possibly as they frequently dissolve incongruently.

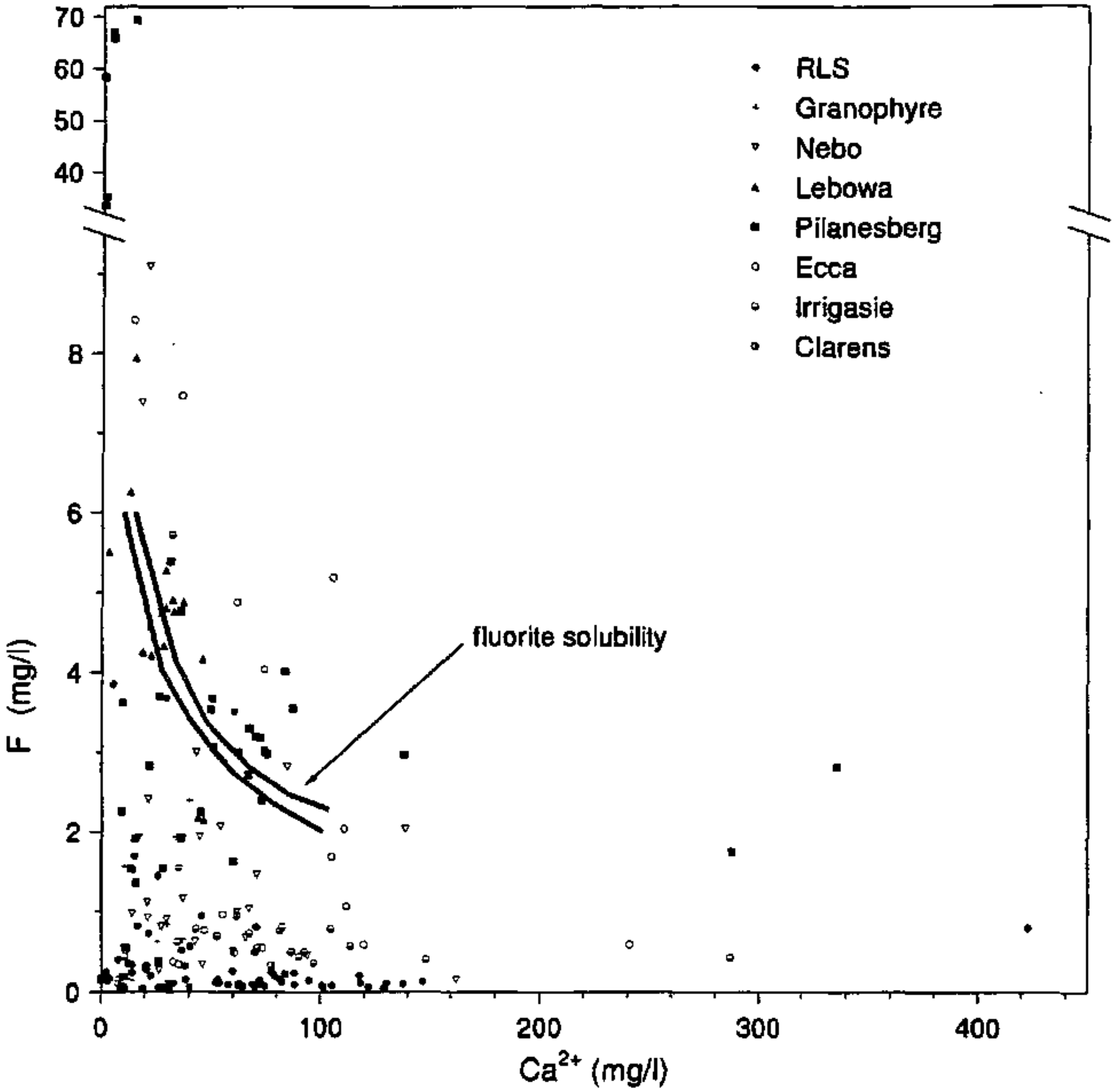


Figure 5.13. A plot of Ca^{2+} against F^- for groundwaters from the field area. Estimate of fluorite solubility plus experimental error, from Pekdeger *et al.* (1992).

5.3.3 Fluorite dissolution kinetics

Brown and Roberson (1977) found that over a three year period fluorite did not fully reach equilibrium with dilute sodium perchlorate solutions, but had reached an approximation of equilibrium after 34 days. Hamza and Hamdona (1991) showed that the dissolution rate of fluorite was dependent on the relative degree of undersaturation with respect to fluorite (Figure 5.14). The data show that the dissolution rate decreases as the solution approaches saturation with respect to fluorite, and that dissolution of fluorite in very undersaturated solutions is rapid. In their experiments the surface area of the crystals presented to the solution seemed to have a negligible effect (Figure 5.15). The experiments of Hamza and Hamdona (1991) were inconclusive on the question of the effect of fluid flow across the crystals.

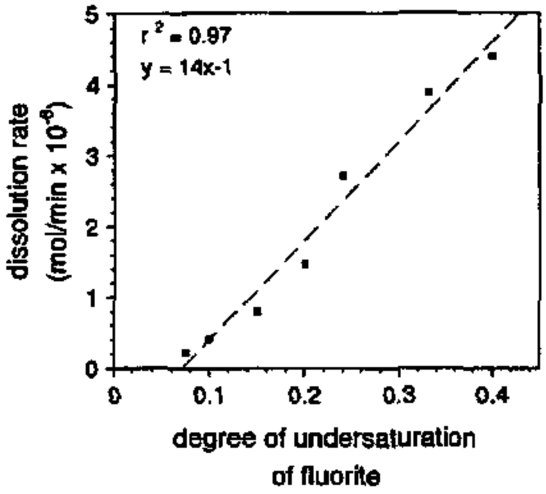


Figure 5.14. Effect of degree of undersaturation on dissolution rate of fluorite, for 16 crystals/g. Data from Hamza and Hamdona (1991).

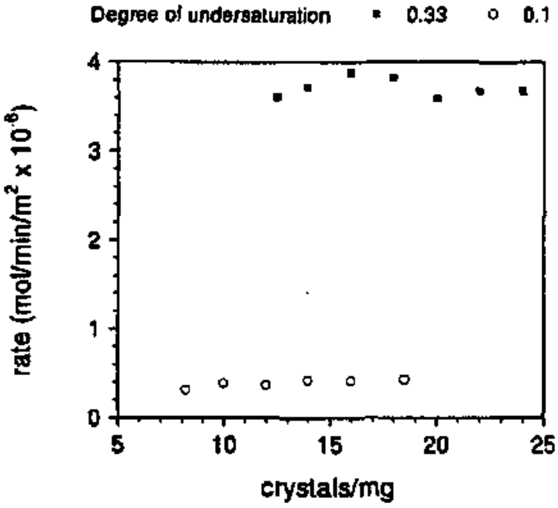


Figure 5.15. Effect of crystal size on dissolution rate of fluorite. Ionic strength 0.5 mol NaCl/ℓ, at 25°C. Ca = 0.129x10^{-3} mol/ℓ, F = 0.258.x10^{-3} mol/ℓ. Data from Hamza and Hamdona (1991).

Peng *et al.* (1996) showed that, since most natural fluorite contains solid inclusions of calcite, the kinetics of fluorite dissolution in nature (4 > pH < 9) are probably controlled by the activities of F^-, Ca^{2+} *and* HCO_3^-. In the ternary system CaF_2-H_2O-$CaCO_3$, complexation of F was not considered of significance in fluorite dissolution kinetics.

5.3.4 Thermodynamic modelling of mineral controls on groundwater composition

As shown in Chapter 3, the lithologies of the study area have a wide range of chemical and mineralogical compositions. The degree to which groundwater is saturated with respect to certain minerals with which it is in contact has been modelled using the computer programme MINTEQA2 (Allison *et al.*, 1991). Most calculations are made assuming a closed system. Table 5.10 gives the chemical composition of minerals of importance in this study. A selection of the results is shown graphically in Figures 5.16 to 5.20. A negative saturation index for a particular mineral implies that it is undersaturated in the solution, whilst a positive index implies that the solution is supersaturated with respect to the mineral (as shown in Figure 5.16). A saturation index close to zero implies that the solution is saturated with a mineral. Langmuir (1971) in his study of carbonate waters states that an error of ±0.05 pH units will result in a calculated error of ≈ ±0.05 saturation index units, for calcite, for example. With other uncertainties, such as in the analysis of cations, and the uncertainties in *p*K for calcite and dolomite, he put a total uncertainty on his saturation index calculations of ≈0.1 and he therefore assumed that all values within 0.1 of zero are saturated. The same is assumed to be so in this study.

In almost all cases, halite and natron are very undersaturated, in accordance with their high solubility and scarcity in the rocks of the field area. Although deposits of halite and natron are found only within the Pretoria Saltpan in the field area, estimations of the saturation index for these minerals give an impression of the salinity of the groundwaters.

Table 5.10 Fluorine-bearing minerals and minerals involved in the thermodynamic modelling of mineral controls on groundwater composition. Solubility product (*p*K) from the MINTEQA2 thermodynamic database (Allison *et al.*, 1991).

Mineral	Chemical formula	*p*K
Calcite	$CaCO_3$	3.15
Strontianite	$SrCO_3$	9.25
Magnesite	$MgCO_3$	8.03
Dolomite	$CaMg(CO_3)_2$	17.03
Natron	$Na_2CO_3.10H_2O$	1.31
Trona	$NaHCO_3.Na_2CO_3.2H_2O$	not used
Halite	$NaCl$	-1.58
Sylvite	KCl	not used
Fluorite	CaF_2	10.96
Sellaite	MgF_2	not used
Villiaumite	NaF	-0.0044
Gypsum	$CaSO_4.2H_2O$	4.85

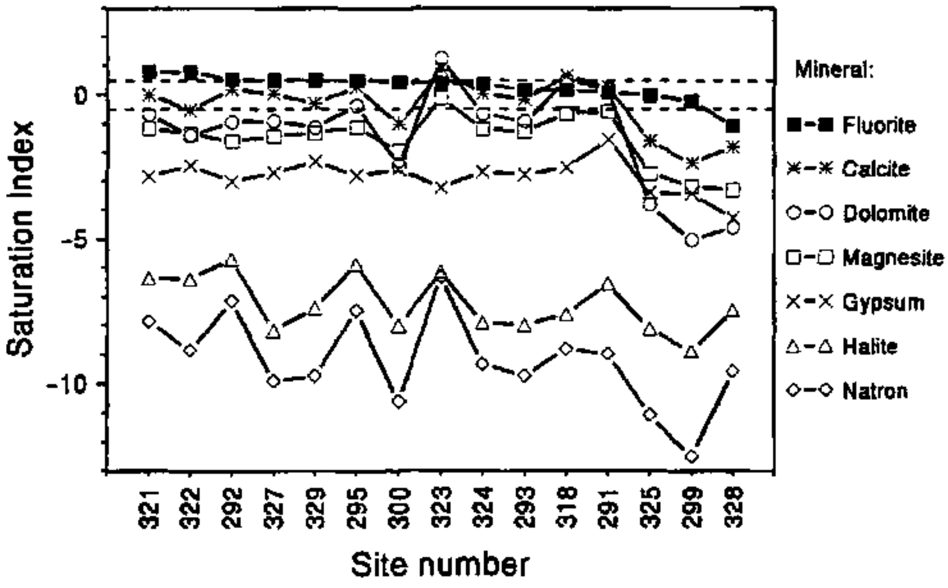


Figure 5.16. Saturation indices for selected minerals calculated for groundwater analyses from the Lebowa Granite. Dashed lines indicate range of saturation.

5.3.4.1 Lebowa Granite

In the Lebowa Granite the groundwater is generally saturated with respect to fluorite and calcite, whilst Mg-containing minerals are just undersaturated (Figure 5.16). Sites 325, 299 and 328 are the most undersaturated with respect to all minerals, indicating either shorter groundwater residence times, proximity to a recharge area or dilution with very fresh water.

5.3.4.2 Nebo Granite

Groundwater hosted in Nebo Granite is mostly undersaturated with respect to fluorite, while calcite is mainly saturated (Figure 5.17). Dolomite, magnesite and gypsum are close to saturation or slightly unsaturated.

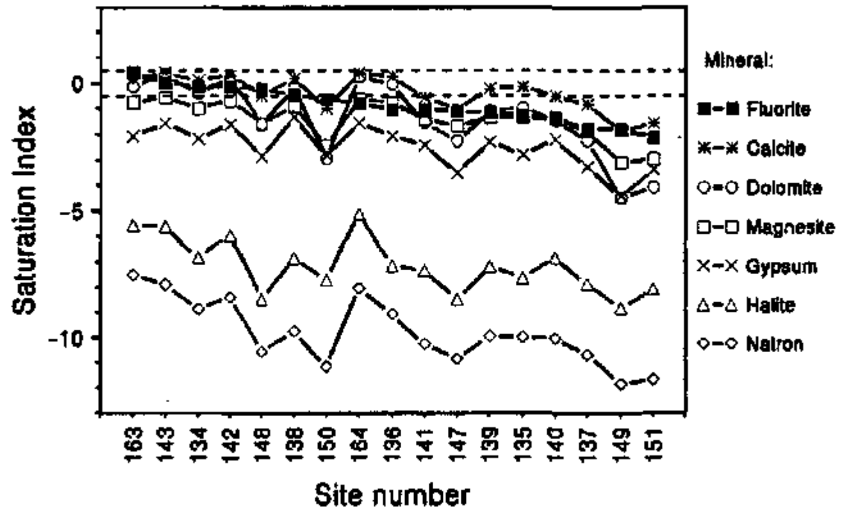


Figure 5.17. Saturation indices for selected minerals calculated from groundwater analyses from the Nebo granite.

5.3.4.3 Pilanesberg

Fluoride concentrations in Pilanesberg groundwater are likely to be controlled by fluorite solubility, since all samples are approximately saturated with respect to the mineral (Figure 5.18). Decreasing fluorite saturation is accompanied by a decrease in halite and natron and an increase in gypsum saturation. Most groundwaters are close to saturation with respect to dolomite, calcite and magnesite. Groundwaters 15 and 12 are anomalous. Groundwater 15 is unusual in that it is close to saturation with respect to fluorite but undersaturated with respect to carbonate minerals, *i.e.* calcite, dolomite and magnesite. This may indicate that, in this instance, $CaCO_3$ precipitation, which must take place when the samples are saturated with respect to $CaCO_3$, is not an active process in upsetting the Ca^{2+}- F^- equilibrium, thereby boosting F^- concentrations. Sample 12 is similar to samples 288, 287 and 34, only in that it is oversaturated with dolomite.

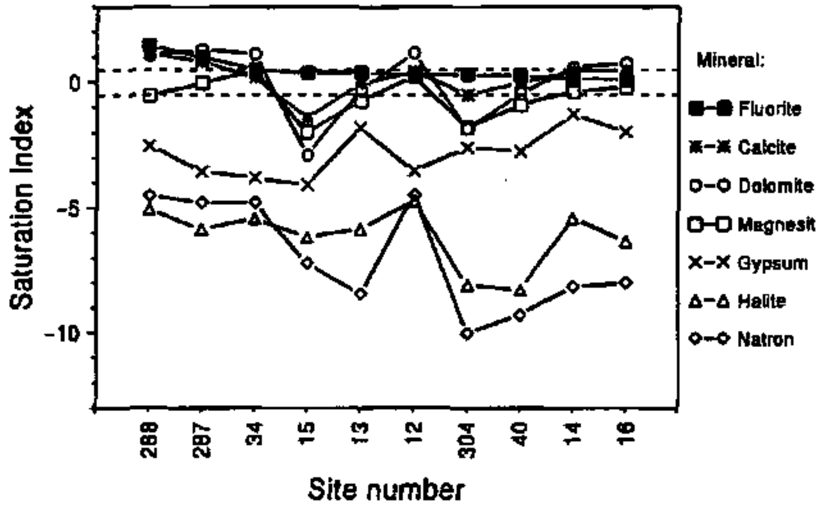


Figure 5.18. Saturation indices of common minerals for selected groundwater samples, sorted by saturation index of fluorite, from the Pilanesberg Complex.

5.3.4.4 Rustenburg Layered Suite

RLS groundwaters are all undersaturated with respect to fluorite but generally close to saturation with respect to calcite and magnesite, and saturated to oversaturated with respect to dolomite (Figure 5.19). Fluorite is not found in the RLS, whilst the rocks have abundant Ca- and Mg-bearing silicate minerals. Since Si was not determined in the groundwater samples, it is unfortunately not possible to calculate the saturation indices for silicate minerals.

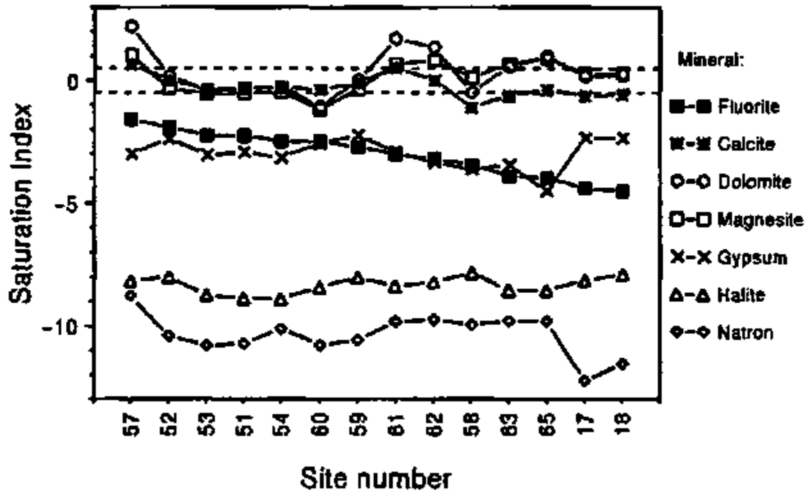


Figure 5.19. Saturation indices for seven minerals for selected groundwater samples from the Rustenburg Layered Suite.

5.3.4.5 Carbonatites

The Nooitgedacht Carbonatite, which is remarkable for the absence of fluorite, is the only carbonatite from which groundwater was collected in this project. All samples from the Nooitgedacht carbonatite are undersaturated with fluorite, with sample 334 showing the greatest degree of saturation (Figure 5.20). Natron is as undersaturated in groundwater from the Nooitgedacht carbonatite as in groundwater from other rock types. This may indicate that the Nooitgedacht carbonatite is poor in soluble sodium minerals. Groundwaters associated with the Kruidfontein carbonatite complex, which is notable for the abundance of fluorite, are expected to be fully saturated with respect to fluorite.

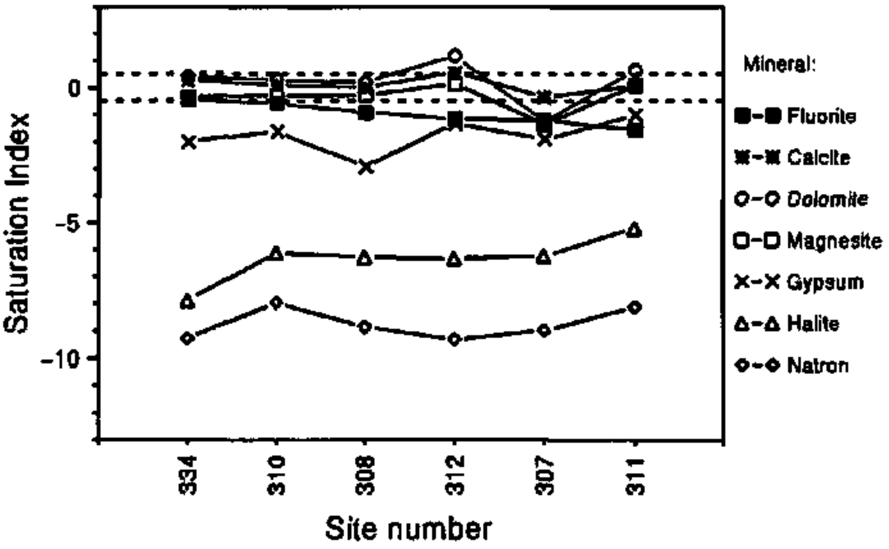


Figure 5.20. Saturation indices for seven minerals for all groundwater samples from the Nooitgedacht carbonatite in the field area, calculated using MINTEQA2.

5.3.4.6 Groundwater in the Pretoria Saltpan area

The Nebo Granite groundwater in the vicinity of the Pretoria Saltpan has a variable series of saturation indices (Figure 5.21). The Saltpan brine (site 230) is supersaturated with respect to fluorite, calcite and dolomite. The brine is closer to saturation with villiaumite (NaF) than any other sample considered here (see next section). Groundwaters in the area show variable saturation indices. Samples from sites 242 (Mr Theledi's Farm) and 335 (Saltpan artesian borehole) are undersaturated with respect to fluorite, and show decreasing saturation with respect to halite and natron, indicative of either mixing with fresh water or a shorter residence time. The Stinkwater sample (243) is undersaturated with fluorite.

5.3.5 Modelling Villiaumite (NaF) solubility

It has been shown that some of the groundwaters in the study area are supersaturated with respect to fluorite. It can be postulated that in such cases the fluoride concentration is being controlled by another fluoride mineral more soluble than fluorite. The most likely mineral is villiaumite. Stormer and Carmichael (1970) reviewed the occurrence of villiaumite and related minerals in igneous rocks. They stated that villiaumite may be controlled by the reactions represented in the following equations:

$$2NaF + 4SiO_2 + CaAl_2Si_2O_8 \leftrightarrow 2NaAlSi_3O_8 + CaF_2 \qquad (5.10)$$

$$\text{villiaumite} + \text{silica} + \text{anorthite} \leftrightarrow \text{albite} + \text{fluorite} \qquad (5.11)$$

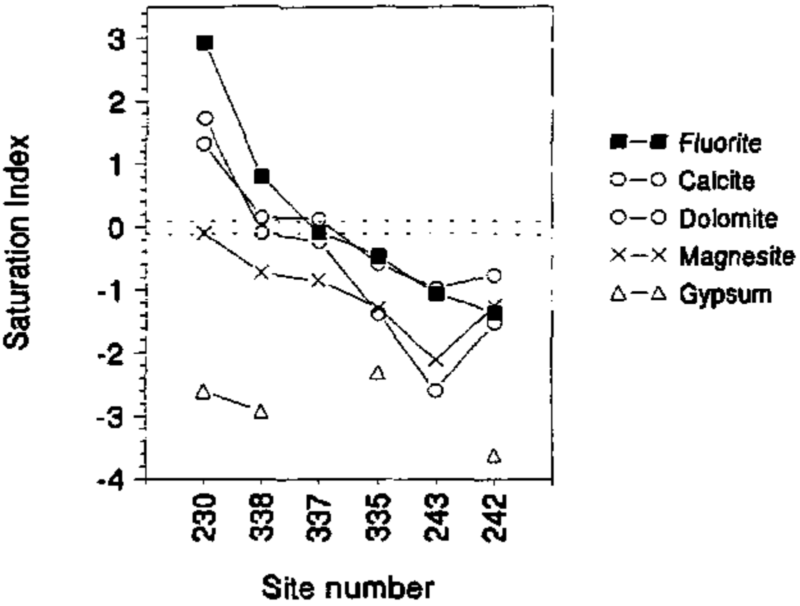


Figure 5.21. Saturation indices for selected minerals for groundwaters from the vicinity of the Pretoria Saltpan crater (hosted in Nebo Granite), calculated using MINTEQA2.

Villiaumite is, therefore, restricted to silica- and calcium- poor rocks, such as peralkaline nepheline syenites and phonolites. Pilanesberg rocks in general conform to these criteria, having mean SiO_2 and CaO contents of 52.4 and 2.9 wt%, respectively (n=23, calculated from Lurie, 1974). The phonolite of the Pilanesberg is a prime candidate to host villiaumite, as is the carbonatitic fluorite ore described in Chapter 4. Given that this ore has large amounts of fluorite, silica concentration is only 10% and the plagioclase composition is close to 100% albite, villiaumite is very likely to occur in the rock.

The thermodynamic databases which are included with the computer package MINTEQA2 do not include villiaumite as a mineral species, and so the relevant thermodynamic data had to be collated, calculated and inserted in the correct format. Woods and Garrels (1987) compiled a list of thermodynamic values which included enthalpy of formation ($\Delta H°_f$), also known as enthalpy of reaction, of inorganic compounds calculated from free elements. MINTEQA2 makes use of enthalpy calculated from aqueous species, and so a new $\Delta H°_f$ had to be calculated. The values used are shown in Table 5.11. Woods and Garrels (1987) stated that although absolute enthalpy values may change between researchers, the enthalpy of formation calculated using values from different sources is often similar, *i.e.* the enthalpy values are internally consistent. Table 5.11 illustrates this effect; the enthalpy values for F^- vary by 6.3 kJ/mol between sources, whereas the resulting enthalpy of formation values vary by only 0.7 kJ/mol. The Rossini *et al.* (1952) value is clearly an outlier, whilst the two most recent compilations yield a calculated $\Delta H°_f$ of -0.9 kJ/mol, the value used in the MINTEQA2 database. Since the temperatures of all the groundwaters modelled were very close to 25°C, the temperature corrections based on the calculated $\Delta H°_f$ values at 25°C were not large.

Table 5.11. Thermodynamic enthalpy values used in the calculation of ΔH°_{f} (enthalpy of formation) used in MINTEQA2. Units are kJ/mol.

Source	Na^+	F^-	NaF	ΔH°_{f}
Rossini *et al.* (1952)	-239.6	-329.1	-569.0	-0.3
Naumov *et al.* (1974)	-240.4	-333.8	-575.2	-1.0
Robie *et al.* (1978)	-240.3	-335.4	-576.6	-0.9
Wagman *et al.* (1982)	-240.1	-332.6	-573.6	-0.9
Babushkin *et al.* (1985)	-240.4	-333.8	n/a	n/a
Mean	-240.2	-332.9	-573.6	-

5.3.5.1 Application of Villiaumite saturation index

A plot of villiaumite (NaF) saturation indices *vs* calcite, natron, fluorite and halite saturation indices shows that groundwaters have very contrasting indices of saturation with respect to these minerals (Figure 5.22). All groundwaters are undersaturated with respect to villiaumite, but Pilanesberg groundwater shows less undersaturation than other groundwaters. Pilanesberg and Lebowa groundwaters are generally saturated to supersaturated with respect to fluorite but have a range of undersaturated values with respect to NaF; Nebo groundwater is saturated to undersaturated with respect to fluorite. The plots can be misleading as all the Na could come from albite and the F from CaF_2 or mica. Consequently the plots give no definite indication that NaF exists as a discrete mineral phase in the rocks in the study area.

5.3.5.2 Comparison of saturation indices calculated by MINTEQA2 and JESS

The results of two speciation modelling programmes have been compared in this study to determine the degree of agreement. The public-domain software package MINTEQA2 (Allison *et al.*, 1991) uses 'best estimate' formation constants and enthalpy values in its database, and it is claimed that the thermodynamic data often lacks internal consistency (Dr P Wade, CSIR, *pers. comm.*, 1995). A more sophisticated speciation modelling program named JESS (Joint Expert Speciation System) has been implemented by the CSIR and Murdoch University of Western Australia (May and Murray, 1991a,b). JESS features a very large thermodynamic database which has been produced by the systematic collation of data from the literature. Thermodynamic values are checked for internal consistency before being added to the database; all values are retained, but are weighted for validity, invalid data being given a zero weighting. Because the computer code for JESS is not in the public domain, Dr Peter Wade of the CSIR was commissioned to model a subset of the water analyses produced in this study. Specifically, the saturation indices for major minerals were required for comparison with the MINTEQA2 results.

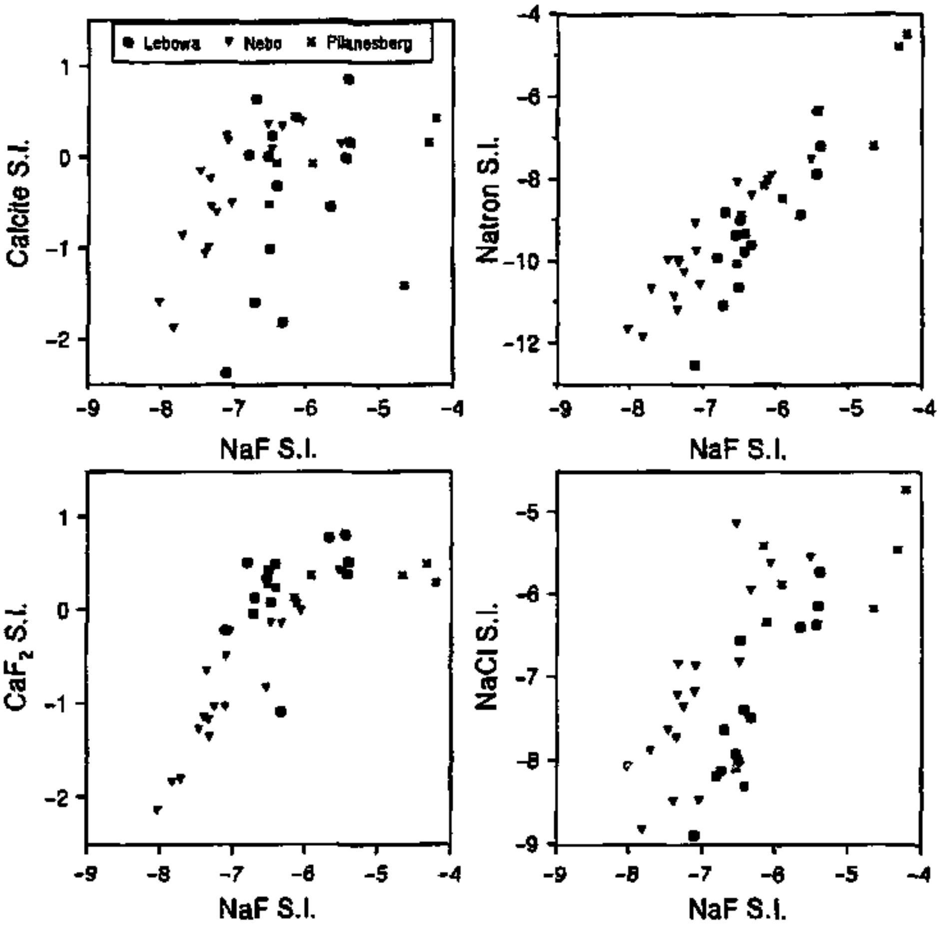


Figure 5.22. Plots of NaF saturation *vs* saturation of calcite, natron, fluorite and halite for groundwaters from the Lebowa and Nebo Granites and from the Pilanesberg.

JESS produced very similar results to MINTEQA2 for non-carbonate minerals (*e.g.* fluorite; Figure 5.23). The only significant difference was a slight systematic bias, the intercept on the y-axis being −0.37. The calculated saturation indices for carbonate minerals sometimes differed considerably between the two packages. For example, there was a good correlation between the two sets of saturation indices for calcite, with the exception of eight samples (one is off scale on the JESS axis, calcite S.I. = −12.1) which clustered well away from the regression line (Figure 5.23).

Several reasons could account for the difference. For MINTEQA2 modelling, the alkalinity as measured in the field was used as a measure of carbonate concentration. For the JESS modelling, carbonate concentration was estimated iteratively from the measured alkalinity. In most cases the alkalinity and the estimated carbonate concentration were within 0.1% relative of one another, but in several cases (groundwater analyses from sites 13, 17, 18, 59, 243, 311, 312 and, notably, 230) the JESS carbonate concentrations were much higher. This may have caused JESS to calculate different saturation indices for carbonate minerals for these analyses (*e.g.* calcite, Figure 5.23). The results give considerable confidence in the MINTEQA2 calculations for fluorite saturation indices but somewhat less for calcite saturation indices.

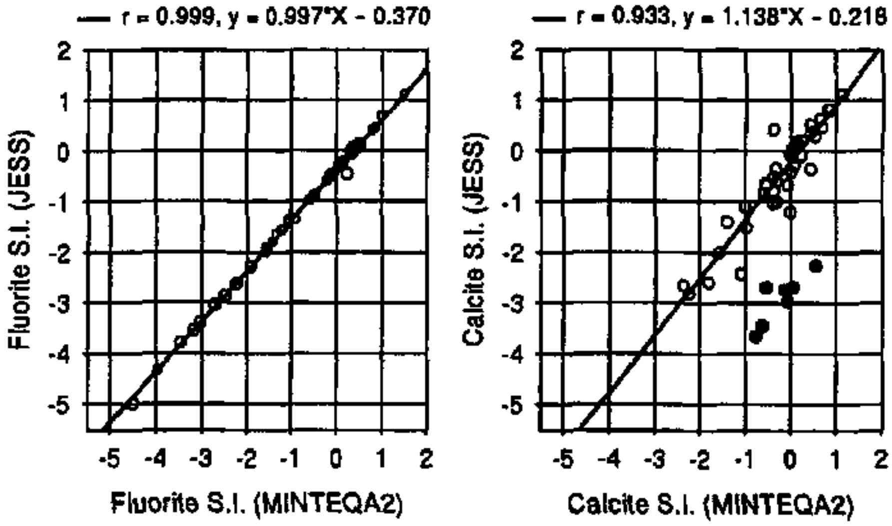


Figure 5.23. Comparison of saturation indices calculated by MINTEQA2 and JESS for selected groundwater analyses from the western Bushveld. In the calcite plot the solid data points were excluded from the regression line calculation.

5.3.6 Aqueous chemical control

It is apparent that dissolution of fluorite provides much of the F^- in groundwater. If this is the case, why are so many groundwaters either supersaturated with respect to fluorite, or far from simple stoichiometric dissolution of fluorite? The possibility that other, more soluble fluorine compounds are responsible for high fluorine concentrations has already been discussed. Other reactions, apart from mineral dissolution, can also affect F^- concentrations. These include displacement of F^- by OH^- on clay surfaces at high pH, precipitation of $CaCO_3$, ion exchange on clays, and precipitation upon evaporation.

5.3.6.1 pH

In general the pH of the groundwater does not correlate with F^- concentration, as shown in Figure 5.24. No clear trend is seen at near neutral pH ($6 < pH < 8$). Although the regression lines in Figure 5.24 are statistically significant, they are controlled by relatively few data points with high F^- concentrations. It must be concluded that F^- is not correlated with pH at near-neutral pH values.

Little work has been done on the solubility of F-bearing minerals at high pH, but it seems likely that increased OH^- activity might displace F^- from adsorbed sites in clay minerals and from structural sites in mica and amphibole. The good correlation between many of the high pH and high F^- values in the groundwaters supports the suggestion that anion exchange (OH^- for F^-) may have occurred.

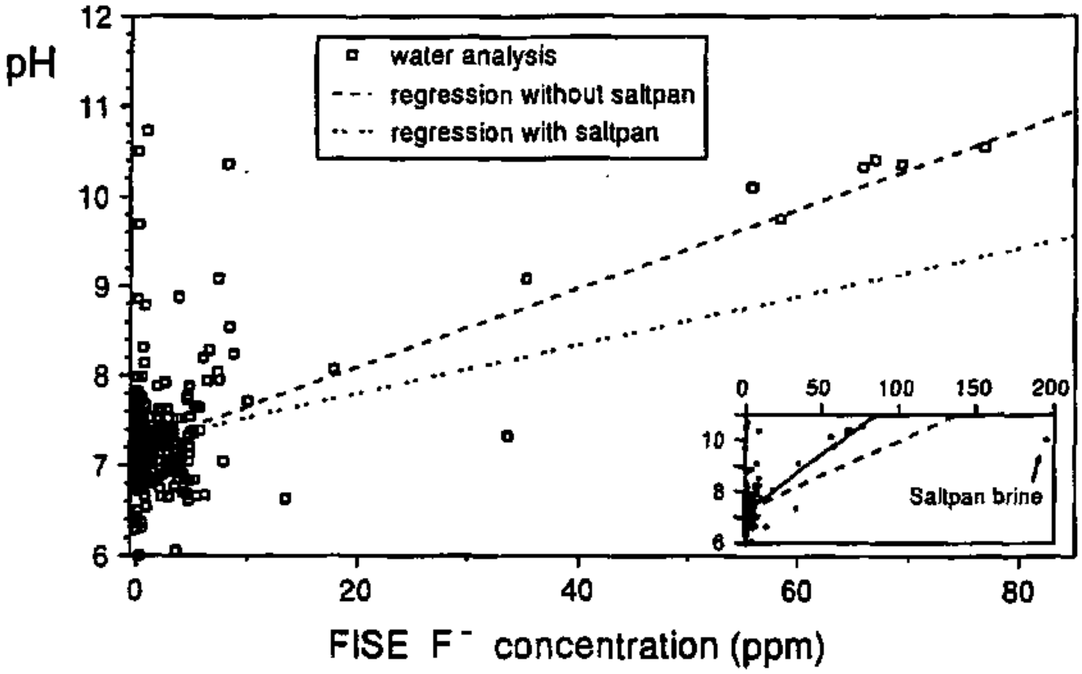


Figure 5.24. Fluoride concentration plotted against pH for groundwater. Two regression lines are given: one does not include the Saltpan data. The regression lines are strongly influenced by a few high F⁻ values.

5.3.6.2 $CaCO_3$ precipitation and its effect on the Ca:F ratio in groundwater

F⁻ concentrations in groundwater can increase as a result of precipitation of $CaCO_3$ at high pH, which removes Ca from solution allowing more fluorite (CaF_2) to dissolve. For an aqueous system in equilibrium with the atmosphere and fluorite, the following equations governing equilibrium reactions can be written:

$$H_2O + CO_2 \rightleftharpoons HCO_3^- + H^+ \quad (5.12)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (5.13)$$

$$CaF_2 \rightarrow Ca^{2+} + 2F^- \quad (5.14)$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (5.15)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (5.16)$$

The $\Delta G°_f$ of equations 5.15 and 5.16 are +12.6 and -46.36 kJ/mol, respectively, and, therefore, the formation of $CaCO_3$ from Ca^+ and CO_3^{2-} occurs spontaneously, but not from Ca^{2+} and HCO_3^-.

When the pH is increased to above 8, fluorite dissolves to release Ca^{2+} ions and CO_3^{2-} combines with the Ca^{2+} to form $CaCO_3$, which then precipitates. The lowered activity of Ca^{2+} means that more CaF_2 can dissolve, thereby increasing the F/Ca ratio of the solution. At neutral pH the concentration of CO_3^{2-} is negligible, and $CaCO_3$ precipitation does not take place. At low pH $CaCO_3$ is unstable and the stripping of Ca^{2+} ions from solution by the precipitation of $CaCO_3$ cannot take place. Therefore, at low pH the F^- concentration and Ca:F ratio are unaffected by $CaCO_3$ precipitation.

5.3.6.3 Ion Exchange

Boyle (1992) showed that very high levels of F^- in groundwater (up to 25 mg/ℓ) were the result of base exchange softening of groundwater in a sedimentary basin. Cation (or 'base') exchange of Ca^{2+} (and Mg^{2+}, Sr^{2+}) for Na^+ and K^+ on clays reduces the Ca^{2+} concentration in solution, thus promoting dissolution of CaF_2. Unlike the studies of Cederstrom (1946) and Foster (1950), Boyle (1992) showed that base exchange could take place at a shallow depth (as little as 15m below the surface) and without a long apparent residence time or flow path. However, Freeze and Cherry (1979) stated that, depending on conditions, several million years may pass before the exchange medium is in *equilibrium* with inflowing groundwater. Boyle (1992) found that with progressive softening of the waters, pH increased up to 9.8 and Ca and Mg concentrations decreased to less than 1 mg/ℓ. He ascribed this to the exchange of Ca^{2+} and Mg^{2+} on 'solid phases' for Na^+, and the involvement of H^+ in satisfying the exchange capacity of the sediments towards the end of the exchange process.

The evidence for the action of ion exchange in the field area is good. The groundwaters of the Pilanesberg Complex with very high F^- contents have very low Ca^{2+} (Figure 5.13) and Mg^{2+}, high Na^+ and pH, and moderately high HCO_3^-. Such a composition is characteristic of groundwater which has undergone cation and anion exchange (e.g. Gascoyne and Kamineni, 1994). Water-bearing fractures in the Pilanesberg Complex are known to be often lined with clays, and flow paths in the order of 5 kilometres are possible (McCaffrey, 1994). The conceptual model of the geohydrology of the area (outlined previously) does not indicate long flow paths or high porosity in the rest of the Bushveld Complex, which would limit the action of cation exchange. The probability of cation exchange is highest in the vicinity of the Karoo basin. Groundwaters of the Lebowa and Nebo Granites, saturated with respect to fluorite, would flow from the granitic highlands into the porous and clayey sediments of the Irrigasie and Ecca formations of the low-lying Karoo basin.

When plotted on a trilinear diagram ('Piper diagrams'; Piper, 1944) hydrochemical processes can be more clearly seen (Lloyd and Heathcote, 1985). Figure 5.25 shows simple divisions into which the groundwaters can be divided. To plot all the data points would result in a confusing and cluttered graph, so only the mean analyses have been plotted. Figure 5.26 shows mean groundwater analyses of the 8 major lithologies of the field area. Most of the groundwaters fall in the 'No Dominant Type' area. Mean groundwater from the RLS is of the $Ca+Mg+Cl+SO_4$ type. Mean Pilanesberg groundwater has no dominant anion, but the cations are dominated by Na+K. This is not in itself evidence that Pilanesberg groundwaters have been subject to ion exchange (the sodium rich, calcium poor rocks of the complex may be the cause), although it is suggestive.

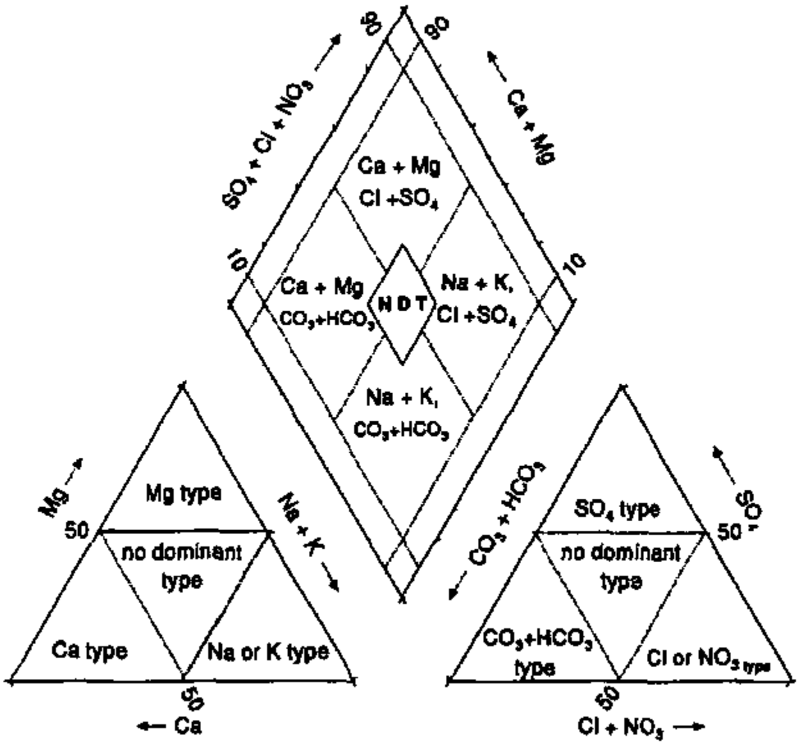


Figure 5.25. Piper diagram divided into descriptive groundwater types. 'NDT' is no dominant type.

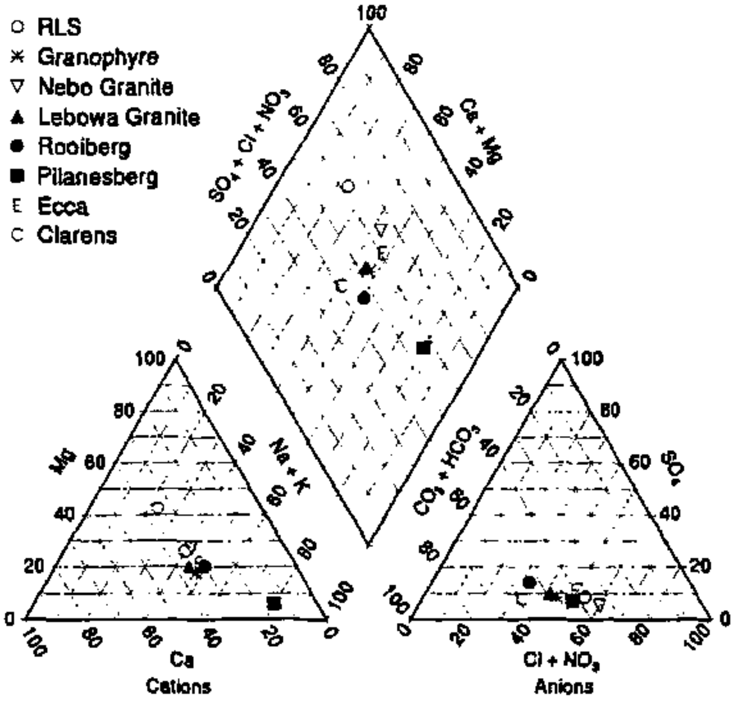


Figure 5.26. Mean groundwater analyses for 8 lithologies plotted on a Piper diagram.

Boyle and Chagnon (1995) used a plot of the ratios of exchangeable cations in water against F^- concentration to demonstrate the variation of exchange capacity of differing aquifers. Figure 5.27 is such a plot with data from this study. The data for the study area as a whole have only a weak covariation ($r=0.517$ at $p<0.001$). However, it is apparent that the very high F^- groundwaters from the Pilanesberg Complex also have very high exchange ratios, strongly suggesting that they have been subject to ion exchange. Conversely, the low F^- groundwaters of the RLS have low exchange ratios, indicating that they have not undergone ion exchange. From this plot, therefore, it seems likely that base exchange is occurring in parts of the Pilanesberg Complex, if not in other parts of the study area.

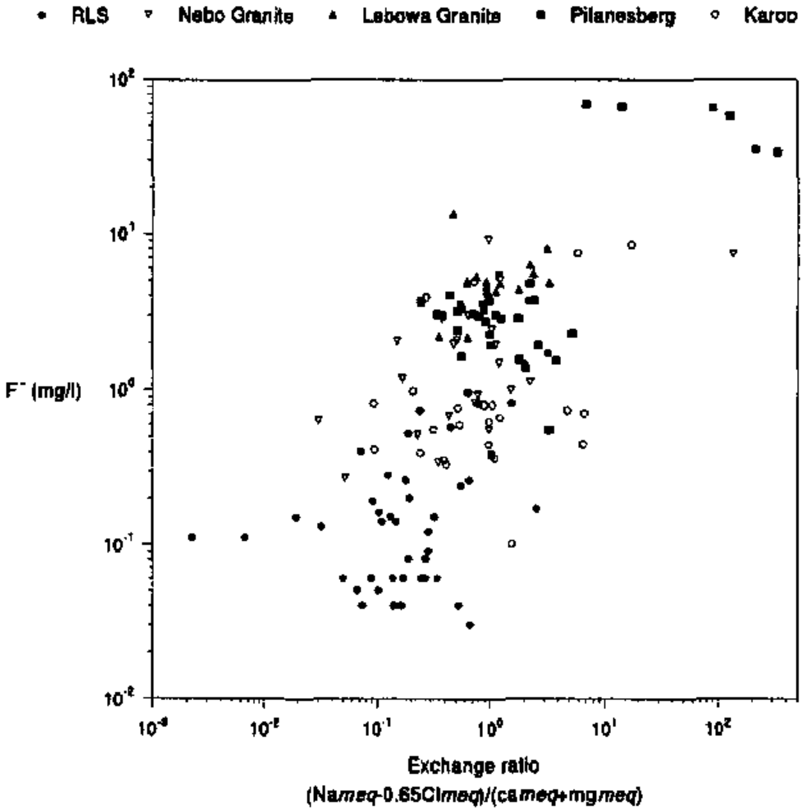


Figure 5.27. Exchange ratio (from Boyle and Chagnon, 1995) against F^- concentration. See text for discussion.

5.3.6.4 Evaporation

Evaporation of groundwater with Ca^{2+}, Na^+ and F^- in solution may result in precipitation of relatively insoluble calcium minerals, whilst Na^+ forms a highly soluble ion-pair with F^-. NaF_2 solubility is 3 orders of magnitude greater than that of CaF_2, and the following reaction would take place:

$$Ca^{2+}_{(aq)} + 2F^-_{(aq)} + 2Na^+_{(aq)} + M^{2-}_{(aq)}O \overset{evaporation}{\Rightarrow} CaM_2\downarrow + 2F^-_{(aq)} + 2Na^+_{(aq)} \quad (5.17)$$

where M is a product of chemical weathering such as sulphate, SO_4^{2-}. This reaction would result in the precipitation of gypsum and an increase in F^- and Na^+ in solution. High values of chloride in the groundwater of the perimeter of the Pilanesberg occur with high values of sodium, strengthening somewhat the argument for evaporative or evapotranspirative concentration, given the absence of sedimentary evaporitic rocks in the area.

5.3.7 Other factors controlling F^- concentration in groundwater

Most studies have shown that the source of F^- in groundwater is the dissolution of F-bearing minerals. However, some studies have shown fluorosis to occur in areas of volcanic exhalations (*e.g.* Vasak, 1992; Fridriksson, 1983), and to be connected to fluorite dust from mining (Davies, 1994) and industrial emissions. These sources will now be briefly discussed.

5.3.7.1 Volcanic exhalation

No volcanic activity currently exists in South Africa, and so HF from volcanic exhalations can be discounted as a source of F^- in groundwater.

5.3.7.2 Industrial emissions

Although many fluorite prospects occur in the Lebowa Granite Suite and Rooiberg felsite (Crocker and Martini, 1976), few large working fluorite mines still exist in the study area. Major fluorite mines are still active in the Malmani Dolomite of the Chuniespoort Group, on the edge of the study area. The impact of dust generated by blasting and processing the ore is likely to be restricted to areas close to the mines, and no gaseous emissions are generated.

Two other large fluorine-handling industries exist in the study area, namely the Atomic Energy Corporation's uranium enrichment plant at Pelindaba in the south, and a major ore smelter in the centre of the area. At Pelindaba, uranium oxide was converted to uranium hexafluoride, which was then enriched by a diffusion process. Much activity occurred at the plant in the 1960's and 70's, but production has since been scaled down, if not terminated. A request for information on the magnitude of fluoride emissions from the plant has remained answered. Use of hydrofluoric acid (commercial grade, 31-32% HF by mass) by one of the metal smelters (which provided information on condition of anonymity) amounts to about 2.5 m^3 per year. Ninety five percent of this is deposited in an evaporative plastic-lined dam, and no leakage to groundwater from this dam has yet been reported. According to the reply, gases emitted from the smelter stacks are fluorine free. 5% remains unaccounted for, equivalent to 125 ℓ HF per year.

To put this in perspective, a rapid calculation can be made using estimated parameters. It might be assumed that all the HF not accounted for reaches the groundwater table; that groundwater is being affected to a depth of 10 m within a radius of 10 km from the smelter; and that the rock has a porosity of 0.5%. If it is further assumed that the smelter has 'lost' 125 ℓ HF per year for the last 50 years, then groundwater fluoride concentration would have been increased by less than 0.1 mg/ℓ F^-. Clearly, this amount is negligible. If the same assumptions are made with the exception that the radius of affected groundwater is reduced to 1 km, groundwater concentrations would be increased by 6.4 mg/ℓ F^-, which would be unacceptable. Groundwater gradients in the RLS are quite low and transmissivity can also be low. Therefore, groundwater flow velocities are likely to be slow, which could result in increased F^--contaminated groundwaters close to the smelters. There is an obvious need to establish accurately the rate of groundwater flow in the area.

5.3.7.3 Fluoride in rainwater

Fluoride occurs in rainwater at very low concentrations, between 2 and 20 $\mu g/\ell$ (Barnard and Nordstrom, 1982a). The origin of F^- in rainwater has been the subject of some controversy. Carpenter (1969) found that fluoride originated from the ocean and is injected into the atmosphere at the air-sea interface. The studies of Wilkniss and Bressan (1971, 1972) totally contradicted this result. Barnard and Nordstrom (1982b) found that the majority of fluoride in precipitation in the United States is anthropogenic in origin and that fluoride is not injected at the air-sea interface.

No rainwater samples suitable for fluoride analysis were taken for this study. However, it is likely that, given the distance from the ocean and the absence of major fluorine-handling industries in the area, fluoride concentration in rainfall would be near the background concentrations of 8 $\mu g/\ell$ F^- found by Barnard and Nordstrom (1982a).

5.3.7.4 Dissolution of atmospheric fluorine compounds

Fluorine exists in the atmosphere in the form of F_2 at concentrations between <0.01 and $0.4\,\mu g/m^3$ (Bowen, 1966; Oelschläger, 1966). Concentrations near industrial plants increase markedly (*e.g.* Machoy *et al.*, 1991). In South African coal up to 90% of the fluorine is volatilised upon combustion, either as HF, CaF_2 or often combining with boron to form BF_3. Most South African coals have F concentrations between 75 and 200 ppm (Kunstmann *et al.*, 1963). It is possible that F emitted into the atmosphere by the burning of South African coals could affect groundwater concentrations significantly. Values given in DMEA (1995) indicate that in 1993, 130 million tonnes of coal were burnt each year in South Africa. This corresponds to between 8.775×10^9 and 2.34×10^{10} g F released into the atmosphere each year. However, most of this coal is burnt on the Transvaal Highveld (approximately 300 km to the east of the study area), and with the prevailing wind systems coming from the southwest, is very unlikely to influence groundwater F^- in the study area (Prof. H. Annegarn, Schonland Centre for Nuclear Research, University of the Witwatersrand, *pers. comm.*).

5.3.7.5 Temporal factors

Chemical analysis of repeat samples taken from boreholes after almost 2 years show great variation for most major ions, but comparatively little variation in F^- levels. This indicates that the F^- concentration is effectively buffered by mineral-water equilibria during short term fluctuations.

5.3.7.6 Hydrological factors

Brown and Roberson (1977) found that over a three year period fluorite (CaF_2) did not fully reach equilibrium with dilute sodium perchlorate solutions, but had reached approximate equilibrium after 34 days. Infiltrating rainwater is undersaturated with respect to CaF_2, and so actively recharging groundwater will not to be in equilibrium with the mineral; it should reach approximate equilibrium with fluorite-containing rocks within 34 days of reaching the water table.

5.3.7.7 Borehole depth

It was noted in Chapter 4 that the fluoride concentrations in groundwater from boreholes located in the outcrop area of the Karoo sediments had a very varied spatial distribution. It is suggested that this is due to the possibility that some boreholes penetrate the low fluoride Ecca shales and tap water from the underlying high fluoride Nebo and Lebowa granites (shown schematically in Figure 5.28). The groundwaters in Karoo sediments in the central part of the basin, namely the Irrigasie and Clarens Formations, have lower mean fluoride concentrations, 1.0 and 0.9 mg/ℓ F^-, respectively, than the Ecca Formation (2.3 mg/ℓ F^-, Chapter 4), and have fewer high fluoride outlier values than the Ecca shales. This suggests that boreholes in the areas of increased sediment thickness are not deep enough to penetrate to the high F^- groundwaters in the underlying granites.

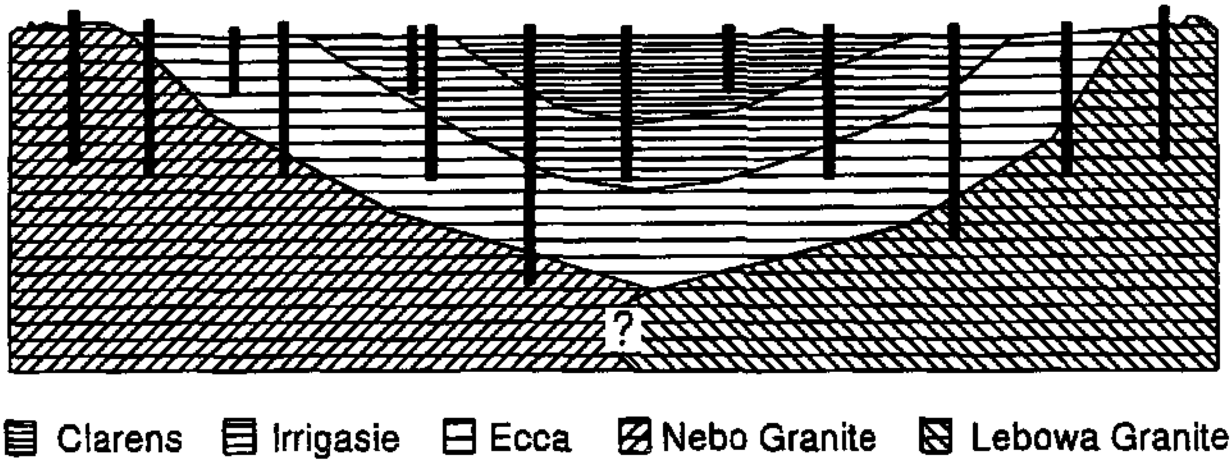


Figure 5.28. Schematic cross section of the geology of the Karoo basin, with boreholes of varying depths reaching the high fluoride groundwater of the underlying granites.

The absence of depth information associated with any of the groundwater samples is a major disadvantage of the current data set. The deficiency all but prevents any speculation of the variation of F^- concentration with depth. Whilst the data of Boyle (1992) appears to show little or no correlation of F^- concentration with depth, Hitchon (1995) found that F^- concentrations increased in deeper groundwaters. Salinisation is known to occur in most crystalline basement massifs at depths between 500 and 1000 m below the earth's surface (e.g. Smalley *et al.*, 1988; Gascoyne and Kamineni, 1994). If depth data could be supplemented to the current data set it would be reasonable to expect higher F^- concentrations with depth.

5.3.7.8 Leakage of fluid inclusions

Waber and Nordstrom (1992) proposed that deep granitic groundwaters were geochemically influenced by the release of fluid from fluid inclusions. In saline, high pH waters with high F^- concentrations, they found that up to 3.8% of ions may have been derived from fluid inclusions. However, their method of calculating the composition of fluid inclusions is flawed, being based on a circular argument involving fluid inclusion contribution to groundwater, and fluid inclusion composition based on groundwater chemistry (Waber and Nordstrom (1992) p244, paragraph 4).

The possibility that fluid inclusions contribute significant amounts of dissolved ionic species to Bushveld groundwater cannot be ruled out. All of the samples collected had inclusion trails, most notably in quartz grains. However, no data on F^- concentrations in fluid inclusions exist for the area.

Although F^- concentrations in fluid inclusions in the study area have not been measured, the F^- concentrations are likely to be controlled by equilibration with fluorite, ubiquitous in these rocks (H. Frimmel, UCT, 1996, *pers. comm.*). Given the retrograde solubility of CaF_2 above 100°C (Strübel, 1965), it is predicted that the medium to high temperature fluid inclusions present in rocks in the study area are not likely to contain more than about 5 mg/ℓ F^-. To actually measure the F^- concentration of fluid inclusions would be difficult and was not attempted in this project.

5.3.7.9 Soil

The leaching experiments described in Chapters 3 and 4 have confirmed that soil is a source of F^-, but that it contains an order of magnitude less soluble-F than associated fresh rock. Soil as a source of F^- is therefore of proportionately less significance than the fresh rock of the host aquifer. However, if soil water is partially evaporated whilst in contact with F salts, higher concentrations of F^-, as well as distinct stable isotope ratios, in groundwater may result.

5.4 Hydrogen and Oxygen Isotopes

The previous discussion has shown that evaporation is a potentially important process in increasing F^- concentrations in groundwater. The study of the stable isotopes of H and O allows an estimation of the extent of any evaporation. The expense of isotope analysis constrained the number of samples which could be analysed. The following discussion is therefore based on a limited sample set, and additional analyses would help to clarify the relationships found here.

5.4.1 Correlation with elevation and temperature

The δ^2H and $\delta^{18}O$ values found in groundwater in this study are weakly correlated to sampling point elevation (Figure 5.29), with considerable scatter around the calculated regression line. The correlation of $\delta^{18}O$ with elevation is significant at the 95% confidence level, whilst for δ^2H it is significant at the 99% level. The scatter may be due to variable vertical flow away from the recharge area, which cannot as yet be quantified because of uncertainty about the location and elevation of the recharge areas of these groundwaters. The regressions shows that there is a decrease in $\delta^{18}O$ of 0.2‰ per 100 m increase in elevation. With a typical lapse rate in summer of 1°C per 100 m, the resultant relationship for $\delta^{18}O$ of 0.2‰/°C is comparable to the value of 0.4‰/°C found by Heaton *et al.* (1986) for groundwater along the southern coast of South Africa. The relationship of δ^2H to temperature for the study area is 3.6‰/°C.

5.4.2 Isotopic signature of rock types

The rock type with which groundwaters interact may control the oxygen and hydrogen stable isotope signature of the water. A summary diagram plotting hydrogen and oxygen isotopes, in groups according to their host rock, is shown in Figure 5.30. Although there is some overlap between groundwaters from different rock types, there is sufficient separation to allow groundwaters from different rock types to be distinguished from one another with a considerable degree of certainty on the basis of their stable isotope composition. The Pilanesberg perimeter groundwaters and those of the Nebo Granite have very different δ^2H and $\delta^{18}O$ values. It should be possible to identify the

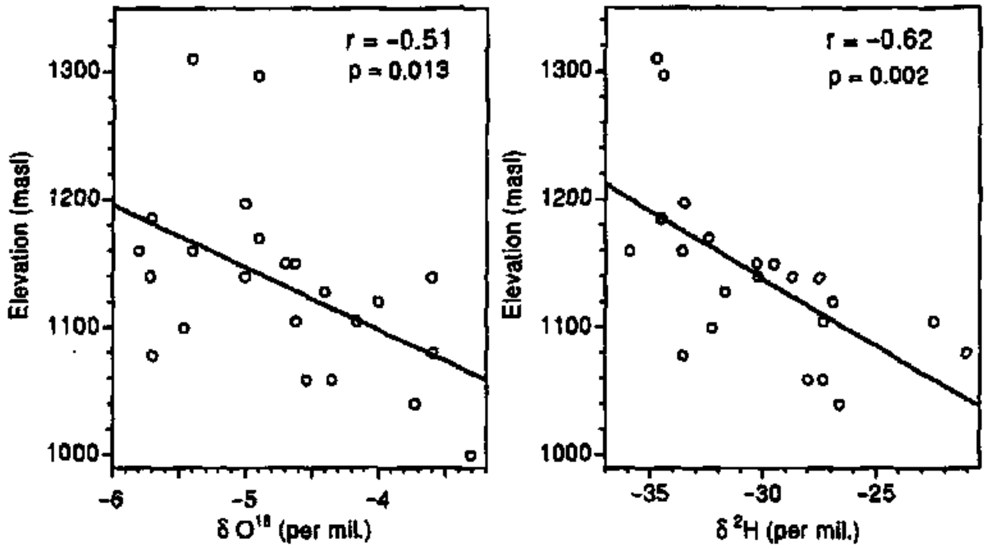


Figure 5.29. $\delta^{18}O$ and $\delta^{2}H$ plotted against elevation of *sampling point*. Some of the scatter may be explained by groundwater flow away from the point of recharge.

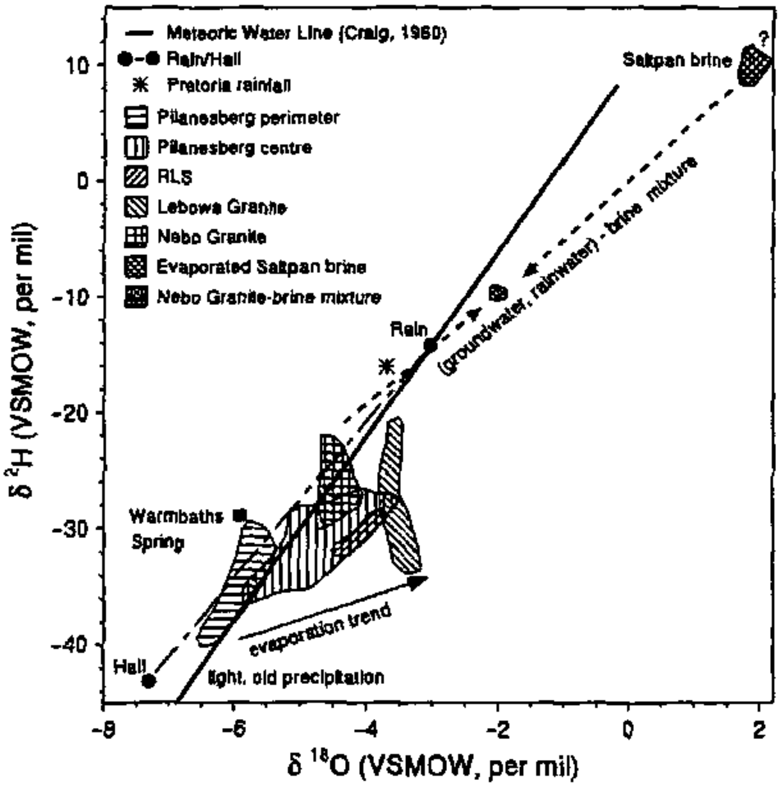


Figure 5.30. Interpretive diagram of hydrogen and oxygen isotopes. Some groundwaters may be the result of mixing between freshly recharged groundwater and evaporated brines. Central Pilanesberg data from McCaffrey (1993).

Pilanesberg Perimeter groundwater type, if encountered in boreholes in the surrounding RLS or Nebo Granite, based on its 'light' isotopic signature. The Nebo granite samples are tightly grouped around -4.4‰ $\delta^{18}O$ and -27‰ $\delta^{2}H$, and any deviations from these values are considered significant. Central Pilanesberg groundwater has a much larger spread and shows evidence of having been subjected to evaporation (McCaffrey, 1993).

The Pretoria Saltpan brine is isotopically very much heavier than the precipitation falling in the area and has been subjected to large amounts of evaporation. One groundwater sample, taken from a borehole situated in Nebo Granite at Mr Mon's store close to the Pretoria Saltpan, has a significantly heavier isotopic signature than other Nebo Granite water, and lies on a mixing line between Saltpan brine and Nebo Granite groundwater and/or rain water. This is taken as evidence that the Saltpan brines are somehow leaving the crater environs and mixing with local groundwater.

The analyses of rain and hail from the same thunderstorm highlight the variability of O and H isotopes in precipitation, with respect to both time and elevation. The differences between rain and hail are unlikely to influence groundwater isotope composition, since no conceivable mechanism exists which would allow recharge by rainwater and not melted hail, at least in the current climate. Hail melts within minutes or hours of falling to the ground, and so effectively becomes part of the rain recharge event. The slight delay in infiltration due to melting might conceivably lead to different layers of an infiltration front having different isotopic values, but they would be quickly mixed in the unsaturated zone.

5.4.3 Isotopic difference between hail and rain

The difference in $\delta^{18}O$ and $\delta^{2}H$ between rain and hail from the same thunderstorm, noted in Chapter 4, may be due to several processes. The ^{18}O fractionation factor (α) for ice in equilibrium with water is 1.002 at 0°C (Faure, 1987); if hail formed in a simple one-step equilibrium freezing process from a large volume of water droplets, then the hail would have a $\delta^{18}O$ of -2‰ relative to rain. The measured difference of -4.3‰ could imply that, since the fractionation factors for ^{18}O and ^{2}H become greater at lower temperatures, the hail formed from supercooled water vapour. Supercooled water vapour does occur in thunderclouds (Preston-Whyte and Tyson, 1988).

It was observed that the hail analysed in this study fell about 1 hour after the rain from the same storm system. Fractionation of the water vapour in the cloud during that time, by preferential removal of the "heavier" molecules, would result in the remaining water vapour becoming isotopically lighter with time. Hence, the differences between hail and rain may be due either to the large fractionation factor at low temperature or to the "rainout effect".

5.5 Radiogenic isotopes

This section attempts firstly to use radiocarbon to gauge the mean residence time of groundwater, and thus the rate of reactions which affect groundwater composition. Secondly, the section includes an attempt to characterise groundwater from the field area using Sr isotopes.

5.5.1 Radiocarbon - ^{14}C

5.5.1.1 Mean Residence Time

The ^{14}C results presented in Chapter 4 may be used simplistically as a chemical parameter to indicate a particular groundwater type (A. Issar, Ben-Gurion University, *pers. comm.*, 1995). More usefully, ^{14}C may be used to calculate the mean residence time (T) of a groundwater flow unit.

Where the recharge area of a confined aquifer is of a similar cross sectional area to the flow path, and where ^{14}C is not depleted by interaction with ^{14}C-free aquifer material, or augmented by ongoing recharge along the flow path, the mean residence time can be modelled with the equation:

$$C_s = C_o(t - t_u - T)e^{-\lambda(t_u + T)} \tag{5.18}$$

where C_s is the ^{14}C activity at the time of sampling, C_o is the input concentration (initial ^{14}C activity), λ the decay constant, T the mean residence time, t the time of sampling and t_u is the delay time in the unsaturated zone (Verhagen *et al.*, 1991). Mook (1980) and others use A_o to denote the original specific radioactivity of the sample, but the notation of Verhagen *et al.* (1991) is used here. The model is known as the 'piston flow' model. Equation 5.18 can be rearranged and simplified to:

$$T = 8267 \ln\left(\frac{C_o}{C_s}\right) \tag{5.19}$$

where C_o is the initial ^{14}C activity and C_s is the activity at the time of sampling.

This simplified equation is valid when the delay time in the unsaturated zone is small (Verhagen *et al.*, 1991). In the field area such conditions are probably only fulfilled in the tuff bands of the Pilanesberg, which are confined on either side by impermeable syenite.

The open fracture system of the granitic rocks of the field area suggests that a discreet recharge area does not exist for these rocks. Rather, rainwater infiltrates over the entire outcrop and much of the suboutcrop of the granite, mixing with groundwater on its way to the discharge area. The mean residence time of a groundwater flow unit in such a system can be calculated using the equation:

$$C_s = \frac{e^{-\lambda t_u}}{T}\int_0^\infty C_o(t - t_u - t^*)e^{-(\lambda + 1/T)t^*}dt^* \tag{5.20}$$

where t* is the transit time of a groundwater volume element (Verhagen, *pers. comm.*). This equation can be rearranged and simplified to:

$$T = \frac{C_o - C_s}{C_s \lambda} \qquad (5.21)$$

where λ is the decay constant of ^{14}C, equal to 0.000121 and calculated from

$$\lambda = \frac{\ln 2}{T_h} \qquad (5.22)$$

The half life (T_h) of radiocarbon used here is 5730 years (Faure, 1987).

5.5.1.2 Estimation of C_o

Equations 5.18 to 5.21 assume that C_o is known. In most hydrologic studies of ^{14}C, soils derived from aquifer material contain appreciable quantities of fossil C (^{12}C), diluting the ^{14}C activity of infiltrating rainwater. This reduces C_o from 100 pmc to as low as to 50 pmc. However, most igneous rocks and the soil derived from them are comparatively free of carbonate. Therefore, at a first approximation it might be assumed that C_o is between 90 and 100 pmc; McCaffrey (1993) assumed that C_o was 90 pmc for Pilanesberg groundwater. Although this study has shown for the first time (Chapter 3, Appendix A6) that carbonate minerals occur in the Pilanesberg, their distribution is likely to be very limited and their importance in terms of their effect on ^{14}C is therefore minimal. Several samples from the Pilanesberg have ^{14}C above 90 pmc. McCaffrey (1993) explained this as due either to an absence of carbonate in the soils of the complex or to the influence of the increased atmospheric ^{14}C since the nuclear weapons tests of the 1960's.

To use the radiocarbon method as a means of dating groundwater, it must be possible to affirm that ^{14}C has not been reduced by an increase in inorganic carbon content resulting from the dissolution of carbonates contained within the aquifer, as opposed to within soil derived from aquifer material. Figure 5.31 shows that the total alkalinity of the sample is not correlated to ^{14}C activity. This observation suggests that the assumption implicit in equations 5.18 to 5.21, that ^{14}C activity is reduced only by radioactive decay, is correct, and suggests that ^{14}C can be used to estimate mean residence time.

A method which has been used to gauge the initial activity of radiocarbon, C_o, is that of isotope dilution correction (Mook, 1980). The quantitative use of ^{13}C to gauge radiocarbon dilution is fraught with difficulties, and indeed its quantitative use is considered to be suspect when the hydrological parameters of a system are poorly known (Prof. B. Th. Verhagen, Schonland Centre for Nuclear Research, University of the Witwatersrand, *pers. comm.*). Typically, the extra parameters involved in the isotope dilution correction equations introduce extra uncertainty and errors into calculations of residence time, errors possibly greater than the actual correction. Isotope dilution corrections also sometimes produce apparent negative residence times, which are obviously impossible. It is with these limitations in mind that an isotope dilution correction is attempted here. In this method the $\delta^{13}C$

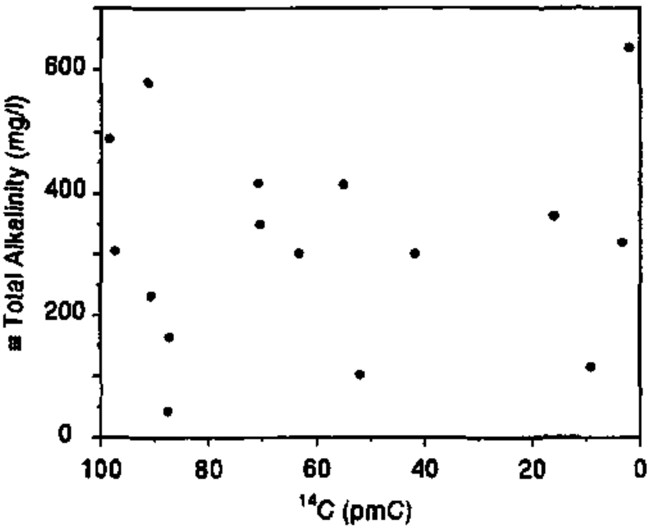


Figure 5.31. Plot of total alkalinity against ^{14}C, showing no significant trend in the data. This confirms that ^{14}C can be used to estimate residence time.

value of the groundwater is used to gauge the degree to which the original ^{14}C has been diluted after infiltration. The dilution factor $^{14}C_\Sigma/^{14}C_o$ is equivalent to

$$\frac{^{14}C_\Sigma}{^{14}C_o} = \frac{(\delta^{13}_\Sigma - \delta^{13}_l)}{(\delta^{13}_o - \delta^{13}_l)} \tag{5.23}$$

where δ^{13}_Σ is the $\delta^{13}C$ value of carbonate in solution in the groundwater, δ^{13}_l is the $\delta^{13}C$ value in aquifer carbonate and δ^{13}_o is the $\delta^{13}C$ of soil CO_2. The $\delta^{13}C$ value for groundwaters (δ^{13}_Σ) is shown in Table 5.12. The table also includes the data of McCaffrey (1993). The value of δ^{13}_l is set at −2.7‰, the $\delta^{13}C$ value for carbonate in the Pilanesberg (Section 3.5.2). Difficulties ensue when estimating the value of δ^{13}_o (the $\delta^{13}C$ of soil CO_2). No direct measurements of this value have been made in any Bushveld soils (Prof. W. Stock, Department of Botany, University of Cape Town, *pers. comm.*). However, as the Bushveld is a semi-arid area of open grassland and Acacia trees, the resulting soil CO_2 $\delta^{13}C$ values are likely to be between −17 and −12‰ (Mook, 1980). The uncertainty in δ^{13}_o propagates into an uncertainty in the dilution factor, and thus C_o.

Table 5.12 shows that several groundwaters apparently have, after the ^{13}C correction described above, initial radiocarbon activities above 100 pmc. Although this seems to confirm that they contain bomb-generated ^{14}C, the lack of hydrological information and the current poor understanding of Bushveld groundwaters makes this a questionable interpretation.

Table 5.12 Data used in the calculation of initial ^{14}C activity (C_o), the minimum and maximum value of C_o (min C_o and max C_o, respectively), and groundwater residence times for the Piston Flow and Exponential models. Sites in italics are from McCaffrey (1993). The superscripts $^{l \text{ or } u}$ indicate to which trend (lower or upper, respectively) in Figure 5.32 the groundwater belongs. No $\delta^{13}C$ was measured for Stinkwater or Tswaaneng groundwaters, and the value of −14.5‰ is a best estimate, being the middle of the range for semi-arid Hache-Slack type vegetation. Minimum and maximum errors for Piston flow model is 1588 and 1968 years respectively for all groundwaters.

Site: site no.	^{14}C	$\delta^{13}C$	C_o	min C_o	max C_o	Piston	Expon-ential	Min error	Max error
Units:	pmc	‰	pmc			Years			
Klipvoor: 299^{u}	87.5	-14.7	102	84	129	1243	1341	1679	2582
Stinkwater: 243^{l}	63.3	(-14.5)	100	83	127	3780	4792	2283	3510
Tswaaneng: 286^{u}	55	(-14.5)	100	83	127	4942	6762	2627	4039
Slipfontein: 300^{l}	51.9	-8.8	52	43	66	-33	-33	1439	2213
Makoropeja: 292^{l}	9	-7.8	43	36	55	12972	31424	6938	10669
Mr Theledi's Farm:242^{l}	3.2	-5.8	26	22	33	17405	59585	11862	18239
Quarantine Camp: 287^{u}	2	-9.1	54	45	69	27283	215857	39182	60248
Mankwe Camp^{u}	98.5	-7.3	39	32	49	-7663	-4994	572	879
Gravel Pit^{u}	97.4	-10.6	67	55	85	-3099	-2584	993	1527
Bakgatla Gate^{u}	91.3	-10.5	66	55	84	-2670	-2281	1046	1608
Ruighoek Staff Acc.^{u}	90.6	-13.5	92	76	116	84	84	1460	2244
Bakubung Gate^{u}	88.6	-14.3	98	81	125	859	905	1603	2465
Tshukudu Camp^{u}	87.2	-11.4	74	61	94	-1387	-1277	1222	1878
Nkakana Int.^{u}	70.8	-10.9	69	57	88	-154	-153	1418	2181
FOP^{l}	70.5	-14.1	97	80	123	2605	3061	1980	3044
Mankwe Dam H/P^{l}	55.9	-9.1	54	45	69	-250	-246	1402	2156
Kololo Camp^{l}	41.8	-10.4	65	54	83	3682	4637	2256	3468
Ruighoek ELC: 35^{u}	15.8	-8.7	51	42	65	9663	18332	4650	7150

5.5.1.3 Variation of F with residence time

Figure 5.32 shows residence times of groundwaters, estimated from equations 5.19 and 5.21 and the ^{14}C data, plotted against F^- concentration. The assumptions and drawbacks of radiocarbon dating and isotope dilution corrections should be remembered when attempting to interpret these graphs.

Notably, the graphs show 'negative' residence times (obviously impossible), resulting from the application of the isotope dilution equation, and have error bars which reflect the likely range of initial radiocarbon values (C_o).

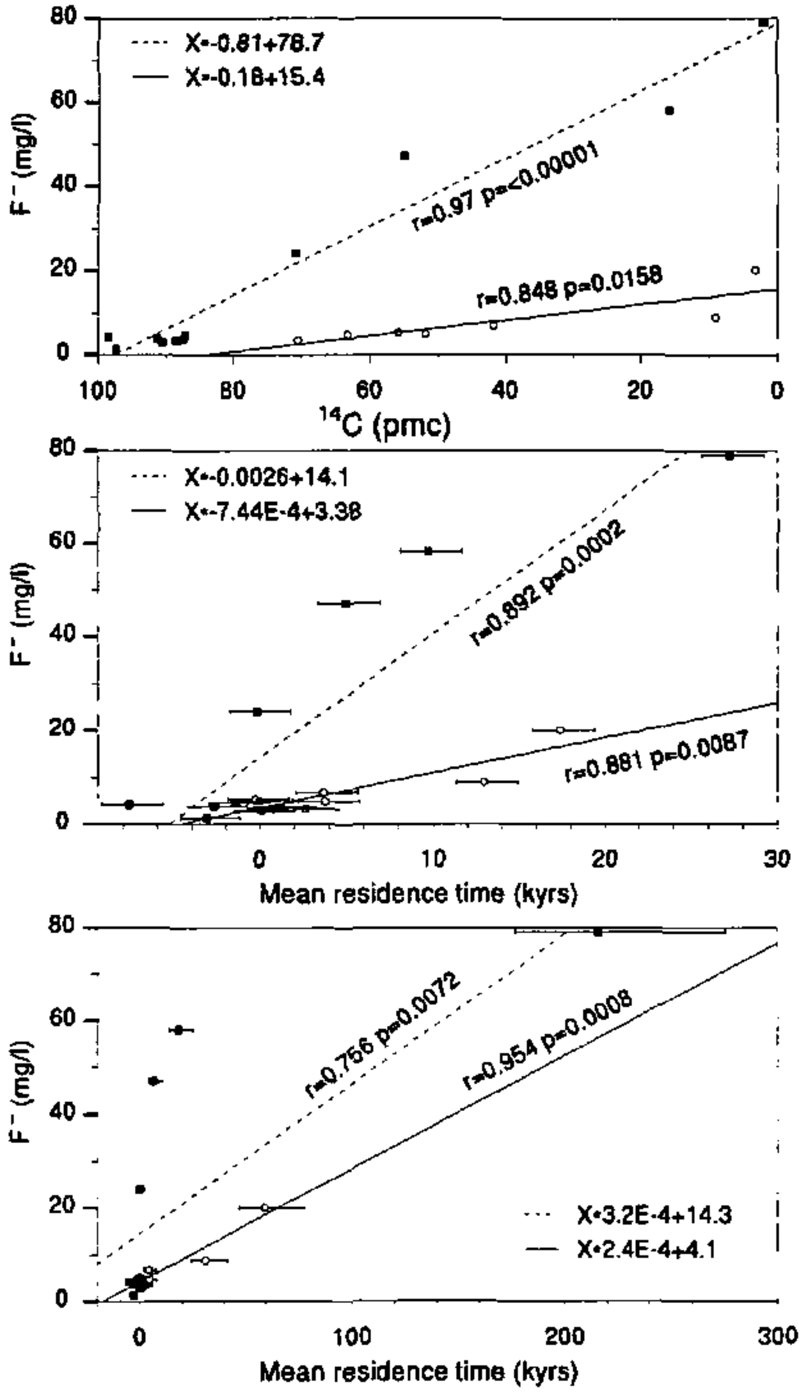


Figure 5.32. Correlation of F$^-$ with ^{14}C and with mean residence time ('age') estimated using the 'Piston Flow' and 'Exponential' equations. '●' is upper trend, '○' is lower trend.

The upper plot in Figure 5.32 clearly shows that two trends are present; a high F^- and a low F^- trend. When ^{14}C activity is used to estimate a mean residence time, it is possible to interpret the two trends as two different rates for reactions which release F^- into solution.

For piston type flow, the equations for the regression lines indicate that the slower reaction releases 7.4×10^{-4} mg/ℓ/yr, whilst the faster reaction releases 2.6×10^{-3} mg/ℓ/yr F^- into solution. The intercept on the y axis of 3.4 mg/ℓ is interpreted as the result of the dissolution of rapidly dissolving, relatively soluble F-bearing minerals. In the context of the long time period under consideration, this may represent the dissolution of fluorite. The *p*K calculated from the intercept of the lower trend is very close to the *p*K of −10.4 calculated for fluorite by Gill (1996), while the *p*K for the upper trend is an order of magnitude higher. When the 'exponential' equation is used to model residence time, the *p*K calculated for both trends is similar to those calculated using 'piston flow' conditions.

5.5.1.4 Variation of other ions with residence time

Several other chemical parameters (Na, pH, Ca and Mg) are correlated with ^{14}C and mean residence time, and bivariate plots of these components are shown in Figures 5.33 and 5.34. It has previously been noted that Na, pH and Ca are involved in reactions which increase F^- above the concentrations expected from the simple stoichiometric dissolution of CaF_2. These reactions are either ion exchange reactions, where Ca in solution is removed by exchange with Na on clay, and the release of F^- from clay surfaces at high pH, or reactions which precipitate $CaCO_3$ or gypsum. The regression equations shown in Figures 5.33 and 5.34 show that Na^+ in these groundwaters increases with residence time ten times faster than Ca^{2+} is removed, suggesting that a simple two-for-one swap of Na^+ for Ca^{2+} on ion-exchanging clays is not the only mechanism for hydrochemical change in these groundwaters. In each case, the reaction or exchange rate calculated using the piston flow model is generally an order of magnitude faster than that calculated from the exponential flow model.

Compared to the dissolution of fluorite, which in this time frame reaches equilibrium quickly, the processes operating here are very slow. Regressions calculated for these parameters are always more significant for the piston flow model than for the exponential flow model. The cation data is generally poorly correlated with residence time.

5.5.2 $^{87}Sr/^{86}Sr$ isotope ratios

The geohydrology of the Bushveld area is not known in any detail (Chapter 1), and the migration of F^- bearing groundwaters from one aquifer to another cannot be ruled out. The likeliest places where this may have occurred are from the Nebo and Lebowa Granites into the low lying Karoo sediments of the Springbok Flats, and from the Pilanesberg into the surrounding Nebo Granite and RLS. This study has attempted to characterise groundwater hosted in different rock types by their Sr isotope ratios, and to use these ratios to study hypothetical groundwater flow and provenance. Unfortunately the number of groundwater $^{87}Sr/^{86}Sr$ samples per rock type is very small, limiting the veracity of the conclusions. The samples were chosen for their geographic isolation from other rock types, so that the resulting Sr isotope values can be treated as a typical signature. Future workers will be able to use these signatures in studies on the provenance of groundwater along flow paths.

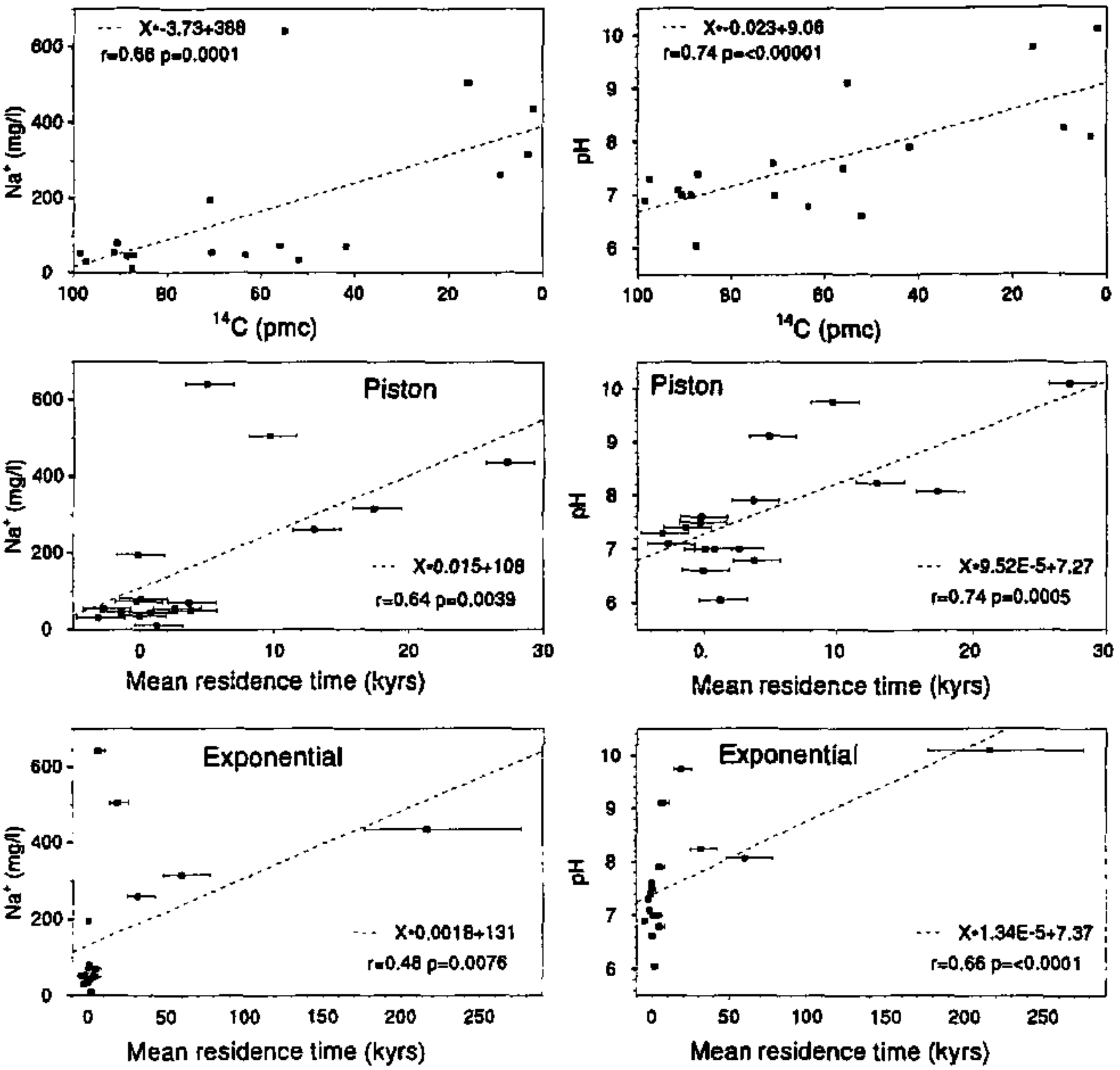


Figure 5.33. Correlation of Na and pH with ^{14}C and with mean residence time, calculated using the 'Piston Flow' and 'Exponential' models.

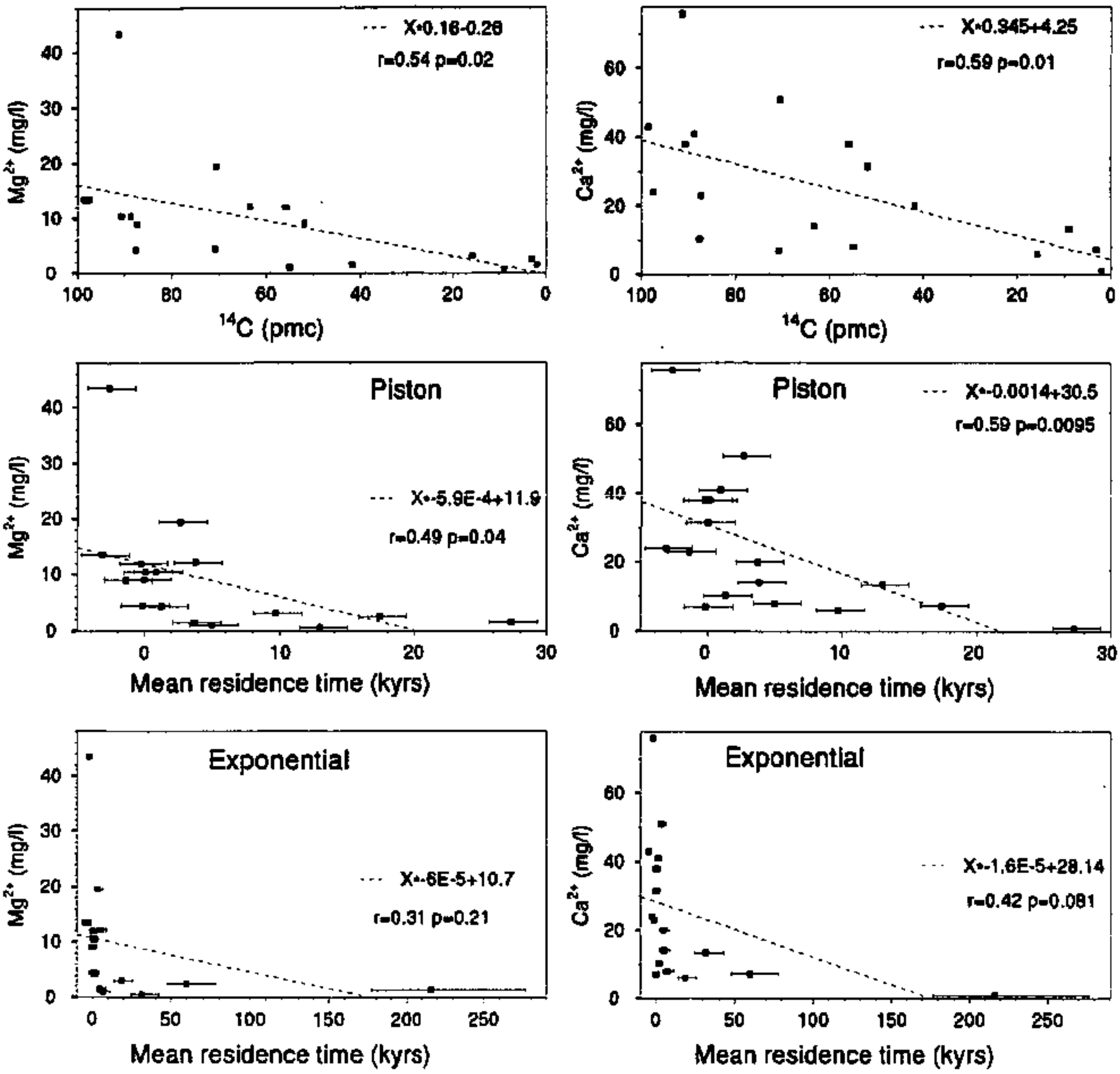


Figure 5.34. Inverse correlation of Ca and Mg with ^{14}C and mean residence time, calculated from 'Piston Flow' and 'Exponential' equations.

Dissolution of Sr-bearing minerals is the main source of Sr in groundwater. Modelling of the dissolution of such minerals can indicate the evolution of Sr isotope ratios over time (e.g. Fritz *et al.*, 1992). These workers indicated that groundwater Sr isotope ratios reach equilibrium with their host rocks within days to months, so that groundwaters (with residence times of centuries to millennia) can be regarded as in equilibrium with the aquifer.

The first influence on groundwater Sr is the Sr content of rain water and this will be briefly discussed.

5.5.2.1 Rainwater Sr

No rainwater $^{87}Sr/^{86}Sr$ ratios are available for the study area and it is therefore not possible to calculate input into the groundwater system from that source. The $^{87}Sr/^{86}Sr$ ratio of modern seawater is 0.70906 (Faure, 1987); rainwater from New Mexico and Scotland had similar ratios, between 0.70917 and 0.71042 (Graustein and Armstrong, 1983; Bacon and Bain, 1995). However, Sr occurs at very low concentrations in rainwater (e.g. Bacon and Bain (1995) found between 2 and 210 Sr µg/ℓ in Scottish rainwater). Because of the very low Sr concentration in rainwater, the $^{87}Sr/^{86}Sr$ ratio of the solution rapidly changes upon dissolution of Sr-bearing minerals in rock and soil, and so the rainwater $^{87}Sr/^{86}Sr$ input into groundwater can effectively be ignored.

5.5.2.2 Mixing of groundwaters with differing $^{87}Sr/^{86}Sr$ and Sr concentrations

The $^{87}Sr/^{86}Sr$ ratio of a mixture of two groundwaters A and B ($^{87}Sr/^{86}Sr_M$) having Sr concentrations Sr_A and Sr_B and Sr isotope ratios of $^{87}Sr/^{86}Sr_A$ and $^{87}Sr/^{86}Sr_B$ is equivalent to (Faure, 1987):

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_M = \frac{Sr_A\,Sr_B\left[\left(\frac{^{87}Sr}{^{86}Sr}\right)_B - \left(\frac{^{87}Sr}{^{86}Sr}\right)_A\right]}{Sr_M\,(Sr_A - Sr_B)} + \frac{Sr_A\left(\frac{^{87}Sr}{^{86}Sr}\right)_A - Sr_B\left(\frac{^{87}Sr}{^{86}Sr}\right)_B}{Sr_A - Sr_B} \tag{5.24}$$

The parameter Sr_M (concentration of Sr in the mixture) is calculated from

$$Sr_M = Sr_A f + Sr_B(1 - f) \tag{5.25}$$

where f is equivalent to

$$f = \frac{V_A}{V_A + V_B} \tag{5.26}$$

The parameters V_A and V_B are the volumes of each groundwater in a given mixture. Figure 5.35 shows the application of these equations to the results presented at the end of Chapter 4, Table 4.4.

It should be stressed that the values for $^{87}Sr/^{86}Sr$ in groundwater from each lithology in Figure 5.35 are probably members of a continuum. Without further sampling and analysis it will not be possible to assert whether the values analysed in the current study are 'end-members' or perhaps more central to that continuum. In Figure 5.35, Pilanesberg groundwater, with high Sr concentration and low $^{87}Sr/^{86}Sr$ ratio, retains a low Sr isotope ratio in mixtures with Nebo Granite groundwaters, because of the relatively low Sr concentration of Nebo Granite groundwater. In contrast, saline groundwater from the perimeter of the Pilanesberg Complex (from a site known as the Quarantine Camp) readily loses its Sr isotope signature when mixed with Nebo Granite groundwater, because of the low Sr concentration in Quarantine Camp groundwater. It is apparent from Figure 5.35a that Quarantine Camp groundwater does not result from the simple mixing of Nebo Granite and Pilanesberg groundwaters. Figure 5.35b shows that, although the Lebowa Granite groundwater has the highest $^{87}Sr/^{86}Sr$ ratios of any groundwater in the study area, the low Sr concentration of this water means that it easily loses its Sr isotope signature when mixed with small quantities of a groundwater with moderate Sr concentration and lower $^{87}Sr/^{86}Sr$ ratio, such as that which occurs in the Irrigasie Formation of the Karoo.

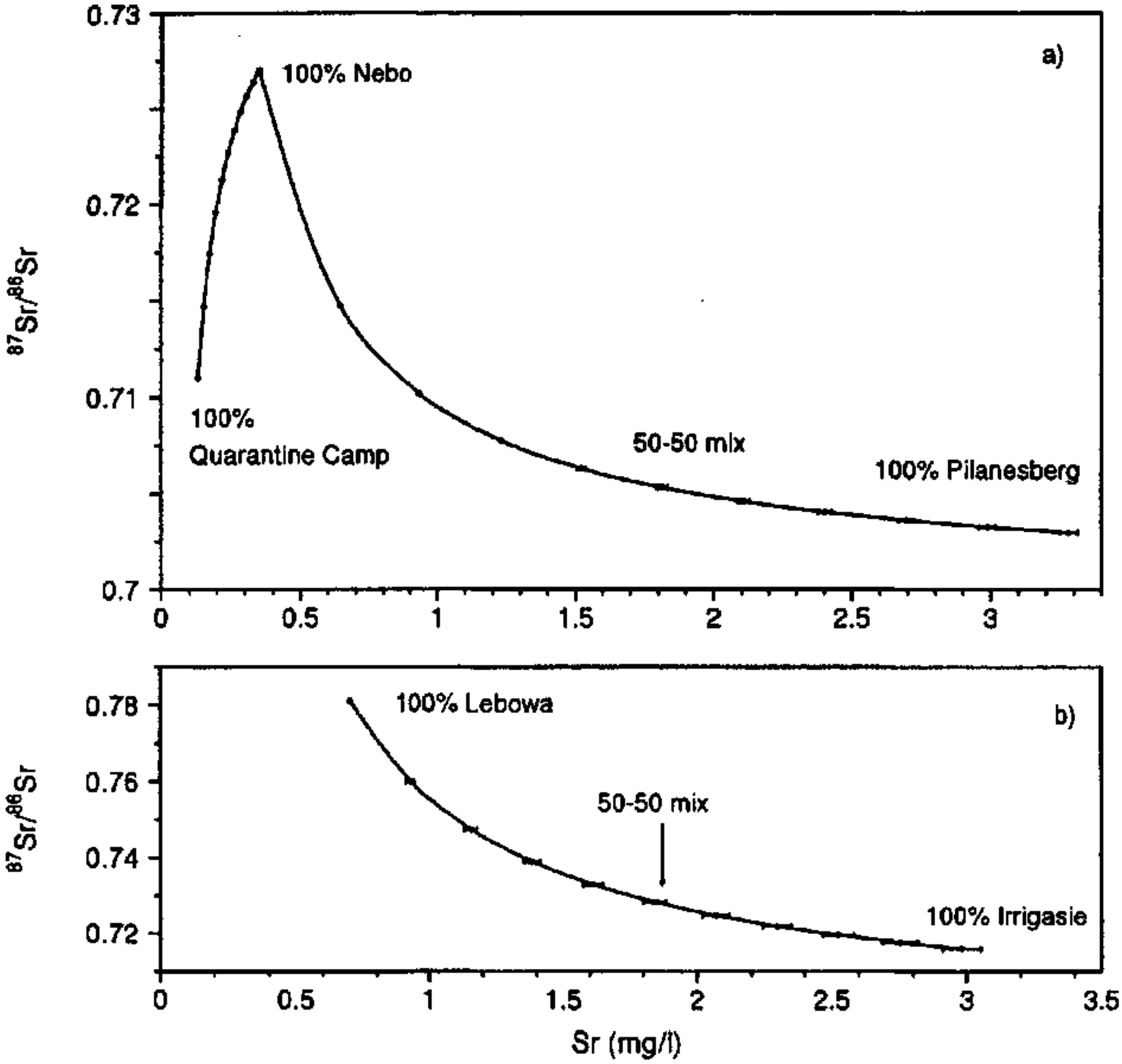


Figure 5.35. $^{87}Sr/^{86}Sr$ ratios in mixtures of various groundwater types. Points represent admixtures of 10 vol% and 90 vol%, 20 vol% and 80 vol%, etc. Error bars are ±1 s.d. Errors smaller than symbols are not shown.

It should be stressed that the values for $^{87}Sr/^{86}Sr$ in groundwater from each lithology in Figure 5.35 are probably members of a continuum. Without further sampling and analysis it will not be possible to assert whether the values analysed in the current study are 'end-members' or perhaps more central to that continuum. In Figure 5.35, Pilanesberg groundwater, with high Sr concentration and low

$^{87}Sr/^{86}Sr$ ratio, retains a low Sr isotope ratio in mixtures with Nebo Granite groundwaters, because of the relatively low Sr concentration of Nebo Granite groundwater. In contrast, saline groundwater from the perimeter of the Pilanesberg Complex (from a site known as the Quarantine Camp) readily loses its Sr isotope signature when mixed with Nebo Granite groundwater, because of the low Sr concentration in Quarantine Camp groundwater. It is apparent from Figure 5.35a that Quarantine Camp groundwater does not result from the simple mixing of Nebo Granite and Pilanesberg groundwaters. Figure 5.35b shows that, although the Lebowa Granite groundwater has the highest $^{87}Sr/^{86}Sr$ ratios of any groundwater in the study area, the low Sr concentration of this water means that it easily loses its Sr isotope signature when mixed with small quantities of a groundwater with moderate Sr concentration and lower $^{87}Sr/^{86}Sr$ ratio, such as that which occurs in the Irrigasie Formation of the Karoo.

The low-lying Karoo basin is surrounded to the north, west and south by elevated outcrops of the Nebo and Lebowa Granites, and it is probable that groundwater moves from these granites into the sediments of the Karoo basin. The groundwater will have equilibrated with the granites and will have the Sr isotope signatures described in the previous sections. Figure 5.36 shows a hypothetical mixing diagram for groundwaters from the Nebo and Lebowa Granites, and from the Irrigasie Formation of the Karoo basin. The diagram is plotted in coordinates of $^{87}Sr/^{86}Sr$ and 1/Sr concentration to give straight mixing lines. The diagram shows that, using just these 3 selected analyses, these groundwaters can be distinguished from each other quite readily using $^{87}Sr/^{86}Sr$ and Sr concentration.

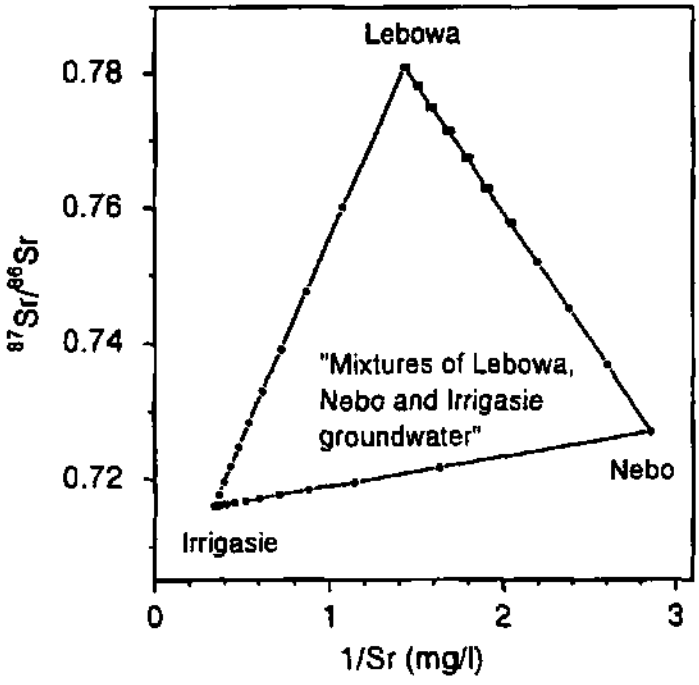


Figure 5.36. Hypothetical mixing diagram for 3 groundwater samples from the Nebo and Lebowa Granites, and from the Irrigasie Formation of the Karoo, based on Sr isotope ratios and Sr concentration.

However, when the full range of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations are plotted, it becomes clear that large ranges of strontium concentration make this method inapplicable (Figure 5.37). The area on this graph where, for instance, Karoo and Lebowa groundwaters mix also includes the two analyses of Nebo Granite groundwater,. producing ambiguous mixing relationships. The same problem occurs for Pilanesberg and Nebo Granite groundwater mixtures, which, when taking into account the 'end-members', encloses the analysis of Rustenburg Layered Suite groundwater. With only two analyses of $^{87}Sr/^{86}Sr$ for groundwater from each rock type, it is very unlikely that the full range of variability has been sampled. With further sampling, the ranges of Sr concentration and isotope value are likely to become larger, making the exercise futile. It is concluded that, even given the small number of samples, Sr isotope and Sr concentration characterisation of groundwater is unlikely to be of use in the Bushveld area.

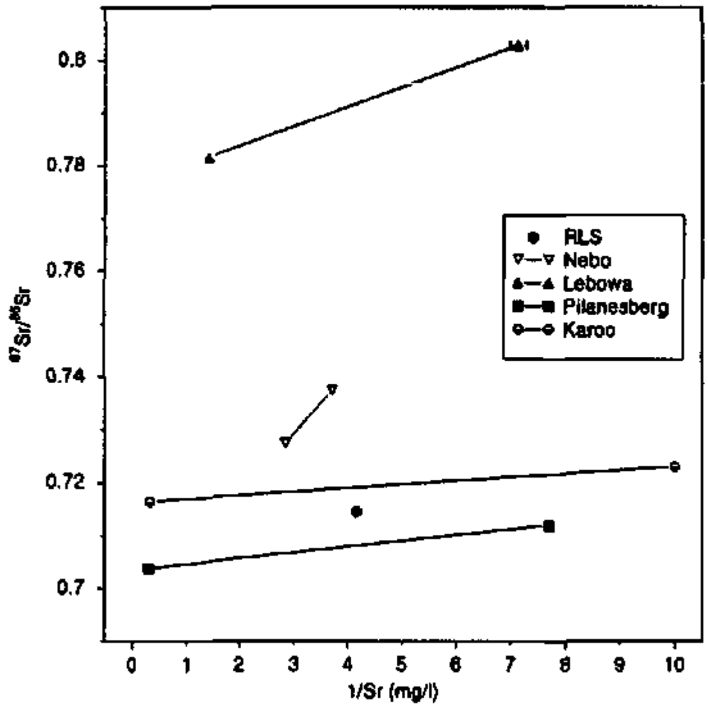


Figure 5.37. The range of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations for groundwater from specific rock types of the area.

6 CONCLUSIONS

6.1 Introduction

This chapter presents a synthesis of the findings of previous chapters. Groundwater data acquisition and data quality is summarised followed by a discussion of the results. The distribution of F in soils, rocks and minerals is linked to the distribution of F^- in groundwater, and other causes of high F^- groundwater are reviewed. An evaluation of the impact on human health of the ubiquity of high F^- groundwater in the Bushveld is reiterated. The main conjectures of this research are then presented. In the next chapter a series of suggestions are made for further research which would answer questions arising from the current body of work.

6.2 Synthesis

This section summarises the findings of previous chapters. The most important conclusions are presented schematically in Figure 6.1.

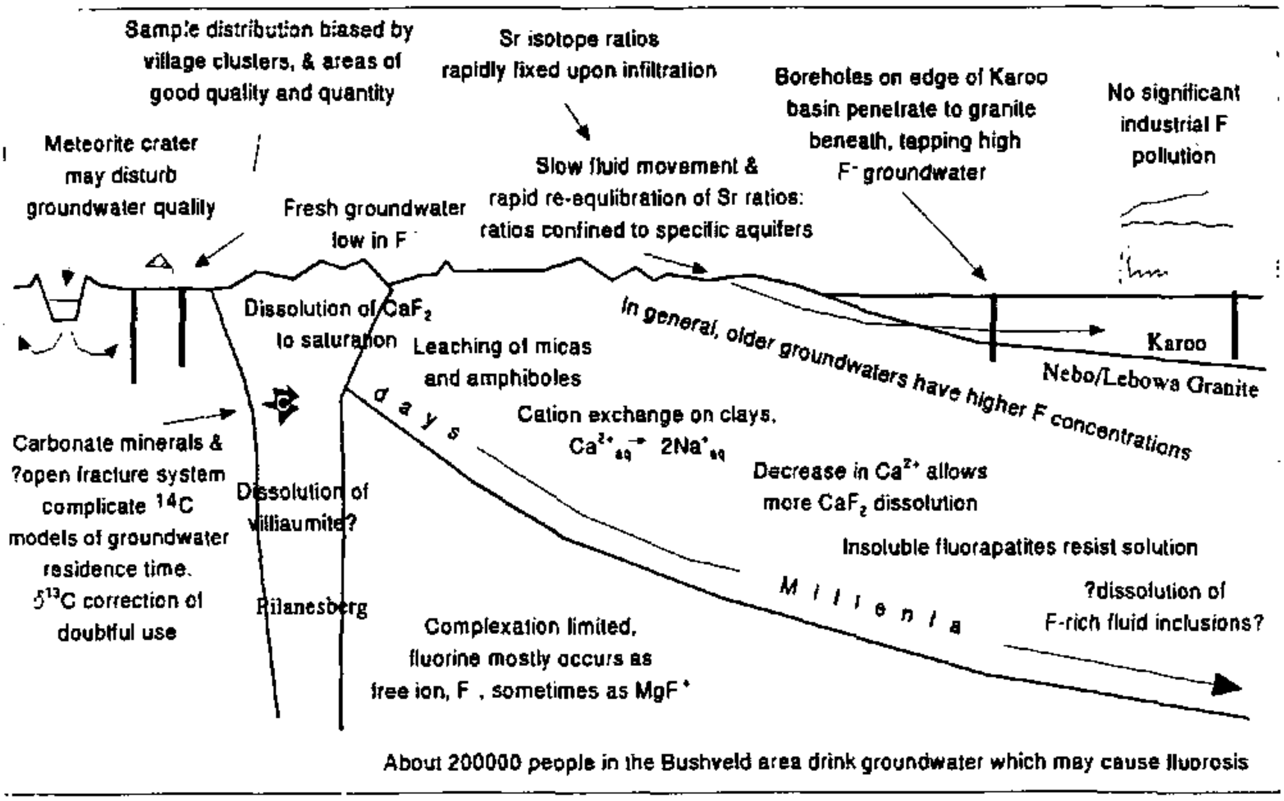


Figure 6.1 A schematic representation of the major conclusions arising from this work.

6.2.1 Groundwater

It was shown that analysis of F$^-$ in groundwater using FISE with a standard buffer solution provided satisfactory analyses of typical Bushveld groundwaters, with no significant interference from Al. However, using a carbonate/bicarbonate eluent with HPIC often over-estimates the concentration of F$^-$ relative to FISE. The presence of a water dip in the carbonate/bicarbonate chromatogram generally complicates the process of determining a baseline for the fluoride peak and is the probable cause of the overestimation, which is removed completely when a sodium tetraborate eluent is used. However, although using sodium tetraborate as an eluent gives an accurate and precise determination of fluoride in solution, the method is slower and other anions cannot be determined in the same run.

Two pre-existing data sets were combined with the data obtained in this work; each had distinct differences in ion balance error. The combined data set is the largest available for F$^-$ in the Bushveld.

Several factors affect the spatial quality of the data, namely humanity, availability and quality of groundwater, and rivers. Firstly, there is a clustering of the data since boreholes are most common in villages. Secondly, a low data density in some areas occurs because of the absence of boreholes, such as in the granite areas to the northeast of the Pilanesberg due to low success rates and low yields. Thirdly, boreholes with 'good' quality water are maintained and more boreholes are drilled in the area. Boreholes with 'poor' quality water tend to be abandoned after drilling, or are equipped but fall into disrepair, and naturally act as a disincentive for further drilling in the area. Finally, few boreholes exist in the vicinity of the perennial rivers, such as the Apies, since water is usually available from the river all year round.

Any data concerning groundwater chemistry collected from rural areas anywhere in the world might be affected in these ways. The current data set is, therefore, highly biased towards clustered boreholes with high yields and good water quality. In this instance, 'good' quality water is measured solely by palatability, as many of the boreholes drilled by local people undergo no other quality test than taste. The results from this study are of the 'best scenario' type.

The median concentration of F$^-$ in groundwater of the western Bushveld is 0.3 mg/ℓ, whilst the mean is 1.43 mg/ℓ; the population is highly skewed towards low concentrations. Fluoride is found at low concentrations in most groundwaters from the RLS (mean of 0.4 mg/ℓ F$^-$). Groundwater F$^-$ concentrations are high in the acid intrusive phases of the BIC. Nebo Granite groundwater has a mean concentration of 2.0 mg/ℓ F$^-$, whilst that from the Lebowa Granite has a higher mean value of 5.0 mg/ℓ with a maximum over 10 mg/ℓ.

The Pilanesberg complex has the highest mean groundwater F$^-$ concentration (15 mg/ℓ). Concentrations around the perimeter of the Complex reach 80 mg/ℓ, although values for the perimeter are generally in the range of 30 to 60 mg/ℓ. Fluoride concentrations of groundwater within the geographic boundaries of the Complex range from 2 to 7 mg/ℓ.

Bushveld groundwaters have concentrations of several trace elements often in excess of South African drinking water guidelines. Of these trace elements, Zn and Al are the likeliest to interact with F$^-$. Zinc occurs in surprisingly high concentrations in these groundwaters, with the highest concentrations in those of the Pilanesberg Complex. At pH 3.0 and 37°C, representative of conditions in the human stomach, all Zn is likely to be in the form Zn^{2+}, which can be readily metabolised. No significant zinc-fluoride complexes are likely to form at the concentrations reported in these groundwaters, and complexation of F^- by Al is of little biological significance in the field area. In most groundwaters, less than 5% of F^- is complexed by Al, Ca or Mg, but Mg is the usual complexing ion. The majority of F exists in the form of the free fluoride ion, F^-.

6.2.2 F in rock, soil and minerals

High F concentrations occur in the Lebowa granite and Pilanesberg Complex, whilst the Nebo granite has scattered high values. The RLS is uniformly low in fluorine and the sedimentary rocks of the area generally have F concentrations well below 1000 ppm. The distribution of F in rock and soil is very similar to the distribution of F^- concentrations in groundwater hosted in the rocks.

Fluorine was determined in paired rock and topsoil samples which showed that fluorine concentrations in soils are generally lower than parental rock fluorine concentrations by up to an order of magnitude. High F concentrations in soil have a similar distribution to high F in rock. Some contamination of soil by tailings has occurred in the vicinity of fluorite mines.

The rocks of the RLS and the Pretoria Group generally contain no major fluoride-bearing minerals. The granophyres, granites and alkaline complexes all contain fluorite (CaF_2) which can have a major effect on groundwater at very low volume percentages. Fluorapatite should occur in the granitic rocks but microscopic examination failed to reveal its presence. Fluorapatites in fluorite ore from the Pilanesberg were shown to have an unusually high Sr concentration, up to 6.8 wt%.

All F concentrations in micas analysed from the Pilanesberg complex and Lebowa Granite were below the detection limit (0.17 wt%), and the micas are presumably hydroxy-micas. Fluorine in amphibole ranged from below the detection limit of 0.17 wt% in Lebowa Granite to 2.69 wt% in the Pilanesberg Complex. Much of the F in the Lebowa Granite is contained in fluorite.

Leaching experiments were conducted on all rock and soil samples. The highest concentrations of F^- in the leachate came from rocks and soils with the highest fluorine concentrations. In the rock leaching experiment, several of the samples had leachate with very high F^- concentrations (>30 mg/ℓ), but concentrations in leachate derived from soil samples was generally below ≈5 mg/ℓ. Soluble F was approximately 1% of the total F in rocks but only 0.1% of the total in soils, indicating that the soils had been effectively leached of soluble F^-.

6.2.3 Origins of high F^- groundwaters

There are three main reasons why fluorite is of prime importance in controlling fluoride solubilities in natural waters: fluorite is the most ubiquitous and abundant fluoride containing mineral; it is sparingly soluble; and Ca is generally always present in natural waters. These three factors also show why fluorapatite is not frequently cited as a controlling factor in fluoride concentration, because fluorapatites are relatively uncommon, they are insoluble and phosphate is found at very low concentrations in natural waters. The possibility that other, more soluble fluorine minerals (such as villiaumite, NaF) are responsible for very high fluoride concentrations (>30 mg/ℓ) is strongly suggested by dissolution experiments on powdered rock samples. Pilanesberg and Lebowa groundwaters are generally saturated to supersaturated with respect to fluorite, while Nebo Granite groundwater is generally less saturated. All groundwaters are undersaturated with respect to NaF.

Speciation and saturation index calculations were undertaken using the thermodynamic modelling package JESS, designed and operated by the CSIR. The package produced very similar results to MINTEQA2, produced by the US EPA, for minerals not containing carbonate. Confidence is expressed in the results of modelling by MINTEQA2.

Other reactions, apart from mineral dissolution, can also affect F^- concentrations. These include: anion exchange of F^- by OH^- on clay surfaces at high pH; precipitation of $CaCO_3$; cation exchange on clays (replacing Ca^{2+} with Na^+), and precipitation of gypsum upon evaporation. The latter three processes remove Ca^{2+} from solution and allow CaF_2 to dissolve further, beyond stoichiometric dissolution. Strong evidence was found for the operation of ion exchange processes in some of the groundwaters.

There is little anthropogenic addition of F to groundwater in the area. Few large working fluorite mines still exist in the Lebowa Granite Suite and Rooiberg felsite, but major fluorite mines are still active in the Malmani Dolomite of the Chuniespoort Group, on the edge of the study area. The impact of dust generated by blasting and processing the ore is likely to be local, and no gaseous emissions are generated. Two other large fluorine-handling industries exist in the study area; a uranium enrichment plant in the south, and a major platinum ore smelter in the centre of the area. Neither of these facilities are likely to add significant F^- concentrations to groundwaters of the region.

Fluoride concentration in rainfall should be near the background concentrations of 8 μg/ℓ, insignificant in terms of fluorosis risk. Infiltrating rainwater is undersaturated with respect to CaF_2, and so recharging groundwater will actively dissolve the mineral. Groundwater should reach equilibrium with fluorite within one month of infiltration.

Some workers have suggested an influence on groundwater compositions from the dissolution of fluid inclusions. Given the retrograde solubility of CaF_2 above 100°C, it is predicted that medium to high temperature fluid inclusions are not likely to contain more than about 5 mg/ℓ F^- and the contribution from weathering fluid inclusions is expected to be negligible.

The Pilanesberg perimeter groundwaters and those of the Nebo Granite have very different δ^2H and $\delta^{18}O$ values, and it should be possible to identify the Pilanesberg perimeter groundwater type, if encountered in boreholes in the RLS or Nebo Granite near the Pilanesberg, based on its 'light' isotopic signature. Nebo granite groundwaters are tightly grouped isotopically, and deviations are considered significant. Central Pilanesberg groundwater has a much larger spread and shows evidence of being subjected to evaporation. The Pretoria Saltpan brine is isotopically much heavier than the precipitation falling in the area and has been subject to large amounts of evaporation. One groundwater sampled in the vicinity has a significantly heavier isotopic signature than other Nebo Granite waters, and lies on a mixing line between Saltpan brine and Nebo Granite groundwater. This is taken as evidence that the Saltpan brines are somehow leaving the crater environs and mixing with local groundwater.

Radiocarbon (^{14}C) activity was used to estimate mean residence times for groundwaters, after correction for variation in initial activities using an isotope dilution correction method. It is possible to interpret the associated groundwater composition data as evidence for different rates for various water-mineral reactions. These reactions appear to increase F^- concentrations in groundwater at two different reaction rates. If piston type flow is assumed, the slowest reaction releases 7.4×10^{-4} mg/ℓ/yr F^-, whilst the faster reaction liberates 2.6×10^{-3} mg/ℓ/yr F^- into solution. An implied solubility of at least 3.4 mg/ℓ is interpreted as the dissolution of a rapidly dissolving, relatively soluble F-bearing mineral. In the context of the long time period under consideration, this probably represents the dissolution of fluorite. Two values of *p*K may be calculated from the data, one of which is very close to the *p*K of ~10.4 calculated for fluorite by other workers.

The large range in Sr isotope ratios and Sr concentrations found in the few samples analysed suggests that natural variability will complicate further use of Sr in tracing groundwater provenance in the Bushveld area. Based on the current Sr isotope data, groundwater from the Quarantine Camp, on the perimeter of the Pilanesberg, with a F^- concentration of 80 mg/ℓ, does not result from a mixture of 'typical' Nebo Granite and Pilanesberg Complex groundwaters.

6.2.4 The possible extent of fluorosis

The optimal F^- concentration in drinking water for several of the towns within the field area was estimated using an equation which related the optimal F^- concentration to the maximum mean temperature. The variation in the value between towns is only 0.07 mg/ℓ, and the mean optimum concentration of 0.65 mg/ℓ F^- is almost identical to the maximum safe concentration of 0.7 mg/ℓ calculated by Du Plessis (1995) for the Free State goldfields.

Spatial analysis by GIS shows that groundwater underlying 17000 km^2 of the western Bushveld has a F^- concentration >0.7 mg/ℓ, the optimum fluoride concentration in drinking water for the area. Over 540 of the 3000 groundwater samples have a F^- concentration >0.7 mg/ℓ. Since between 150 and 200 people are supplied by each borehole, between 82 000 and 109 000 people are drinking groundwater which may induce fluorosis in the long term.

Using a Thiessen polygon method, three hundred areas have been delineated where there is a medium or higher risk of dental fluorosis. The resulting 'fluorosis risk map' will be of use to water supply planners.

6.3 General

The project was brought to a successful conclusion and extended over a very large area of approximately 150,000 km^2.

All the aims of the project have been successfully addressed, namely:

(i) a comprehensive database of the concentrations of F^- and other common anions and cations, together with data on pH, temperature, EC and alkalinity, has been produced for a further 323 groundwater sites over the study area. In addition F^- concentrations over the extended area have been collated and evaluated.

(ii) The source and mobility of F^- in the hydro-geochemical environment of the study area was established, and also the spatial relations between F^--enriched groundwaters and fluoride sources in rocks, mineralised areas and soils.

(iii) Existing epidemiological information on the health related F^- effects have been reviewed and compiled in a F^- concentration *vs.* effect plot.

(iv) The results have been successfully utilised to provide maps of areas of zero, low, medium, high and very high fluorosis risk. These should be of use to engineers and planners concerned with the supply of drinking water to the rural population in the study area, and hopefully will result in considerable cost-savings in the future supply of water in the study area. The results should bring about, over the next generation, a marked improvement in the dental and skeletal health of the local populace.

By implementing a very wide variety of analytical techniques to gain information on physical and geochemical characteristics of both groundwaters and their host rocks, by interpreting the results of chemical and isotopic analyses, and by the use of theoretical modelling calculations of element speciation, the project has both created and successfully integrated a huge database of knowledge of the study area. It is believed that the work has contributed significantly to the knowledge of fluoride in South African groundwaters, and that the results will be of use in studying groundwaters in other parts of the country.

7 RECOMMENDATIONS

7.1 Recommendations for further work

7.1.1 Groundwater studies

Spatial gaps still exist in the data base, especially in the areas underlain by Archaean Granite. Further groundwater sampling in these areas could be undertaken to improve data density. However, the cost-benefit relationship of further sampling would have to be carefully considered. Silica was not determined in this study, and the absence of silica data meant that saturation indices for silicate minerals could not be calculated. The analysis of a sub-set of samples for silica would improve understanding of mineral-water interaction in the area. The extension of the study to include the rest of the South African groundwater database, which holds ≈45 000 groundwater analyses, would enable further high F^- areas to be delineated. The translation from the Chinese of the potentially important text by Fuhong *et al.* (1996) should be undertaken by a specialist.

7.1.2 Analysis of rock, soil and minerals

The lack of analyses for F in rocks from the field area is apparent, and the fact that the Regional Geochemical Mapping Programme (RGMP) of the Council for Geoscience does not include the analysis of F is regrettable. The analysis of F in just 1% of the thousands of soil samples taken by the RGMP, which coincidentally covers most of the high groundwater fluoride areas shown in Figure 5.2, would provide a very valuable data set.

The Moepo Fluorite mine in the Pilanesberg has been shown to contain an unusual assemblage of minerals and rare mineral types (high-Sr calcite and high Sr-apatite) which have not been reported previously in South Africa. Additional mineralogical and geochemical investigation may produce further interesting results.

The characterisation of clays and/or zeolites lining fractures in Bushveld Igneous Complex and Pilanesberg Complex rocks would help to define possible cation exchange processes taking place in the groundwater regime. The use of XRD to identify the clays and the determination of cation exchange capacities would be of use in delimiting ion exchange processes in the area.

An investigation into the presence of NaF in rocks of the Pilanesberg Complex and Lebowa Granite would test the theory that groundwater F^- concentrations have been influenced by dissolution of this mineral.

7.1.3 Groundwater isotopes

The geohydrology of the hard rock aquifers of the western Bushveld has been comparatively poorly researched. The area is, therefore, a prime target for the large scale application of isotope hydrology. The wide range of radiocarbon activities in the Pilanesberg and Lebowa Granite Suite is still a conundrum, and the accurate estimation of groundwater residence time requires more accurate knowledge of the local geohydrology. Given the relative cheapness of oxygen and hydrogen isotope analyses, these parameters should be measured on the whole sample set to show regional trends, and possibly recharge/discharge areas. The uncertainty in recharge areas and groundwater movement in the study area might be solved by the analysis of such stable isotope data. Sr isotope analyses of a greater number of samples from groundwaters from the western Bushveld would help to show the range of natural variation in this parameter.

7.1.4 Geohydrology of the western Bushveld

The lack of water level and borehole depth data has been one of the major limitations of this study. An analysis of all available water-table elevation data should delineate flow directions. The glimpse of the hydrological systems existing around a recent meteorite crater should be followed up with a total hydro-census of the area, intensive sampling for major and trace elements, and stable isotopes, and computer modelling of the results.

7.1.5 General

It is clear from this study that there is a very high probability of groundwaters from the Pilanesberg Complex and the Lebowa Granite having a F^- concentration above the maximum safe limit for human consumption (3 mg/ℓ F^-. **It is recommended that any further installation of boreholes by the Department of Water Affairs and Forestry in these areas should be accompanied by suitable defluoridation procedures.**

Since the start of this study the Pilanesberg area has been the subject of water quality remediation measures, in the form of the Saulspoort pipeline scheme. The population in this area now have access to good quality water supplied from the Vaalkop Dam. The population resident on the outcrop areas of the Lebowa Granite have had no such attention. **It is strongly recommended that a district-wide alternative water supply scheme be instituted for the Lebowa Granite area.**

The Nebo Granite and parts of the Karoo sub-basin have scattered high fluoride concentrations. A district-wide alternative water supply scheme in these areas is not required, since good quality boreholes do exist in the area. **It is recommended that poor quality boreholes are either closed down or have borehole-scale defluoridation measures implemented on them.** Good quality boreholes have been identified and it is recommended that these boreholes be **publicly identified**, *e.g.* by being painted green, and developed as a primary source of human drinking water.

Understanding and awareness of the risk of fluorosis from the ingestion of high fluoride groundwater is limited to a few specialists. The general population of the field area is almost entirely unaware of these problems, although the job-seeking population in the Pilanesberg area are rapidly coming to realise that a smile spoilt by dental fluorosis can severely limit a person's job opportunities.

It is recommended that a 'technology transfer' programme be initiated. This should could take the form of health education comics, talks, community meetings and so on. It is recommended that suitably qualified members of the local population be trained to do this in a manner acceptable to the local populace. At these meetings it should be explained exactly what the problem is, how it can be overcome, and what the local government is planning to do to solve the problem.

Where necessary and cost-effective, *e.g.* in areas of isolated boreholes, house-based defluoridation should be implemented, possibly through the utilisation of the 'clay pot' method, as developed in Scandinavia, or through more technologically advanced methods. **House-based defluoridation should be encouraged, possibly through Province-sponsored training sessions and the development of local clay resources.** This would provide much-needed job opportunities in rural areas. More research into the occurrence and suitability of local clay resources is needed.

It was apparent from the small variations in F^- over a time scale of two years that there is likely to be very little change in F^- with time. However, it became clear from discussions with local village chiefs and headmen that the groundwater from many boreholes had never bee analysed since the boreholes were first installed. Even then the results had never been communicated to the local populace. It would seem prudent to put in place a plan to monitor the F^- content of boreholes every five to ten years. It would be even better if a simple, rapid and cheap test, similar to a litmus paper test for pH, could be developed for the determination of F^- in groundwater. Suitable kits could be distributed to local authorities who could arrange for testing on a regular basis. When water quality was adequate, this would generate confidence in the local populace in the suitability of their drinking water. When the quality was unacceptable the regular testing would provide an early warning system, allowing timely remedial steps to be taken.

Water quality in the Lebowa Granite area has been shown to be of poor quality and to have levels of molybdenum above the high risk limit for human consumption. **It is recommended that further sampling and study of this area be undertaken.**

Finally, it is recommended that this report be brought to the attention of all governmental, provincial and local authorities, and also to all non-governmental organisations, operative in the area.

8 REFERENCES

Acker, JG and Bricker OP (1992) The influence of pH on biotite dissolution and alteration kinetics at low temperature. *Geochim. Cosmochim. Acta*, **56**, 3073-3092.

Ahrens, LH (1952) The use of ionization potentials, Part 1: Ionic radii of the elements. *Geochim. Cosmochim. Acta*, **2**, 155-169.

Al-Aasm, IS, Taylor, BE and South, B (1990) Stable isotope analysis of multiple carbonate samples using selective acid extraction. *Chemical Geology*, **80**, 119-125.

Allison, JD, Brown, DS and Novo-Gradac, KJ (1991) *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems, version 3.0 users manual.* US Environmental Protection Agency, Athens, Georgia. 106pp.

Allman, R and Koritnig, S (1974) *Fluorine. In:* Wedepohl, KH (ed.) *Handbook of Geochemistry, Vol. II/1.* Springer-Verlag, Berlin.

Anderson, C (1991) Fluoride given the all clear. *Nature*, **349**, 732.

APHA [American Public Health Association] (1995) *Standard methods for the examination of water and wastewater, 19th edition.* American Public Health Association, American Water Works Association and Water Environment Federation, Washington D.C.

Arnold, FA, Dean, HT and Knutson, JW (1953) Effect of fluoridated public water supplies on dental caries prevalence: results of the seventh year of study at Grand Rapids and Muskegon, Michigan. *Public Health Report*, **68**, 141-148.

Ashley, RP and Burley, MJ (1994) Controls on the occurrence of fluoride in groundwater in the Rift Valley of Ethiopia. 45-54 *In:* Nash, H and McCall, GJH (*eds.*) *Groundwater Quality 17th Special Report.* Chapman and Hall, London. 204pp.

Ashton, PJ and Schoeman, FR (1983) Limnological studies on the Pretoria Salt Pan, a hypersaline maar lake. *Hydrobiologia*, 99, 61-73.

Auméras, M (1927) Etude de l'equilibre fluorure de calciu-acide chlorhydrique etendu - contribution a l'étude des équilibres ioniques. *J. Chim. Phys.*, **24**, 548-571.

Babushkin, VI, Matveyev, GM and Mchedlov-Petrossyan, OP (1985) *Thermodynamics of silicates.* Springer Verlag, Berlin. 459pp.

Backer Dirks, O (1992) Biokinetics of fluoride in relation to dental and skeletal fluorosis. *In:* Frencken, JE (*ed.*) *Endemic fluorosis in developing countries.* Report of a symposium held in Delft, the Netherlands, April 27th, 1990, 20-30.

Bacon, JR and Bain, DC (1995) Characterization of environmental water samples using strontium and lead stable isotope compositions. *Environmental Geochemistry and Health*, **17**, 39-49.

Bailey, JC (1977) Fluorine in granitic rocks and melts: a review. *Chem. Geol.*, **19**, 1-42.

Banner, JL, Musgrove, M and Capo, RC (1994) Tracing ground-water evolution in a limestone aquifer using Sr isotopes: effects of multiple sources of dissolved ions and mineral-solution reactions. *Geology*, **22**, 687-690.

Barker, DS (1989) Field relations of carbonatites. *In:* Bell, K (*ed.*) *Carbonatites: Genesis and Evolution*. Unwin Hyman, 38-69.

Barker, DS (1993) Diagnostic magmatic features in carbonatites: implications for the origins of dolomite- and ankerite-rich carbonatites. *S Afr. J. Geol.*, **96**, 131-138.

Barnard, WR and Nordstrom, DK (1982a) Fluoride in precipitation - 1. Methodology with the fluoride-selective electrode. *Atmospheric Environment*, **16**, 99-103.

Barnard, WR and Nordstrom, DK (1982b) Flouride [*sic*] in precipitation - 2. Implications for the geochemical cycling of fluorine. *Atmospheric Environment*, **16**, 105-111.

BDWA, [Bophuthatswana Department of Water Affairs] (1992) *Moretele Water Plan*. Unpubl. Report.

Birch, GF (1981). The Karbonat-Bombe: a precise, rapid and cheap instrument for determining calcium carbonate in sediments and rocks. *S Afr. J. Geol.*, **84**, 199-203.

Blavoux, B and Letolle, R (1995) Apports des techniques isotopiques a la connaissance des eaux souterraines. *Géochronique*, **54**, 12-15.

Blum, JD, Erel, Y and Brown, K (1994) $^{87}Sr/^{86}Sr$ ratios of Sierra Nevada stream waters: Implication for relative mineral weathering rates. *Geochim. Cosmochim. Acta.*, **58**, 5019-5025.

Bond, GW (1947) A Geochemical Survey of the Underground Water Supplies of the Union of South Africa. *Department of Mines, Geological Survey Memoir*, **41**. 203pp.

Botchway, CA, Ansa-Asare, OD and Antwi, LA (1996) Natural fluoride and trace metal levels of ground and surface waters in the greater Accra region of Ghana. *West Afr. J. Med.*, **15**, 204-209.

Botha, CJ, Naude, TW, Minnaar, PP, Van Amstel, SR and Janse van Rensburg, SD. (1993) Two outbreaks of fluorosis in cattle and sheep. *J.S.Afr. Vet. Assoc.*, **64**, 165-168.

Boudreau, AE, Mathez, EA and McCallum, IS (1986) Halogen geochemistry of the Stillwater and Bushveld Complexes: evidence for transport of the platinum-group elements by Cl-rich fluids. *J. Petrology*, **27**, 967-986.

Bowen, HJM (1966) *Trace elements in biochemistry*. Academic Press, London.

Boyle, DR (1976) *The geochemistry of fluorine and its applications in mineral exploration.* PhD Thesis, Imperial College, University of London. 386pp.

Boyle, DR (1992) Effects of base exchange softening on fluoride uptake in groundwaters of the Moncton Sub-Basin, New Brunswick, Canada. *In:* Kharaka, YK and Maest, AS (*eds.*) *Symposium on Water-Rock interaction*, Volume 1. Balkema, Rotterdam. 771-774.

Boyle, DR and Chagnon, M (1995) An incidence of skeletal fluorosis associated with groundwaters of the maritime carboniferous basin, Gaspé region, Quebec, Canada. *Environmental Geochemistry and Health;* 17, 5-12.

Brandt, D and Reimold, WU (1995) The geology of the Pretoria Saltpan impact structure and the surrounding area. *S Afr. J. Geol.*, **98**, 287-303.

Brantley, SL and Chen, Y (1995) Chemical weathering rates of pyroxenes and amphiboles. *In:* White, AF and Brantley, SL (*eds.*) Chemical weathering rates in silicate minerals. *Reviews in Mineralogy*, **31**, 119-172.

Broecker, WS (1995) Cooling the tropics. *Nature*, **376**, 212-213.

Brouwer, ID, Backer Dirks, O, De Bruin, A and Hautvast, JGAJ (1988) Unsuitability of World Health Organisation guidelines for fluoride concentrations in drinking water in Senegal. *The Lancet*, 1 **(8579)**, 223-225.

Brown, DW, and Roberson, CE (1977) Solubility of natural fluorite at 25°C *J. Res. US Geol. Surv.*, **5**, 509-518.

Cameron, EN (1980) Evolution of the lower Critical Zone, central sector, eastern Bushveld Complex, and its chromite deposits. *Econ. Geol.*, **75**, 845-871.

Campbell, AD (1987) Determination of fluoride in various matrices. *Pure and Appl. Chem.*, **59(5)**, 695-702.

Campbell, IH, Naldrett, AJ and Barnes, SJ (1983) A model for the origin of the platinum-rich sulfide horizons in the Bushveld and Stillwater complexes. *J. Pet.*, **24**, 133-165.

Cao, J, Bai, X, Zhao, Y, Liu, J, Zhou, D, Fang, S, Jia, M and Wu, J (1996) The relationship of fluorosis and brick tea drinking in Chinese Tibetans. *Environ. Health Perspect.*, **104**, 1340-1343.

Carpenter, R (1969) Factors controlling the marine geochemistry of fluorine. *Geochim. Cosmochim. Acta*, **33**, 1153-1167.

Carstens, IL, Louw, AJ and Kruger, E. (1995) Dental status of rural school children in a sub-optimal fluoride area. *J. Dent. Assoc. S. Afr.*, **50**, 405-411.

Cawthorn, RG (1988) *The Geology of the Pilanesberg*. National Parks Board of Bophuthatswana, Mafikeng. 24pp.

Cederstrom, DJ (1946) Genesis of groundwaters in the coastal plain of Virginia. *Economic Geology*, **41**, 218-245.

Charter, RH (1928) Solubilities of some inorganic fluorides in water at 25°C. *Ind. Engng. Chem.*, **20**, 1195. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2). *Neues Jahr. Miner.*, **3**, 83-95.

Chaumba, JB (*in prep.*) *A stable isotope study of the northern limb of the Bushveld Complex.* Unpubl. PhD thesis, University of Cape Town.

Collerson, KD, Ullman, WJ and Torgersen, T (1988) Ground waters with unradiogenic $^{87}Sr/^{86}Sr$ ratios in the Great Artesian Basin, Australia. *Geology*, **16**, 59-63.

Coplen, TB (1995) Discontinuance of SMOW and PDB. *Nature*, **375**, 285.

Corbett, RG and Manner, BM (1984) Fluoride in the ground water of northeastern Ohio. *Ground Water*, **22**, 13-17.

Correns, CW (1956) Geochemistry of the Halogens. *Phys. Chem. Earth*, **1**, 181-233.

Craig, H (1961) Isotopic variations in meteoric waters. *Science*, **133**, 1702-1703.

Crocker, IT and Martini, JEJ (1976) Fluorspar. *In:* Coetzee, CB (*ed.*) *Mineral resources of the Republic of South Africa.* The Government printer, Pretoria, 357-363.

CSIR [Centre for Scientific and Industrial Research] (1991) *Recommendations to the Department of Water Affairs, Bophuthatswana on criteria for drinking water quality.* Internal report **10/8/4/3/32508**, CSIR, Pretoria, 9pp.

Dansgaard, W (1964) Stable isotopes in precipitation. *Tellus*, **16**, 436-468.

Datta, PS, Deb, DL and Tyagi, SK (1996) Stable isotope (^{18}O) investigations on the processes controlling fluoride contamintaion of groundwater. *J. Contaminant Hydrol.*, **24**, 85-96.

Davies, RD, Allsop, HL, Erlank, AJ and Manton, WI (1970) Sr-isotopic studies on various layered mafic intrusions in Southern Africa. *Geol. Soc. S Afr., Special publication*, **1**, 576-593.

Davies, TC (1994) Water quality characteristics associated with fluorite mining in the Kerio Valley area of western Kenya. *Int. J. Env. Health Res.*, **4**, 165-175.

Dawson, JB and Fuge, R (1980) Halogen content of some African primary carbonatites. *Lithos*, **13**, 139-143.

Day, TK and Powell-Jackson, PR (1972) Fluoride, water hardness, and endemic goitre. *The Lancet*. **1 (7763)**, 1135-1138.

Dean. HT, Arnold FA and Elvove, E (1942) Domestic water and dental caries. V. Additional studies of the relation of fluoride domestic waters to dental caries experience in 4,425 white children aged 12-14 years, of 13 cities in 4 states. *Public Health Reports*, **57**, 1115-1179.

Dean, HT (1954) Fluorine in the control of dental caries: some aspects of the epidemiology of the fluorine-dental caries relationship. *Int. Dent. J*, **4**, 311-326.

Deer, WA, Howie, RA and Zussman, J (1977). *An introduction to the rock forming minerals.* Longman, London. 528pp.

Dia, AN, Castrec, M, Boulègue, J, and Boudou, JP (1995) Major and trace element and Sr isotope constraints on fluid circulations in the Barbados accretionary complex. Part 1: Fluid origin. *Earth and Planetary Science Letters*, **134**, 69-85.

Dissanayake, CB (1996) Water quality and dental health in the Dry Zone of Sri Lanka. *In:* Appleton, JD, Fuge, R and McCall, GJH (*eds.*) Environmental geochemistry and health. *Geol. Soc. Spec. Publ.*, **113**, 131-140.

DMEA, [Department of Mineral and Energy Affairs, Eskom Marketing Intelligence] (1995) *South African energy statistics 1950-1993, no. 2.* Department of Mineral and Energy Affairs, Pretoria. 101pp.

Dodd, NF, Levy, DW, Jackson, WPU and Traut, ML (1960) Environmental bone disease hitherto undescribed type. *S.A. Med. J*, 606-611.

Driscoll, WS, Heifetz, SB, Horowitz, HS, Kingman, A, Meyers, RJ and Zimmerman, ER (1983) Prevalence of dental caries and dental fluorosis in areas with optimal and above-optimal water fluoride concentrations. *J. Am. Dental Assoc.*, **107**, 42-47.

Duncan, AR, Erlank, AJ and Betton, PJ (1984) Appendix 1: Analytical techniques and database descriptions. 389-395. *In:* Erlank, AJ (*ed.*) *Petrogenesis of the volcanic rocks of the Karoo Province.* Geol. Soc. S Afr., Spec. Publ., **13**, 395pp.

Du Plessis, JB (1995) What would be the maximum concentration of fluoride in water that will not cause dental fluorosis. p4. *In:* McCaffrey, LP (*ed.*) *Fluoride and fluorosis: the status of South African research.* Abstract volume of a Workshop held on 10th August 1995 in the Pilanesberg National Park, South Africa. 11pp.

Du Plessis JB, van Rooyen JJ, Naude DA and van der Merwe CA (1995) Water fluoridation in South Africa: will it be effective? *J. Dent. Assoc. S. Afr.*, **50**, 545-549.

DWAF, [Department of Water Affairs and Forestry] (1996) *Draft of South African Water Quality Guidelines, Volume 1: Domestic Use (second edition).* The Government Printer, Pretoria. 37pp.

Eales, HV, Botha, WJ, Hattingh, PJ, de Klerk, WJ, Maier, WD and Odgers, ATR (1993) The mafic rocks of the Bushveld Complex: a review of emplacement and crystallization history, and mineralization, in the light of recent data. *J. Afr. Earth Sci.*, **16**, 121-142.

Edgar, AD (1989) Barium- and strontium-enriched apatites in lamproites from West Kimberley, Western Austrlia. *Am. Miner.*, **74**, 889-895.

Ehhalt, D (1967) Deuterium and tritium content of hailstones: additional information their growth. *Trans. Am. Geophys Union.*

Elfimov, AS, Kravchenko, SM and Vasih'eva, ZV (1962) Strontium apatite: a new mineral.

Akademiya Nauk SSSR Doklady, **142**, 439-442.

Ellis, AJ and Mahon, WAJ (1977) *Chemistry and Geothermal Systems.* Academic Press, New York. 375pp.

Elrashidi, MA and Lindsay, WL (1986) Chemical equilibria of fluorine in soils: a theoretical development. *Soil Science*, **141**, 274-280.

Eriksson, PG, Hattingh, PJ and Altermann, W (1995) An overview of the geology of the Transvaal Sequence and Bushveld Complex, South Africa. *Mineralium Deposita*, **30**, 98-111.

Fanning, DS and Keramidas, VZ (1977) Micas. *In:* Dixon, JB and Weed, SB (*eds.*) *Minerals in Soil Environments.* Soil Science Society of America, Wisconsin. 195-258.

Faure, G (1987). *Principles of isotope geology.* John Wiley and sons, New York. 589pp.

Fayazi, M (1995) Distribution of fluoride in groundwater of the northern Springblok Flats. p1. *In:* McCaffrey, LP (*ed.*) *Fluoride and fluorosis: the status of South African research.* Abstract volume of a Workshop held on 10th August 1995 in the Pilanesberg National Park, South Africa. 11pp.

Fejerskov, O, Manji, F, Baelum, V and Moller, IJ (1988) *Dental fluorosis - a handbook for health workers.* Munksgaard, Copenhage. 123pp.

Felsenfeld, AJ and Roberts, MA (1991) A report of fluorosis in the United States secondary to drinking well water. *J. Am. Med. Assoc.*, **265**, 486-488.

Ferguson, J (1973). The Pilanesberg Alkaline Igneous Complex. *S Afr. J. Geol.*, **76**, 249-270.

Feuchtwanger, T (1973) *Zoutpan: carbonatite-alkaline volcano.* Unpubl. Honours Thesis, Uni. Witwatersrand, 41pp.

Filippov, LV, Savimova, YN, Kapitonova, TA and Andreyeva, TP (1974) Fluorine in Mg-Fe micas from granitoids of various magmatic formations in the folded belt of Central Asia. *Geochem Int.*, **11**, 185-194.

Fluhler, H, Polomski, J and Balser, P (1982) Retention and movement of fluoride in soils. *J. Environ. Qual.*, 11, 461-468.

Foss, PJ and Pittman, JM (1986) Efficacy of fluoride on dental caries reduction by means of a community water supply. *J. Dent. Child.*, **53**, 219-222.

Foster, MD (1950) The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plains. *Geochim. Cosmo. Acta*, **1**, 32-48.

Fourie, N, Basson, AT, Basson, KM, Ferreira, GC, van der Berg, H, Smith, JC and Labuschagne, L (1996) Poisoning of wildlife in South Africa. *J. S. Afr. Vet. Assoc.* **50**, 467-471.

Franke, J, Runge, H and Fengler, F (1978) Endemic and industrial fluorosis *In:* Courvoisier, B, Donath, A and Baud, CA (*eds.*) *Fluoride and Bone*. Hans Huber, Bern. 129-143.

Frant, MS and Ross, JW (1966) Electrode for sensing fluoride ion activity in solution. *Science*, **154**, 1553-1554.

Freeze, RA and Cherry, JA (1979) *Groundwater*. Prentice-Hall, New Jersey. 604pp.

French, BM (1990) Absence of shock-metamorphic effects in the Bushveld Complex, South Africa: Results of an intensive search. *Tectonophysics*, **171**, 287-301.

Freni, SC and Gaylor, DW (1992) International trends in the incidence of bone cancer are not related to drinking water fluoridation. *Cancer*, **70**, 611-618.

Fridriksson, S (1983) Fluoride problems following volcanic eruptions. *In:* Sharpe, JL, Peterson, HB and Leone, NC (*eds.*) *Fluorides - effects on vegetation, animals and humans*. Paragon Press, Salt Lake City. 339-344.

Friedman, I and O'Neil, JR (1977) Compilation of stable isotope fractionation factors of geochemical interest. *In*: *Data of Geochemistry*. US Geol. Surv. Prof. Paper 440-KK, 6th ed.

Fritz, B, Richard, L and McNutt, RH (1992) Geochemical modelling of Sr isotopic signatures in the interaction between granitic rocks and natural solutions. *In:* Kharaka, YK and Maest, AS (*eds.*) *Symposium on Water-Rock interaction*, Volume 1. Balkema, Rotterdam. 927-930.

Fritz, P, Gale, JE and Reardon, EJ (1979) Comments on Carbon-14 dating of groundwaters from crystalline environments. *Geoscience Canada*, **6**, 10-15.

Frommurze, HF (1937) The water bearing properties of the more important geological formations in the Union of South Africa. *Department of Mines, Geological Survey Memoir*, **34**. 252pp.

Fudali, RF, Gold, DP and Gurney, JJ (1973) The Pretoria Salt Pan: astrobleme or cryptovolcano? *J. Geol.*, **81**, 495-507.

Fuge, R (1988) Sources of halogens in the environment, influences on human and animal health. *Env. Geochem. and Health*, **10**, 51-61.

Fuge, R (1989) Iodine in waters: possible links with endemic goitre. *Applied Geochemistry*, **4**, 203-208.

Fuge, R (1996) Geochemistry of iodine in relation to iodine deficiency diseases. *In:* Appleton, JD, Fuge, R and McCall, GJH (*eds.*) Environmental geochemistry and health. *Geol. Soc. Spec. Publ.*, **113**, 201-211.

Fuhong, R, Jianhui, Z, Wensheng, L and Cuiyun, Z (1996) Hydrogeochemical environment of high fluorine groundwater and the relation between the speciation of fluorine and the diseased ratio of endemic fluorosis - a case study of the North China Plain. *Acta Geoscientia Sinica*, **17**, 85-97.

Gaciri, SJ and Davies, TC (1993) The occurrence and geochemistry of fluoride in some natural waters of Kenya. *Journal of Hydrology*, **143**, 395-412.

Galagan, DJ and Lamson, GG (1953) Climate and endemic fluorosis. *Publ. Health Report*, **68**, 497-508.

Galvin, RM (1996) Occurrence of metals in waters: an overview. *Water SA*, **22**, 7-18.

Garven, G (1995) Continental-scale groundwater flow and geological processes. *Annu. Rev. Earth Planet. Sci.*, **23**, 89-117.

Gascoyne, M and Kamineni, DC (1994) The hydrogeochsmistry of fractured plutonic rocks in the Canadian Shield. *Applied Hydrogeology*, **2**, 43-49.

Gat, JR (1980) The isotopes of hydrogen and oxygen in precipitation. 21-45 *In:* Fritz, P and Fontes, JCh (*eds.*) *Handbook of environmental isotope geochemistry*. Volume 1A. Elsevier, Amsterdam.

Gelberg, KH, Fitzgerald, EF, Hwang, S and Dubrow, R (1995) Fluoride exposure and childhood osteosarcoma: a case-control study. *Am. J. Public Health*, **85**, 1678-1683.

Gessner, BD, Beller, M, Middaugh, JP and Whitford, GM (1994) Acute fluoride poisoning from a public water system. *New Eng. J. Med.*, **330**, 95-99.

Geyh, MA (1972) Basic studies in hydrology and ^{14}C and ^{3}H measurements. *Proc. 24th Internatl. Geol. Conf., Montreal*, **11**, 227-234.

Gill, R (1996) *Chemical fundamentals of geology*. Chapman and Hall, London. 290pp.

Ginster, M and Fey, MV (1995) Soil and plant responses to irrigation with a fluoride-rich wate water. *In:* McCaffrey, LP (*ed.*) *Fluoride and fluorosis: the status of South African research.* Abstract volume of a Workshop held on 10th August 1995 in the Pilanesberg National Park, South Africa. 11pp.

Gíslason, SR, Andrésdóttir, A, Andrésdóttir, ÁE, Óskarsson, N, Thordarson, Th, Torssander, P, Novâk, M and Zâk, K (1992) Local effects of volcanoes on the hydrosphere: example from Hekla, southern Iceland. *In:* Kharaka, YK and Maest, AS (*eds.*) *Symposium on Water-Rock Interaction*, Volume 1. Balkema, Rotterdam. 477-481.

Gizaw, B (1996) The origin of high bicarbonate and fluoride concentrations in the waters of the Main Ethiopian Rift Valley, East African Rift system. *J. Afr. Earth Sci.*, **22**, 391-402.

Goldman, SM, Sievers, ML and Templin, DW (1971) Radiculomyopathy in a southwestern Indian due to skeletal fluorosis. *Arizona Medicine*, **28**, 32-48.

Graustein, WC and Armstrong, RL (1983) The use of ^{87}Sr/^{86}Sr ratios to measure atmospheric transport into forested watersheds. *Science*, **219**, 289-292.

Grobler; SR and Dreyer, AG (1988) Variations in the fluoride levels of drinking water in South Africa - implications for fluoride supplemantation. *S. Afr. Med. J.*, **73**, 217-219.

Guidotti, CV (1984) Micas in metamophic rocks. *In:* Bailey, SW (*eds*) Micas. *Reviews in Mineralogy*, **13**, 357-468.

Guntz, M (1884) Recherches thermiques sur les combinaisons du fluor. Ann. Chim. Phys. **6**, p38. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2). *Neues Jahrbuch Mineralogie*, **3**, 83-95

Gupta, RK, Chhabra, R and Abrol, IP (1982) Fluorine adsorption behaviour in alkaline soils: relative roles of pH and sodicity. *Soil Sci.*, **133**, 364-368.

Gupta, SK and Sharma, P (1995) An approach to tackling fluoride problem [*sic*] in drinking water. *Current Science*, **68**, 774.

Hamamoto, E (1957) On bone changes observed in in residents of a high fluorine zone. *In:* Utzino, S (*ed.*) *Medico-Dental researches on fluorides*, Japanese Society for Promotion of Science, Tokyo. 118-130.

Hamilton, PJ (1977) Sr isotope and trace element studies of the Great Dyke and Bushveld mafic phase and their relation to early Proterozoic magma genesis in southern Africa. *J. Petrology*, **18**, 24-52.

Hamilton, W (1970) Bushveld Complex - product of impacts? *Geol. Soc. S. Afr. Spec. Publ.*, **1**, 3667-379.

Hamza SM and Hamdona, SK (1991) Kinetics of dissolution of calcium fluoride crystals in sodium chloride solutions: influence of additives. *J. Phys. Chem.*, **95**, 3149-3152.

Harmer, RE (1985) A Sr isotope study of Transvaal carbonatites. *Trans. Geol. Soc. S Afr.*, **88**, 471-472.

Harmer, RE (1992) *The geochemistry of Spitskop and related alkaline intrusions.* Unpubl. PhD thesis, Uni. Cape Town. 332pp.

Harmer, RE and Farrow, D (1995) An isotopic study on the volcanics of the Rooiberg Group: age implications and a potential exploration. *Mineralium Deposita*, **30**, 188-195.

Harwood, JE (1969) The use of an ion-selective electrode for routine fluoride analyses on water samples. *Water Research*, **3**, 273-280.

Heaton, THE, Talma, AS and Vogel, JC (1986) Dissolved gas paleotemperatures and ^{18}O variations derived from groundwater near Uitenhage, South Africa. *Quaternary Research*, **79**, 79-88.

Henderson, P (1986) *Inorganic Geochemistry.* Pergamon Press, Oxford. 353pp.

Hill, M, Barker, F, Hunter, D, Knight, R (1996) Geochemical characteristics and origin of the Lebowa Granite Suite, Bushveld Complex. *Int. Geol. Rev.*, **38**, 195-227.

Hitchon, B (1995) Fluorine in formation waters, Alberta Basin, Canada. *Applied Geochemistry*, **10**, 357-367.

Hrudey, SE, Soskolne, CL, Berkel, J and Fincham, S (1990) Drinking water fluoridation and osteosarcoma. *Can. J. Public Health*, **81**, 415-416.

Hübner, M (1969) Geochemische Interpretation von Fluorid/Hydroxid-Austauschversuchen an Ton-mineralen. *Freiberger Forschungsheft*, **C244**.

Hudson, TD (1977) Stable isotopes and limestone lithification. *J. Geol. Soc. Lond.*, **133**, 637-660.

Humphrey, WA (1913) The Volcanic Rocks of the Pilanesberg. *Trans. Geol. Soc. S.A.*, **15**, 100-106.

Hunter, DR and Hamilton, PJ (1978) The Bushveld Complex. *In:* Tarling, DH (*ed.*) *Evolution of the Earth's Crust*. Academic Press, London, 107-173.

Ibrahim, YE, Affan, AA and Bjorvatn, K (1995) Prevalence of fental fluorosis in Sudanese children from two villages with 0.25 and 2.56 ppm fluoride in the drinking water. *Int. J. Paediatr. Dent.*, **5**, 223-229.

Jago, BC and Gittins, J (1991) The role of fluorine in carbonatite magma evolution. *Nature*, **349**, 56-58.

Jakosky, BM and Jones, JH (1994) Evolution of water on Mars. *Nature*, **370**, 328-329.

Jenkins, GN (1990) The metabolism and effects of fluoride. *In:* Preist, ND and Van De Vyver, FL (*eds*) *Trace metals and fluoride in bones and teeth*. CRC press, Boca Raton, 142-173.

Jinadasa, KBPN, Dissanayake, CB, Weerasooriya, SVR and Senaratne, A (1993) Adsorption of fluoride on goethite surfaces - implications on dental epidemiology. *Environ. Geol.*, **21**, 251-255.

Kalk, WJ, Sitas, F and Patterson, AC (1997) Thyroid cancer in South Africa - an indicator of regional iodine deficiency. *S. Afr. Med. J.*, **87**, 735-738.

Kazakov, AV and Sokolova, EE (1950) Conditions of formation of fluorite in sedimentary rocks (the fluorite system). *Akad. Nauk SSSR Inst. Geol. Nauk Tr.*, **114**, 22-64. *In:* Nordstrom, DK and Jenne, EA (1977) Fluorite solubility equilibria in selected geothermal waters. *Geochim. Cosmochim. Acta*, **41**, 175-188.

Kilborn, LG, Outerbridge, TS and Lei, HP (1950) Fluorosis with a report of an advanced case. *Can. Med. Ass. J.*, **62**, 135-141.

Kinlen, L (1975) Cancer incidence in relation to fluoride level in water supplies. *Br. Dent. J.*, **138**, 221-224.

Kleeman, GJ and Twist, D (1989) The compositionally-zoned sheet-like granite pluton of the Bushveld Complex: evidence bearing on the nature of A-type magmatism. *J. Petr.*, **30**, 1383-1414.

Kogarko, LN (1993) Geochemical characteristics of oceanic carbonatites from the Cape Verde Islands. *S Afr. J. Geol.*, 96, 119-125.

Kogarko, LN, Krigman, LD and Sharudilo, NS (1968) Experimental investigations of the effect of alkalinity of silicate melts on the separation of fluorine into the gas phase. *Geochem. Int.*, **5**, 782-790.

Kohlrausch, GG (1908) Über gesättigte wäßrige lösungen schwerlöslicher salze II: Die gelösten mengen mit ihrem temperaturgang. *Z Phys. Chem.*, **64**, 129-169. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2) *Neues Jahrbuch Mineralogie*, **3**, 83-95.

Koritnig, S (1951) Ein Beitrag zur Geochemie des Fluor. *Geochim. Cosmochim. Acta*, **1**, 89-100.

Koritnig, S (1974) *Fluorine. In:* Wedepohl, KH *(ed.) Handbook of Geochemistry Vol. II/1.* Springer-Verlag, Berlin.

Kraynov, SR, Mer'kov, AN, Petrova, NG, Baturinskaya, IV and Zharikova, VM (1969) Highly alkaline (pH 12) fluorosilicate waters in the deeper zones of the Lovozero Massif. *Geochemistry International*, **6**, 635-640.

Kunstmann, FH, Harris, JF, Bodenstein, LB and van den Berg, AM (1963) The occurrence of boron and fluorine in South African coals and their behaviour during combustion. *Bull. Fuel Res. Inst.*, **63**, 45pp.

Lane, SJ and Dalton, JA (1994). Electron microprobe analysis of geological carbonates. *American Mineralogist*, 79, 745-749.

Langmuir, D (1971) The geochemistry of some carbonate ground waters in central Pennsylvania. *Geochim. Cosmochim. Acta*, **35**, 1023-1045.

Lasaga, AC (1984) Chemical kinetics of water-rock interactions. *J. Geophys. Res.*, **B89**, 4009-4025.

Launay, L (1913) Traité de Métallogenie: Gites minéraux et métallifères, Paris et Siège. Unknown publisher. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2). *Neues Jahrbuch Mineralogie*, **3**, 83-95.

Le Maitre, RW (1989). *A classification of igneous rocks and glossary of terms. Recommendations of the International Union of Geological Sciences Subcommission on the systematics of Igneous Rocks.* Blackwell, London, 193pp.

Leung, AKC (1988) Water standards for fluoride. *The Lancet*, **1 (8591)**, 935.

Lewis HA and Chikte UM (1995) Prevalence and severity of fluorosis in the primary and permanent dentition using the TSIF. *J. Dent. Assoc. S. Afr.*, **50**, 467-471.

Libby, WF (1955) *Radiocarbon Dating.* University of Chicago Press, Chicago. 175pp.

Lloyd, JW and Heathcote, JA (1985) *Natural inorganic hydrochemistry in relation to ground water*. Clarendon Press, Oxford. 294pp.

Lombaard, BV (1932) The felsites and their relations in the Bushveld Complex. *Trans. Geol. Soc. S. Afr.*, **35**, 165-169.

Lurie, J (1974) *The Pilanesberg: Geology, Rare Element Geochemistry and Economic Potential.* Unpublished PhD thesis, Rhodes Univ.

Lyth, O (1946) Endemic fluorosis in Kweichow, China. *Lancet*, **1**, 233.

Machoy, Z, Dabkowska, E and Nowicka, W (1991) Increased fluoride content in mandibular bones of deer living in industrialised regions of Poland. *Env. Geochem. and Health*, **13**, 161-163.

Mahoney, MC, Nasca, PC, Burnett, WS, Melius, JM (1991) Bone cancer incidence rates in New York State: time trends and fluoridated drinking water. *Am. J. Public Health*, **81**, 475-479.

Manji, F, Baelum, V and Fejerskov, O (1986) Dental fluorosis in an area of Kenya with 2 ppm fluoride in the drinking water. *J. Dent. Res.*, **65**, 659-662.

Mason, B and Moore, CB (1966) *Principles of Geochemistry*. John Wiley & Sons, New York. 344pp.

Mathez, EA, Agrinier, P and Hutchinson, R (1994) Hydrogen isotope composition of the Merensky Reef and related rocks, Atok Section, Bushveld Complex. *Econ. Geol.*, **89**, 791-802.

Matthess, G (1982) *The properties of Groundwater*. John Wiley & Sons, New York.

May, PM and Murray, K (1991a) JESS, a joint expert speciation system - I: Raison d'être. *Talanta*, **38**, 1409-1417.

May, PM and Murray, K (1991b) JESS, a joint expert speciation system - II: the thermodynamic database. Talanta, **38**, 1419-1426.

Mazor, E and Verhagen, B Th. (1983) Dissolved ions, stable and radioactive isotopes and noble gases in thermal waters of South Africa. *J. Hydrology*, **63**, 315-329.

McCaffrey, LP (1993) *The Geohydrology of the Pilanesberg*. Unpubl. MSc dissertation, Univ. Witwatersrand, Johannesburg. 130pp.

McCaffrey, LP (1994) Fluoride electrode versus ion chromatograpic analyses of groundwater. *Abstract volume*, Analitika 94, Stellenbosch, 8-13 December 1994. 87pp.

McCaffrey, LP, Harris, C and Willis, JP (1996) An occurrence of calcite, stontianite and ankerite in the Pilanesberg Complex, North West Province, South Africa. *S. Afr. J. Geol*, **99**, 33-36.

McCrea, JM, (1950). On the isotopic chemistry of carbonates and palaeo-temperature scale. *Journal of Chemical Physics*, **18**, 849-857.

McInnes, PM, Richardson, BD and Cleaton-Jones, PE (1982) Comparison of dental fluorosis and caries in primary teeth of preschool-children living in arid high and low fluoride villages. *Community Dentistry and Oral Epidemiology*, **10**, 182-186.

McKay FS and Black, GV (1916) An investigation of mottled teeth. *Dental Cosmos*, **58**, 477-484.

McKenzie, WJ, Becker, BJP, Dreyer, CJ, du Toit, J, Dowdle, EBD, de Graad, JW and van Deventer, BJS (1966) *Report of the commission of enquiry into fluoridation.* The Government Printe, Pretoria. 174pp.

McNutt, RH, Frape, SK, Fritz, P, Jones, MG and MacDonald, IM (1990) The ^{87}Sr/^{86}Sr values of Candian Shield brines and fracture minerals with applications to groundwater mixing, fracture history, and geochronology. *Geochimica et Cosmochimica Acta*, **54**, 205-215.

Meeussen, JCL, van Riemsdijk, WH, de Wilde, PGM, Aalbers, Th.G (1994) Modeling [*sic*] fluoride transport in soils using ion binding models for oxides. *Transactions of the 15th World Congress of Soil Science, Acapulco, Mexico, July 10-16, 1994*, **3a**, 170-180.

Meunier, PJ, Femenias, M, Duboeuf, F, Chapuy, MC and Delmas, PD (1989) Increased vertebral bone density in heavy drinkers of mineral water rich in fluoride. *The Lancet*, **I (8630)**, p 152.

Meyer, R and de Beer, JH (1987) Structure of the Bushveld Complex from resisitivity measurements. *Nature*, **352**, 610-612.

Molengraaff, GAF (1905) Preliminary Note on the Geology of the Pilandsberg and a Portion of the Rustenburg District. *Trans. Geol. Soc. S.A.*, **8**, 108-115.

Moller, PF and Gudjonsson, SV (1932) Massive fluorosis of bones and ligaments. *Acta Radiol.*, **13**, 269-304.

Mook, WG (1980) Carbon-14 in hydrogeological studies. *In:* Fritz, P and Fontes, J Ch (*eds.*) *Handbook of environmental isotope geochemistry: Volume 1, The Terrestrial environment.* Elsevier, Amsterdam. 49-74.

Moola, MH (1996) Fluoridation in South Africa. *Community and Dent. Health*, **13**, 51-55.

Mougnard, P (1931) Sur le dosage du fluor. Compt. Rend. **192**, 1733-1735. *In* Nordstrom, DK and Jenne, EA (1977) Fluorite solubility equilibria in selected geothermal waters. *Geochim. Cosmochim. Acta*, **41**, 175-188.

Munoz, JL and Ludington, SD (1974) Fluoride-hydroxyl exchange in biotite. *Am. J. Sci.*, **274**, 396-413.

Munsell (1992) Munsell soil color chart. Kollmorgen Instruments Corporation. New York.

Nagy, KL (1995) Dissolution and precipitation kinetics of sheet silicates. *In:* White, AF and Brantley, SL (*eds.*) Chemical weathering rates in silicate minerals. *Reviews in Mineralogy*, **31**, 173-234.

Nash, WP (1976) Fluorine, chlorine and OH-bearing minerals in the Skaergaard Intrusion. *Am. J. Sci.*, **276**, 546-57.

Naumov, GB, Ryzhenko, BN and Khodakovsky, IL (1974) *Handbook of thermodynamic data.* Nat. Tech. Inf. Serv., **Pb-226, 722/7GA**, US Dept. Commerce, 328pp.

Newbrun, E (1989) Effectiveness of water fluoridation. *J. Public Health Dentistry*, **49**, 279-289.

Ng'ang'a, PM and Valderhaug, J (1993) Prevalence and severity of dental fluorosis in primary schoolchildren in Nairobi, Kenya. *Community Dentistry and Oral Epidemiology*, **21**, 15-18.

Nicholson, K and Pasquier, C (1993) The determination of fluoride in water in the presence of organic acids and iron using a fluoride-selective electrode. *Env. Geochem. and Health*, **15**, 185-186.

Nordstrom, DK and Jenne, EA (1977) Fluorite solubility equilibria in selected geothermal waters. *Geochim. Cosmochim. Acta*, **41**, 175-188.

Norrish, K and Hutton, JT (1969) An accurate X-ray spectrometric method for the analyses of a wide range of geological samples. *Geochim. Cosmochim. Acta.*, **33**, 431-453.

NPRL, [National Physical Research Laboratory] (1984) *Annual report.* **FIS 350**, 71.

Ockerse, T (1941) Endemic fluorosis in the Pretoria district. *S.A. Med. J.*, **15**, 261-266.

Ockerse, T and Meyer, HP (1941) Endemic fluorosis in the Pilandsberg area. *S.A. Dent. J*, **15**, 62-72.

Ockerse, T (1943) *Endemic fluorosis in South Africa.* Department of Public Health, Pretoria. 93pp.

Odenthal, H and Wieneke, HL (1959) Chronische fluorvergiftung und osteomyelosklerose. *Deutsche Medizinische Wochenschrift*, **84**, 725-728.

Oldham, PD and Newell, DJ (1977) Fluoridation of water supplies and cancer - a possible association? *Appl. Stat.*, **26**, 125-135.

O'Neil, JR, Clayton, RN and Mayeda, TK (1969) Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.*, **51**, 5547-5558.

O'Neil, JR and Taylor, HP (1967) The oxygen isotope and cation exchange chemistry of the feldspars. *Am. Mineral.*, **52**, 1414-1437.

Pakalns, P and Farrar, YJ (1976) Effects of surfactants on the determination of fluoride in waters. *Water Research*, **10**, 1087-1092.

Pekdeger, A, Özgür, N and Schneider, HJ (1992) Hydrogeochemistry of fluorine in shallow aqueous systems of the Gölcük area, SW Turkey. *In:* Kharaka, YK and Maest, AS (*eds.*) *Symposium on Water-Rock Interaction*, Volume 1. Balkema, Rotterdam. 821-824.

Pelpola, KU, Pienaar, P and Xu, Y (1992) Development of groundwater resources in Bophuthatswana. *In:* Proceedings of the 18th WEDC Conference, Kathmandu, Nepal, 30 August - 3 September 1992.

Pendrys, DG (1995) Risk of fluorosis in a fluoridated population. *J. Am. Dent. Ass.*, **126**, 1617-1624.

Peng, C, Qi, J and Rubin, AJ (1996) Use of fluorspar in water fluoridation. *J. Env. Eng.*, **122**, 132-140.

Petersen, E (1889) Neutralisationswärme der fluoride. *Z Phys. Chem.*, **4**, 384-412. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2). *Neues Jahrbuch Mineralogie*, **3**, 83-95.

Pettifor, JM, Schnitzler, CM, Ross, FP and Moodley, GP (1989) Endemic skeletal fluorosis in children: hypocalcemia and the presence of renal resistance to parathyroid hormone. *Bone Miner.*, **7**, 275-288.

Pickering, WF (1985) The mobility of soluble fluoride in soils. *Environ. Pollut.*, **B9**, 281-308.

Piper, AM (1944) A graphic procedure in the geochemical interpretion of water analyses. *Trans. Am. Geophys. Union*, **25**, 914-923.

Plankey, BJ and Patterson, HH (1986) Kinetics of aluminium fluoride complexation in acidic waters. *Environ. Sci. Technol.*, **20**, 160-165.

Pokrovskii, VA and Helgeson, HC (1995) Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: the system Al_2O_3-H_2O-NaCl. *Am. J. Science*, **295**, 1255-1342.

Preston-Whyte, RA and Tyson, PD (1988) *The Atmosphere and Weather of Southern Africa.* Oxford University Press, Cape Town. 374pp.

Prins, P (1981) The geochemical evolution of the alkaline and carbonatite complexes of the Damaraland Igneous Province, South West Africa. *Annall Uni. Stellenbosch*, series A1, **3**, 145-278.

Qi, J and Knaebel, KS (1989) Dissolution equilibria and kinetics of fluorite and calcite mixtures. *Am. Inst. Chem. Engin. J*, **35**, 1293-1303.

Raubenheimer, EJ, Okonska, ET, Dauth, J, Dreyer, MJ, Lourens, C, Bruwer, CA and de Vos, V (1990) Fluoride concentrations in the rivers of the Kruger National Park: a five year survey. *S. Afr. J. Wildlife Res.*, **20**, 127-129.

Reimold, WU, Koeberl, C, Kerr, SJ and Partridge, TC (1991) The Pretoria Saltpan - the first firm evidence for an origin by impact. *Lunar Planet. Sci.*, **22**, 1117-1118.

Reimold, WU, Koeberl, C, Partridge, TC and Kerr, SJ (1992) Pretoria Saltpan crater: impact origin confirmed. *Geology*, **20**, 1079-1082.

Retief, DH, Bradley, EL, Barbakow, FH, Friedman, M, van der Merwe, EH and Bischoff, JI (1979) Relationships among fluoride concentration in enamel, degree of fluorosis and caries incidence in a community residing in a high fluoride area. *J. Oral Pathol.*, **8**, 224-236.

Retief, EA (1962) Preliminary observations on the feldspars from the Pilanesberg alkaline complex, Transvaal, South Africa. *Norsk. geol. Tidskr.*, **42** (Feldspar-volume), 493-513.

Retief, EA (1963) *Petrological and mineralogical studies in the southern part of the Pilanesberg alkaline complex, Transvaal, South Africa.* Unpub. PhD thesis, Univ. of Oxford.

Riggs, RL, Hodgson, SF, O'Fallon, WM, Chao, EYS, Wahner, HW, Muhs, JM, Cedel, SL and Melton, LJ (1990) Effect of fluoride treatment on the fracture rate in postmenopausal women with osteoporosis. *New England J. Med.*, **332**, 802-809.

Roberson, CE and Hem, JD (1969) Solubility of aluminum in the presence of hydroxide, fluoride, and sulfate *U.S. Geol. Surv. Water Supply Paper*, **1827**, C1-C37.

Robie, RA, Hemingway, BS and Fisher, JR (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *US Geol Surv. Bull.*, **1452**, 456pp.

Robinson, JBD (1978) Fluorine: its occurrence, analysis, effects on plants, diagnosis and control. *Commonwealth Bureau of Soils Spec. Publ.*, **6**.

Roedder, E (1972) Composition of fluid inclusions. *In: Data of Geochemistry, 6th edition.* U.S. Geol. Surv., Prof. Pap. **440-JJ, Ch.JJ**, 164pp.

Rossini, FD, Wagman, DD, Evans, WH, Levine, S and Jaffe, I (1952) *Selected values of chemical thermodynamic properties.* Nat. Bureau Standards Circ. **500**, US Dept. Commerce, Washington DC.

Rozendaal, A, Toros, MS and Anderson, JR (1986) The Rooiberg tin deposits, West-Central Transvaal. 1307-1327. *In:* Anhaeusser, CR and Maske, S (*eds.*) *The mineral deposits of Southern Africa Volume II* Geol Soc. S Afr., Johannesburg. 2335pp.

Rudolph, MJ, Molefe, M, and Chikte, UME (1995) Dental fluorosis with varying levels of fluoride in drinking water. Abstract, *J. Dental Research*, **74**, 1012.

SACS, [South African Council for Stratigraphy] (1980) Stratigraphy of South Africa, Part 1 (Comp. L.E. Kent), Lithostratigraphy of the Republic of South Africa, South West Africa/Namibia, and the Republics of Bophuthatswana, Transkei and Venda. *Handb. Geol. Surv. S. Afr.*, **8**, 690pp.

Schidlowski, M, Hayes, JM and Kaplan, IR (1983). Isotopic inferences of ancient biochemistries: Carbon, sulfur, hydrogen, and nitrogen. *In:* Schopf, JW (*ed.*) *Earth's earliest biosphere*. Princeton University Press, Princeton. 543pp.

Schlatter, Ch (1978) Metabolism and toxicology of fluorides. *In:* Courvoisier, B, Donath, A and Baud, CA (*eds*) *Fluoride and Bone*. Hans Huber, Bern. 1-21.

Schloemann, H (1995) *The Geochemistry of some Western Cape soils (South Africa) with emphasis on toxic and essential elements.* Unpubl. PhD Thesis, Uni. Cape Town, 300pp.

Schreiner, GDL (1958) Comparison of the ^{87}Rb-^{86}Sr ages of the red granite of the Bushveld Complex from measurements on the total rock and seperated mineral fractions. *Proc. Roy. Soc.*, **A245**, 112-117.

Schulz, EE, Libanati, CR and Farley, SM (1984) Skeletal scinitigraphic changes in osteoporosis treated with sodium fluoride: concise communication. *J. Nucl. Med.*, **25**, 651-655.

Schweitzer, JK, Hatton, CJ and de Waal, SA (1995) Regional lithochemical stratigraphy of the Rooiberg Group, upper Transvaal Supergroup: a proposed new subdivision. *S Afr. J. Geol*, **98**, 245-255.

Seemann, F (1905) Studien über die quantitative bestimmung und trennung der Kieselsäure und des fluors. *Z Anal. Chem.*, **44**, 343-387. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2) *Neues Jahrbuch Mineralogie*, **3**, 83-95.

Senewiratne, B, Senewiratne, K, Hettiarachchi, J and Thambipillai, S (1973) Assessment of the fluoride content of water in wells selected randomly and after examining schoolchildren for dental fluorosis. *Bull. WH.O.*, **49**, 419-422.

Shand, SJ (1928) The Geology of Pilansberg (Pilaan's Berg) in the Western Transvaal; A Study of Alkaline Rocks and Ring-Intrusions. *Trans. Geol. Soc. S.A.*, **31**, 97-156.

Sharpe, MR (1985) Strontium isotope evidence for preserved density stratification in the Main Zone of the Bushveld Complex, South Africa. *Nature*, **316**, 119-126.

Shcherba, GN (1970) Greisens. *Int. Geol. Rev.*, **12**, 239-255.

Shortt, HE, McRobert, GR, Barnard, and Mannadi Nayar, AS (1937) Endemic Fluorosis in the Madras Presidency. *Ind. J. Med. Res.*, **25**, 553-568.

Smalley, PC, Blomqvist, R and Råheim, A (1988) Sr isotopic evidence for discrete saline components in stratified ground waters from crystalline bedrock, Outokumpu, Finland. *Geology*, **16**, 345-357.

Smet, J (1992) Fluoride in drinking water. *In:* Frencken, JE (*ed.*) *Endemic fluorosis in developing countries*. Report of a symposium held in Delft, the Netherlands, April 27th 1990. 98pp.

Smyshlyaev, SI and Edeleva, NP (1962) Determination of solubility of minerals I: The solubility product of fluorite. *Izv. Vysshikh Uchebn. Zavedenii Khim. Teknol.*, **5**, 871. *In:* Nordstrom, DK and Jenne, EA (1977) Fluorite solubility equilibria in selected geothermal waters. *Geochim. Cosmochim. Acta*, **41**, 175-188.

Socki, RA, Karlsson, HR and Gibson, EK (1992) Extraction Technique for the determination of Oxygen-18 in water using preevacuated glass vials. *Anal. Chem.*, **64**, 829-931.

Sonnet, CP and Finney, SA (1990) The spectrum of radiocarbon. *In:* Pecker, J and Runcorn, SK (*eds.*) *The Earth's climate and variability of the sun over recent millennia*. Royal Society, London. 692pp.

Speer, JA (1984) Micas in igneous rocks. *In:* Bailey, SW (*eds*) Micas. *Reviews in Mineralogy*, **13**, 299-356.

Stauffer, RE (1982) Fluorapatite and fluorite solubility controls on geothermal waters in Yellowstone National Park. *Geochim. Cosmochim. Acta*, **46**, 465-474.

Stormer, JC and Carmichael, ISE (1970) Villiaumite and the occurrence of fluoride minerals in igneous rocks. *Am. Mineralogist*, **55**, 126-134.

Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2). *Neues Jahrbuch Mineralogie*, **3**, 83-95.

Stuckless, JS, Peterman, ZE and Muhs, DR (1991) U and Sr isotopes in ground water and calcite, Yucca Mountain, Nevada: evidence against upwelling water. *Science*, **254**, 551-554.

Stumm, W, Wehrli, B and Wieland, E (1987) Surface complexation and its impact on geochemical kinetics. *Croatica Chemica Acta*, **60**, 429-456.

Suwa, K, Oana, S, Wada, H and Osaki, S (1975) Isotope geochemistry and petrology of African carbonatites. *Phys. and Chem. of the Earth*, **9**, 735-745.

Suzuki, K and Endo, Y (1995) Relation of Na^+ concentration and $\delta^{18}O$ in winter precipitation with weather conditions. *Gephys. Res. Lett.*, **22**, 591-594.

Sverdrup, HU (1990) *The kinetics of base cation release due to chemical weathering*. Lund Univ. Press.

Taylor, HP (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.*, **69**, 843-883.

Taylor, HP, Frechen, J and Degens, ET (1967) Oxygen and carbon isotope studies of carbonatites from the Laacher See district, West Germany, and the Alno district, Sweden. *Geochim. Cosmochim. Acta*, **31**, 407-430.

Thiessen, AH (1911) Precipitation averages for large areas. *Monthly Weather Rev.*, **39**, 1082-1084.

Thorsden, JJ, Kharaka, YK, Mariner, RH and White, LD (1992) Controls on the distribution of stable isotopes of meteoric water and snow in the greater Yellowstone National Park region, USA. *In:* Kharaka, YK and Maest, AS (*eds.*) *Symposium on Water-Rock Interaction,* Volume 1. Balkema, Rotterdam. 591-595.

Thylstrup, A and Fejerskov, O (1978) Clinical appearance of dental fluorosis in permanent teeth in relation to histologic changes. *Community Dentistry and Oral Epidemiology*, **6**, 315-328.

Tobayiwa, C, Musiyambiri, M, Chironga, L, Mazorodze, O and Sapahla, S (1991) Fluoride levels and dental fluorosis in two districts in Zimbabwe. *Central African J. Medicine*, **37**, 355-361.

Torino, M, Rognini, M and Fornaciari, G (1995) Dental fluorosis in ancient Herculaneum. *The Lancet*, **345**, 1306.

Treadwell, FP and Koch, AA (1904) Über die bestimmung von fluor in wein und bier. *Z Anal. Chem.*, **43**, 114-115. *In:* Strübel, G (1965) Quantitative Untersuchungen über die hydrothermale Löslichkeit van flußspat (CaF_2) *Neues Jahrbuch Mineralogie*, **3**, 83-95.

Trotignon, L and Turpault, MP (1992) The dissolution kinetics of biotite in dilute HNO_3 at 24°C *In:* Kharaka, YK and Maest, AS (*eds.*) *Symposium on Water-Rock interaction*, Volume 1. Balkema, Rotterdam. 123-125.

US Dept of Health and Human Services (1991) *Review of fluoride: benefits and risks.* Report of the Ad Hoc Subcommittee on fluoride of the Committee to Coordinate Environmental Health and Related Programs. Washington DC.

Van der Merwe, EH, Bischoff, JI, Fatti, LP, Retief, DH, Barbakow, FH and Friedman, M. (1977) Relationships between fluoride in enamel, DMFT index and fluorosis in high- and low-fluoride areas in South Africa. *Community Dent. Oral Epidemiol.*, **5**, 61-64.

Van Wyk, PJ, Louw, AJ and Snyman, WD (1983) Dental fluorosis in two communities in S.W.A. (namibia). *J. Dental Res.*, **62**, 508.

Vasak, L (1992) Primary sources of fluoride. *In:* Frencken, JE (*ed.*) *Endemic fluorosis in developing countries.* Report of a symposium held in Delft, the Netherlands, April 27th, 1990. 98pp.

Verdoux, P, Lancelot, J and Faillat, J (1995) Traçage de l'origine des eaux karstiques en bordure d'un massif cristallin à l'aide des isotopes du strontium: Exemple des causses lozériens (France). *CR Acad. Sci. Paris*, **320**, 387-394.

Verhagen, B Th., Geyh MA, Fröhlich, K and Wirth, K (1991) *Isotope hydrological methods for the quantitative evaluation of ground water resources in arid and semi-arid areas - Development of a methodology.* Federal Ministry for Economic Co-operation, Bonn. 164pp.

Verhagen, B Th., Mazor, E and Sellschop, JPF (1974) Radiocarbon and tritium evidence for direct rain recharge to ground waters in the northern Kalahari. *Nature*, **249**, 643-644.

Verwoerd, WJ (1967) The carbonatites of South Africa and South West Africa. *Department* *of Mines, Geological Survey Handbook*, **6**.

Verwoerd, WJ (1993). Update on carbonatites of South Africa and Namibia. *S Afr. J. Geol.*, **96**, 75-95.

Von Gruenewaldt, G, Hatton, CJ, Merkle, CJ and Gain, SB (1986) Platinum-group element - chromitite associations in the Bushveld Complex. *Econ. Geol.*, **81**, 1067-1079.

Waber, N and Nordstrom, DK (1992) Geochemical modeling of granitic ground waters at the Stripa site (Sweden) using a mass balance approach. 243-246. *In:* Kharaka, YK and Maest, AS *(eds.) Water-Rock interaction*, Volume 1. Balkema, Rotterdam.

Wager, LR and Brown, GM (1968) *Layered Igneous Rocks*. Oliver and Boyd, Edinburgh. 588pp.

Wagman, DD, Evans, WH, Parker, VB, Schumm, RH, Halow, I, Bailey, SM, Churney, KL and Nutall, RL (1982) The NBS tables of chemical thermodynamic properties: selected values for inorganic and C_1 and C_2 organic substances in SI units. *J. Phys. and Chem. Ref. data*, **11**, Supplement No. 2, 392pp.

Wagner, PA (1920) Note on the volcanic origin of the Salt Pan on the farm Zoutpan, No.467. *Trans. Geol. Soc. S.A.*, **23**, 52-58.

Wagner, PA (1922) *The Pretoria Salt-Pan, a soda caldera*. Geol. Surv. S.A. Memoir 20.

Walraven, F (1976) Notes on the late-stage history of the western Bushveld Complex. Trans. *Geol. Soc. S Afr.*, **79**, 13-21.

Walraven, F (1981) *The Geology of the Rustenburg area, explanation of sheet 2526*. Geological Survey of South Africa, Pretoria. 37pp.

Walraven, F (1987) Geochronological and isotopic studies of Bushveld Complex rocks from the Fairfield borehole at Moloto, northeast of Pretoria. *S Afr. J. Geol.*, **90**, 352-360.

Walraven, F and Hattingh, E (1993) Geochronology of the Nebo Granite, Bushveld Complex. *S Afr. J. Geol.*, **96**, 31-41.

Warner, TB (1971) Electrode determination of fluoride in ill-characterized natural waters. *Water Research*, **5**, 459-465.

Weast, RC (1975) *Handbook of Chemistry and Physics, 56th Edition*. CRC Press. Cleveland, Ohio.

White, SL (1988) Water standards for fluoride. *The Lancet*, **1 (8583)**, p475.

White, DE and Waring, GA (1963) Volcanic emanations *In: Data of Geochemistry, 6th edition*, U.S. Geol. Surv., Prof. Pap. **440-K, Ch.K**, K1-K29.

Whitford, GM (1996) *The metabolism and toxicity of fluoride*. Karger, Basel. 156pp.

WHO (1984) *Guidelines for drinking water quality, volume 1: Recommendations.* World health Organisation, Geneva.

WHO (1993) *Guidelines for drinking water quality, volume 1: Recommendations.* 2nd edition, volume 1. World health Organisation, Geneva.

Wilkniss, PE and Bressan, DJ (1971) Chemical processes at the air-sea interface: the behaviour of fluorine. *J. Geophys. Res.*, **76**, 736-741.

Wilkniss, PE and Bressan, DJ (1972) Fractionation of the elements F, Cl, Na and K at the air-sea interface. *J. Geophys. Res.*, **77**, 5307-5315.

Willis, JP (1995) *Instrumental parameters and data quality for routine major and trace element determinations by WDXRFS.* Department of Geological Sciences, University of Cape Town, information circular **14**, 7pp.

Woods, TL and Garrels, RM (1987) *Thermodynamic values at low temperature for natural inorganic materials: an uncritical summary.* Oxford University Press, New York. 242pp.

Woolley, AR (1982) A discussion of carbonatite evolution and nomenclature, and the generation of sodic and potassic finites. *Mineral. Mag.*, 46, 13-17.

Yang, Y, Wang, X and Guo, X (1994) Effects of high iodine and high fluorine on childrens intelligence and the metabolism of iodine and fluorine [Chinese]. *Chung Hua Liu Hsing Ping Hsueh Tsa Chih*, **15**, 296-298.

Yong, L and Hua, ZW (1991) Environmental characteristics of regional groundwater in relation to fluoride poisoning in North China. *Environ. Geol. and Water Sci.*, **18**, 3-10.

Yurtsever, Y and Gat, JR (1981) Atmospheric Waters. *In:* Stable Isotope Hydrology, technical report series, **210**. IAEA, Vienna.

Zhang, H, Bloom, PR and Nater, EA (1993) Change in surface area and dissolution rates during hornblende dissolution at pH 4.0. *Geochim. Cosmochim. Acta*, **57**, 1681-1689.

Zhu, C (1991) Biotite ((Mg,FE^{2+},Al^{VI}) (F,Cl,OH) reciprocal mixing properties: evidence from the partitioning of F-Cl-OH between biotite and apatite. *Abstract 5133, Geol. Soc. Amer.*

Zhu, C and Sverjensky, DA (1992) F-Cl-OH partitioning between biotite and apatite. *Geochim. Cosmochim. Acta*, **56**, 3435-3467.

Zietsman, S (1985) *Die verband tussen sekere fisies-geografiese veranderlikes en die voorkoms van tandfluorose in die Odi 1 gebied.* Unpubl. M.Sc. diss., Uni. S. Africa. 327pp.

Zietsman, S (1989) The relationship between the geological variation, the F^- of the water and the spatial variation in the occurrence of dental fluorosis in an endemic area. *S. Afr. Geog. J.*, **71**, 102-108.

Zietsman, S (1991) Spatial variation of fluorosis and fluoride content of water in an endemic area in Bophuthatswana. *J. Dent. Ass. S. Afr.*, **46**, 11-15.

Zipkin, I, McClure, FJ, Leone, NC and Lee, WA (1958) Fluoride deposition in human bones after prolonged ingestion of fluoride in drinking water. *Public Health Report*, **73**, 732-740.

9 APPENDICES

9.1 Appendix A1. Groundwater sample site information

"B/H No." (borehole number) has the following codes; "n/n" is no number; "unk./n" is a borehole with a number but is unclear. Site type has the following codes; "B" for borehole, "F" for spring, "P" for pan or dam, "R" for river or stream, "O" for seepage from opencast mine and "Z" for other. Site equipment has the following codes; "H" for handpump, "M" for mono-type pump, "N" for no equipment, "S" for submersible pump, "W" for windpump, "Z" for other and blank for no information. Non-consecutive site numbers result from either errors in the field maps or duplication of previous sites.

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 1: Bapong, self help garden	26.84806	25.30934	B	H
n/n	site 2: Bapong, southern end	26.84110	25.31384	B	Z
n/n	site 3: Bapong, northern end	26.84807	25.30121	B	H
06-65005	site 7: Mabeeskraal, middle of village	26.79908	25.20140	B	H
06-65184	site 8: Mabeeskraal, Marula Park	26.81794	25.19555	B	H
n/n	site 9: Maneeskraal, Mami's house, zone 4	26.81300	25.18291	B	H
n/n	site 10: Maologane	26.94143	25.26697	B	Z
n/n	site 11: Maologane, Joyce's yard	26.94540	25.27059	B	S
n/n	site 12: Maologane, Private Yard	26.94441	25.27149	B	H
n/n	site 13: Maologane, Private yard	26.94639	25.27194	B	H
n/n	site 14: Maologane, private yard	26.94589	25.27284	B	H
n/n	site 15: Maologane, Private yard	26.94689	25.27329	B	H
06-65307	site 16: Maologane, Dikeme middle school	26.94242	25.27555	B	H
n/n	site 17: Raborife, Mr Raborife's yard	26.90721	25.22407	B	H
n/n	site 18: Raborife, private	26.90970	25.21911	B	S
n/n	site 19: Mmorogong (Tlhatlhaganyane)	26.94045	25.23610	B	Z
n/n	site 20: Mmorogong, Christoff's yard	26.94055	25.23718	B	H
n/n	site 21: Mmorogong, Tapson's yard	26.94045	25.23808	B	H
n/n	site 22: Mmorogong, Johanna's yard	26.94169	25.23899	B	H
n/n	site 23: Mmorogong, Witness' yard	26.94144	25.23989	B	H
n/n	site 24: Mmorogong, animal gear	26.94144	25.24124	B	Z
n/n	site 25: Mmorogong, owner absent	26.94144	25.24260	B	H
n/n	site 26: Mmorogong, Joseph's yard	26.94144	25.24328	B	H
n/n	site 27: Mmorogong, Mthembu's yard	26.94045	25.24395	B	H
n/n	site 28: Mmorogong, Sekgwelea's yard	26.94065	25.24418	B	H

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 29: Mmorogong, Master's yard	26.94065	25.24485	B	H
n/n	site 30: Mmorogong, Public H/P	26.94065	25.24576	B	H
T6234	site 31: Tlhatlhaganyane, Animal gear east	26.93996	25.21822	B	Z
n/n	site 32: Tlhatlhaganyane	26.92061	25.22047	B	H
06-65436	site 33: Tlhatlhaganyane	26.91367	25.20963	B	H
06-65192	site 34: Tlhatlhaganyane, Early learning C	26.94344	25.22138	B	H
n/n	site 35: Ledig, Lena's yard	27.06607	25.36853	B	H
n/n	site 36: Ledig, Lydia's yard	27.07899	25.36943	B	H
n/n	site 37: Ledig, Pilanesberg seepage spring	27.08245	25.35002	F	
n/n	site 38: Ledig, Esky's yard	27.07749	25.35408	B	H
06-65324	site 39: Ledig, public	27.07451	25.36356	B	H
n/n	site 40: Ledig, Nicholas's yard	27.06755	25.35228	B	H
n/n	site 41: Ledig, Joan's yard	27.06756	25.36311	B	H
n/n	site 42: Ledig, Phineas's yard	27.05812	25.35860	B	H
n/n	site 43: Ledig, Jacob's yard	27.05464	25.35454	B	H
n/n	site 44: Ledig, Alexander's yard	27.05116	25.35319	B	H
06-65302	site 45: Ledig, Zulu section	27.04520	25.35274	B	Z
06-65304	site 46: Ledig, public	27.03626	25.34958	B	H
n/n	site 47: Ledig, Onika's yard	27.03079	25.34733	B	H
n/n	site 48: Ledig, Katherine's yard	27.02483	25.34733	B	H
n/n	site 49: Ledig, Moses' yard	27.03427	25.35365	B	H
n/n	site 50: Ledig, Dorothy's yard	27.04769	25.35680	B	H
BB 2035	site 51: Makoshong, northern	26.84369	25.23666	B	H
BB 2033	site 52: Makoshong	26.84418	25.23937	B	H
BB 2031	site 53: Makoshong, next to shop	26.84120	25.24162	B	H
N 204	site 54: Makoshong	26.83971	25.23801	B	H
n/n	site 55: Mahobieskraal	26.96672	25.34642	B	
06-40709	site 56: Mahobieskraal, vegetable garden	26.97268	25.34327	B	H
n/n	site 57: Motlhabe, south east	26.95837	25.07830	B	S
06-65532	site 58: Motlhabe	26.95391	25.06656	B	H
06-65301	site 59: Motlhabe	26.94846	25.06475	B	H
06-65387	site 60: Motlhabe	26.93905	25.06701	B	H
n/n	site 61: Motlhabe	26.95243	25.06295	Z	Z
06-65084B	site 62: Ntswana le Metsing	26.96878	25.05347	B	H
06-65347	site 63: Motlhabe	26.97423	25.05573	B	H

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 65: Makgope Mine	26.92564	25.11891	B	S
n/n	site 66: Makgope mine, domestic supply	26.93853	25.11530	B	S
n/n	site 67: Witkleifontein grazing	26.95043	25.10041	B	W
T6768	site 69: Southeast of Pilanesberg	27.21503	25.32912	B	W
T41731	site 70: Southeast of Pilanesberg	27.22542	25.30608	B	W
T141900	site 71: Sefikile	27.20554	24.99917	B	W
T7693	site 72: Sefikile	27.18276	25.00416	B	W
T6292	site 73: Tsweneng, south	27.01237	24.92437	B	W
n/n	site 74: Leswaaneng spring	27.12398	25.15454	F	
n/n	site 75: Salty spring	27.12595	25.15002	F	
n/n	site 76: Lesetlheng, outside chief's house	27.09917	25.14553	B	H
n/n	site 77: Ramatshaba	27.05206	25.13427	B	H
n/n	site 78: Ramatshaba	27.02975	25.14104	B	H
06-65284	site 79: Ramatshaba	27.04757	25.06114	B	W
n/n	site 80: Ramatshaba	27.05103	25.04534	B	W
n/n	site 81: north of Pilanesberg	27.04954	25.02548	B	W
n/n	site 82: north of Pilanesberg	27.17792	25.07910	B	W
06-65547	site 83: north of Pilanesberg	27.08179	25.10040	B	W
n/n	site 84: Chaneng, next to Agricor	27.12920	25.40776	B	H
n/n	site 87: Robega A (Boshkoppie farm)	27.14909	25.41677	B	W
?2861	site 88: Tsitsing	27.33801	25.44083	B	Z
05-62054	site 89: Maile (Rooikraal farm)	27.24546	25.39768	B	H
T6921	site 90: Rietspruit	27.28714	25.37052	B	W
T6869	site 91: Monnakato	27.27118	25.34302	B	W
05-62041	site 92: Tsitsing	27.32024	25.48871	B	W
05-62162	site 93: KwaSeretube	27.29348	25.52714	B	H
05-62163	site 94: KwaSeretube	27.30591	25.52666	B	H
n/n	site 95: Bospoort Dam	27.34232	25.55953	P	
n/n	site 95: Marikana	27.48562	25.68415	B	S
n/n	site 97: Swartkoppies, Mev Engelbrechts fa	27.47953	25.65528	B	S
05-62167	site 98: Tlapa, grazing lands	27.43562	25.63195	B	H
T6918	site 99: Tlapa, grazing lands	27.40419	25.61218	B	W
RB067	site 100: Tlapa, arable field	27.43957	25.62291	B	H
05-62120	site 101: Tlapa	27.43555	25.61299	B	H
05-62121	site 102: Tlapa	27.43329	25.60623	B	H

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 103: Maumong	27.45337	25.58586	B	H
05-62180	site 104: Lekgalong	27.40941	25.53724	B	H
T6227	site 105: Rankelanyane	27.40926	25.56635	B	Z
05-62013	site 106: Lekjaneng	27.39308	25.56346	B	H
05-62012	site 107: Malejaneng	27.37325	25.58789	B	H
24400	site 108: Thekwane, kraal	27.35490	25.60892	B	
n/n	site 109: Bapong oustad	27.70630	25.69137	B	H
n/n	site 110: Bapong, roberts yard	27.67851	25.71001	B	H
n/n	site 111: Bapong	27.67409	25.72041	B	Z
n/n	site 112: Bapong	27.66659	25.71548	B	H
n/n	site 113: Bapong, Legalawong sub village	27.66255	25.70602	B	H
04-56110	site 114: Modderspruit	27.65220	25.72592	B	H
BB 130	site 115: Modderspruit	27.64769	25.72098	B	H
n/n	site 116: Seqwelane	27.60255	25.66250	B	H
n/n	site 117: Makolokwe, western end	27.61234	25.62770	B	H
T6955	site 118: Bethanie farm	27.56013	25.53471	B	W
BB 1284	site 119: Bethanie cattle post	27.61475	25.51644	B	W
BB1292	site 120: Wilgevonden east cattle post	27.61360	25.48462	B	W
BB 1282	site 121: Bethanie, south east	27.59910	25.56908	B	W
04-59958	site 122: Bethanie, outside church	27.60701	25.55912	B	H
T6231	site 123: Waaikraal farm	27.57705	25.53577	B	W
04-59162	site 124: Modikwe	27.53721	25.52599	B	H
T49020	site 125: Modikwe, south	27.53476	25.53526	B	H
04-57078	site 126: Modikwe	27.53774	25.53479	B	H
n/n	site 127: Gwatlhe River	27.53675	25.53592	R	
n/n	site 128: Modikwe, school	27.53519	25.51968	B	H
T49064	site 130: Modikwe, west	27.50606	25.51121	B	W
04-59080	site 131: Berseba	27.52937	25.55265	B	H
04-59053	site 132: Bethanie	27.61648	25.56134	B	H
n/n	site 133: Krokodile Riv, Hartebeespoort fm	27.67961	25.50690	R	
T4397	site 134: Maboloka, Bafokeng section	27.84883	25.41981	B	H
03-56174	site 135: Maboloka, Taung section	27.86042	25.44321	B	H
03-56370	site 136: Maboloka, Solomon middle school	27.86493	25.44815	B	H
BB 1266	site 137: Maboloka, Phuthanang Primry schl	27.85881	25.42652	B	H
03-56177	site 138: Maboloka grazing	27.86774	25.42421	B	W

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 139: Maboloka, Tumo primary school	27.85803	25.42156	B	H
03-56595	site 140: Maboloka	27.85526	25.41661	B	H
n/n	site 141: Letlhakaneng	27.81882	25.39109	B	H
03-65150	site 142: Letlhakaneng	27.82181	25.39378	B	H
n/n	site 143: Letlhakaneng	27.82826	25.39104	B	H
T4	site 144: Rietgat grazing	27.80553	25.40990	B	W
T4305	site 145: Rietgat grazing	27.80492	25.39343	B	W
4308	site 146: Rietgat grazing	27.79690	25.38309	B	W
unk./n	site 147: Waterval grazing	27.73031	25.37892	B	W
n/n	site 148: Waterval grazing	27.73809	25.35180	B	W
03-56145	site 149: Waterval (Tsogwe)	27.74907	25.36077	B	H
T4860	site 150: Tsogwe	27.75108	25.36460	B	H
03-56143	site 151: Tsogwe, Tsogwe School	27.75356	25.36301	B	H
n/n	site 152: Kgomokgomo (Rooiwal)	27.76121	25.31557	B	H
n/n	site 153: Kgomokgomo	27.75476	25.31696	B	H
03-56383	site 154: Legonyane	27.77133	25.26813	B	H
T46033	site 155: Legonyane	27.77532	25.27082	B	H
03-57331	site 156: Legonyane, outskirts	27.77532	25.27082	B	H
unk./n	site 157: Leganyane, lethabong primary scl	27.77929	25.27034	B	H
03-56331	site 158: Legonyane	27.79021	25.27119	B	H
T46009	site 159: Legonyane	27.78929	25.28248	B	H
T46039	site 161: GaTsefoqe	27.71680	25.10997	B	H
03-56017	site 162: Jericho	27.82928	25.32288	B	
03-56415	site 163: Madinyane, Ramogatla	27.88097	25.39750	B	H
03-56327	site 164: Madinyane	27.87745	25.39166	B	H
n/n	site 165: Fafung	27.78182	25.20037	B	H
n/n	site 166: Bultfontein grazing	27.71097	25.21517	B	W
03-56409	site 167: Jonathan, next to cemetary	27.86970	25.21207	B	H
T4237	site 168: GaHabedi grazing	27.89137	25.18937	B	W
T4876	site 169: Zoutpansleegte grazing	27.88281	25.17182	B	W
unk./n	site 170: GaHabedi	27.90113	25.16855	B	H
n/n	site 171: Sephai grazing	27.82227	25.24122	B	W
n/n	site 172: Sephai	27.80543	25.24606	B	H
n/n	site 173: Sephai	27.80572	25.25170	B	H
03-56356	site 174: Sephai	27.80170	25.24404	B	H

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
T46022	site 175: Mmakau, Tshwara section	27.93212	25.62015	B	H
0036	site 176: Tshwara	27.93486	25.62058	B	Z
n/n	site 177: Mmakau, Mongopeng section	27.95675	25.61954	B	H
n/n	site 178: Mmakau, Polonia Section	27.96071	25.61680	B	H
n/n	site 179: Mmakau	27.93408	25.61607	B	H
n/n	site 180: Mmakau, Tetele subvillage	27.89594	25.60728	B	H
BB1273	site 181: Mmakau, Switch subvillage	27.88837	25.59424	B	H
0032	site 182: Mothuthlung	27.89585	25.59623	B	H
BB1021	site 183: Mothuthlung, Switch subvillage	27.88962	25.59423	B	H
n/n	site 184: btwn Rankotia and Ntswaphelong	27.84688	25.56696	B	S
NO. 2	site 185: Vametco mine	27.89972	25.58154	B	N
n/n	site 186: Lerulaneng	27.89874	25.51655	B	H
T4072	site 187: Lerulaneng	27.90003	25.52196	B	H
n/n	site 188: Lerulaneng	27.90377	25.52419	B	H
BB1226	site 189: Paarlkraal farm	27.79225	24.97147	B	W
BB1313	site 190: Paarlkraal grazing	27.78049	24.99049	B	W
T4636	site 191: Doornfontein grazing	27.76074	25.00052	B	W
BB1204	site 192: Doornfontein grazing	27.73561	25.02186	B	W
BB1264	site 193: Blokspruit grazing	27.74268	25.04485	B	W
n/n	site 194: Goudkoppie Veldspaatmyn	27.77187	25.03748	O	
BB1222	site 195: Ruigterpoort grazing	27.78375	25.03651	B	W
n/n	site 196: Blokspruit grazing	27.76188	25.06416	B	W
BB11	site 197: Blokspruit grazing	27.81223	25.07292	B	W
BB1172	site 198: Die mont van Blokspruit	27.74285	25.11436	B	W
BB1193	site 199: Die mont van Blokspruit	27.74549	25.09900	B	W
T4742A	site 200: Kenkelbos	27.70064	25.05679	B	W
T4852	site 201: Kwarriekraal	27.65559	25.06467	B	W
n/n	site 202: Tolwane River	27.82832	25.32830	R	
n/n	site 203: Shakung	27.91981	25.34310	B	H
T4903	site 204: Shakung	27.90934	25.33866	B	H
03-56404	site 205: Shakung	27.90831	25.33279	B	H
03-65121	site 206: Shakung	27.90037	25.33465	B	H
03-56372	site 207: Moiletswane	27.92207	25.37965	B	H
03-56195	site 208: Moiletswane	27.92703	25.37826	B	H
03-56371	site 209: Moiletswane	27.92458	25.38370	B	H

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
03-56398	site 210: Dipompong	27.94675	25.39168	B	H
03-56397	site 211: Dipompong	27.94599	25.38898	B	H
n/n	site 212: Makgabetlwane	27.94607	25.27253	B	H
03-56395	site 213: Makgabetlwane	27.92966	25.26812	B	H
BB1064	site 214: Rabosula, outside Kalkbank Pr.sc	27.97570	25.37660	B	H
BB1065	site 215: Rabosula	27.98264	25.37519	B	H
03-56382	site 216: Rabosula	27.98293	25.28808	B	H
n/n	site 217: Botshabelo (Vyeboschlaagte no.1)	27.99854	25.31506	B	S
03-56274	site 218: Klippan	28.04664	25.44173	B	H
03-56269	site 219: Winterveld	27.99238	25.41214	B	H
T4066	site 220: Winterveld	27.96519	25.39833	B	H
T4064	site 221: Winterveld, Palatselenyae Mdl sc	28.01992	25.36573	B	H
BB1315	site 222: Winterveld, Matlwareng primary s	28.05601	25.45172	B	H
BB?	site 223: Kgabaletsane	27.95010	25.53270	B	H
BB1084	site 224: Kgabaletsane	27.96532	25.53914	B	H
BB1086	site 225: Kgabaletsane	27.96776	25.53371	B	H
n/n	site 226: Hebron	28.00850	25.54687	B	H
n/n	site 227: Hebron	28.02344	25.54494	B	H
BB1080	site 228: Hebron	28.02615	25.54811	B	H
n/n	site 229: Hebron	28.03060	25.55243	B	H
n/n	site 230: Pretoria Saltpan, surface	28.08316	25.41082	P	
n/n	site 231: Pretoria Saltpan, fountain	28.08170	25.40720	Z	
T4894	site 232: Tamootielaagte	27.87859	25.06667	B	W
T4997	site 233: Tambootielaagte	27.85554	25.06636	B	M
02-53055	site 234: Tambootielaagte	27.82861	25.07780	B	W
n/n	site 235: Tambootielaagte	27.86907	25.05229	B	M
BB0103	site 236: Waterval	27.87611	24.99673	B	W
T49020	site 237: Waterval	27.84197	25.00189	B	M
n/n	site 238: Witpoortje	27.91725	25.00190	B	M
n/n	site 239: Lebitloane	27.92414	25.06234	B	H
02-53591	site 240: Lebitloane	27.92721	25.07496	B	H
n/n	site 242: Stinkwater, Mr Teledi's farm	28.16481	25.38784	B	M
n/n	site 243: Stinkwater, next to Namo Prm Scl	28.16281	25.39009	B	H
n/n	site 244: Stinkwater	28.16228	25.39460	B	H
02-53324	site 245: Mogogelo	28.13668	25.36105	B	H

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 246: Dilopye	28.19292	25.38190	B	H
T442?8	site 247: Suurman	28.21601	25.38361	B	H
T4032	site 248: Makekeng (Syferkuil)	28.22560	25.08531	B	
T4207B	site 249: Syferkuil	28.24378	25.07141	B	
T4376	site 250: Syferkuil A grazing	28.22900	25.05689	B	W
n/n	site 251: Syferkuil grazing	28.19286	25.05264	B	W
n/n	site 252: Mathiebiestad, Senteng Prm schl	28.16915	25.26104	B	H
02-53251A27	site 253: Mathiebiestad, Lepomo Prm schl	28.15674	25.26187	B	
01-53385 (!)	site 254: Mathiebiestad, Regodile ELC	28.15321	25.26952	B	H
02-53384	site 255: Mathiebiestad, south	28.15267	25.27584	B	H
n/n	site 256: Mathiebiestad	28.16899	25.28586	B	H
02-5330?	site 257: Mathiebiestad, Ramogoga ELC	28.19832	25.27880	B	H
02-00093	site 258: Mathiebiestad, Mahobotle Prm sch	28.20082	25.27565	B	
n/n	site 259: Mathiebiestad	28.17754	25.26830	B	H
n/n	site 260: Mathiebiestad	28.16263	25.27183	B	H
n/n	site 261: Potoane (Goedgewacht)	28.15839	25.23841	B	H
n/n	site 262: Mathiebiestad, Geodgewaagd 2	28.17772	25.24213	B	H
T4991	site 263: Slagboom grazing	28.00950	25.12013	B	H
02-53455	site 264: Slagboom	28.00230	25.12144	B	H
n/n	site 265: Bollantlokwe	27.97968	25.06785	B	H
n/n	site 266: Bedwang grazing	28.02492	25.11256	B	
4689	site 267: Tholwe	27.91266	25.11838	B	H
T4546	site 268: De Grens trust	27.93028	25.08848	B	H
02-53581	site 269: De Grens private	27.91682	25.07773	B	H
n/n	site 270: Lefiswane	28.86383	24.96765	B	H
01-50099	site 271: Lefiso	28.88763	24.93878	B	H
01-50098	site 272: Lefiso	28.90100	24.93066	B	H
01-5277?	site 275: Rooikoppies grazing	28.73087	25.09025	B	H
n/n	site 276: Ramantsho, primary school	28.76712	25.05329	B	H
n/n	site 277: Rooifontein grazing	28.67043	25.07839	B	M
01-50771?	site 278: Semohlase	28.70660	25.08208	B	H
T4269	site 279: Semohlase grazing?	28.68158	24.98317	B	W
T42600	site 280: Goedviralles	28.66474	24.98313	B	M
T4507	site 281: Bultfontein grazing	28.52865	25.08839	B	W
T4710	site 282: Bultfontein grazing	28.59841	25.12877	B	W

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 283: Bultfontein grazing	28.51458	25.13754	B	W
n/n	site 284: Klippan grazing	28.49735	25.10860	B	M
n/n	site 286: Tswaaneng Spring west	27.00893	25.14917	F	
n/n	site 287: Quarantine Camp	27.02233	25.23448	B	
n/n	site 288: Letswaaneng spring auger hole, L	27.11058	25.14778	F	
BB2088	site 289: Mabele a Podi	27.20353	25.28039	B	H
NO. 2	site 290: Main Camp borehole, Borakalalo	27.80978	25.15328	B	M
n/n	site 291: Jonathan Camp, Borakalalo Park	27.84812	25.17518	B	S
n/n	site 292: Makoropeja	27.83629	25.11431	B	H
n/n	site 293: Tlolwe Base, Borakalalo	27.88743	25.12530	B	M
n/n	site 294: Blokspruit base, Borakalalo	27.73717	25.11710	B	M
n/n	site 295: Moretele Camp, Borakalalo Park	27.79122	25.12043	B	M
n/n	site 298: Bultfontein	27.81142	25.17539	B	H
n/n	site 299: Klipvoor Primary school	27.80541	25.09192	B	H
n/n	site 300: Slipfontein fluorite mine	27.68452	25.00992	B	M
n/n	Site 302: Mankwe river at Mankwe bridge	27.10969	25.25566	R	
n/n	site 303: Blinkwater, Pilanesberg	27.11063	25.20104	R	
unk./n	site 304: Pilanesberg centre	27.10372	25.24754	B	
unk./n	Site 306: Pilanesberg, Green Tweed	26.98510	25.33559		
n/n	site 307:Nooitgedacht farm	27.51583	25.05800	B	S
n/n	site 308: Nooitgedacht, Wolvaardts	27.51091	25.06659	B	S
n/n	site 309: Nooitgedacht, cattle	27.49156	25.06169	B	
n/n	site 310: Nooitgedacht, Van niekerk	27.51227	25.03770	B	
n/n	site 311: Nooitgedacht, Eloff's	27.53149	25.01416	B	
n/n	site 312: Bakgat Farm	27.52718	25.04803	B	
n/n	site 313: Pienaars river, Buffelspoort	27.62518	25.12664	R	
n/n	site 314: Buffelspoort, Fred de la poorts'	27.63448	25.10313	B	
n/n	site 315: Buffelspoort, Standers	27.61618	25.11178	B	
n/n	site 316: Kwarriekraal	27.64165	25.05254	B	H
n/n	site 317: Mooimeisjiesfontein	27.64588	25.00874	B	
n/n	site 318: Slipfontein, fanigalo	27.65632	25.01592	B	
n/n	site 319: Mooimeisjiesfontein, spruit	27.62446	24.98400	R	
n/n	site 320: Rietfontein	27.59249	24.92636	B	M
n/n	site 321: Weihoek	27.62808	24.91628	B	
n/n	site 322: Driefontein game farm	27.68708	24.93588	B	

B/H No.	Site Number: Location, Description	Long. E	Lat. S	Type	Equip
n/n	site 323: Koperfontein, Shikari game camp	27.64367	24.96496	B	
n/n	site 324: Driefontein	27.71312	24.98722	B	
n/n	site 325: Hartbeesfontein	27.81150	24.96234	B	
n/n	site 326: Rietdal	27.76547	24.96484	B	
n/n	Site 327: Morgenzon	27.85164	24.89531	B	
n/n	site 328: Kromdraai	27.90670	24.91349	B	S
n/n	site 329: Kromdraai, plot 142	27.84262	24.95133	B	
n/n	site 330: Kromdraai, plot 304	27.87693	24.97280	B	
n/n	site 331: Kromdraai, plot 48	27.87115	24.92589	B	
n/n	site 332: Hardekoolbult	27.56136	24.93731	B	
n/n	site 333: Kruidfontein, dam draining hills	27.51617	25.14015	P	
n/n	site 334: Kruidfontein	27.51620	25.14782	B	
n/n	site 335: Pretoria Saltpan, old artesian	28.08122	25.41081	B	N
n/n	site 337: Soutpan	28.07802	25.43291	B	M
n/n	site 338: Soutpan, Mr Mon's	28.09856	25.41137	B	

9.2 Appendix A2. Rock and soil sample locations.

"N" = Nebo Granite, "L" = Lebowa Granite.

No.	Site Name	Rock Type	Long. E.	Lat. S.
1	Bapong	Quartzite	26.8337	25.3035
2	Moreteletsi	Monzonite	26.7895	25.2860
3	Green Tweed	Syenite	26.9841	25.3473
4	Thabayadiotsa	Syenite	27.1677	25.2574
5	Kubu drive Quarry	Syenite	27.0998	25.2837
6	Moepo	Fluorite ore	27.0799	25.2968
7	N of Pilanesberg	Norite	27.1537	25.1324
8	Mabele a podi	Alkali granite	27.1961	25.2854
9	Lesung	Norite	27.3667	25.5166
10	Lesung	Magnetite ore	27.3667	25.5000
11	Modikwe	Alkali granite (N)	27.5242	25.5125
12	Sun city-Lesung	Norite	27.2355	25.3900
13	Smaldale Farm	Dolomitic limestone	26.6043	24.8385
14	Tamboetieshoek Fm	Ironstone	26.5943	24.8692
15	Dwarsberg	Sandstone	26.6683	24.9561
16	Rampapaanspoort	Norite	26.6811	24.9931
17	Holfontein	Garnet-biotite hornfels	26.7361	25.1837
18	Leboaneng	Ironstone	27.4149	25.0989
19	GaRamolorengpoort	Dolomite	27.4183	25.0958
20	Makoropeja	Granite (L)	27.8343	25.1206
21	North block 7	Granite (L)	27.8626	25.1264
22	North block 10	Granite (L)	27.8959	25.1352
23	Slipfontein	Quartz pegmatite	27.6845	25.0108
24	Kwarriekraal	Granophyre	27.6531	25.0561
25	Kenkelbos	Alkali granite (L)	27.6837	25.0465
26	Blokspruit	Alkali granite (L)	27.7467	25.0471
27	Blokspruit	Alkali granite (L)	27.7324	25.0724
28	Borakalalo	Sandstone	27.7998	25.1484
29	Sephai	Limestone	27.7938	25.2418
30	GaTsogwe	Granite (N)	27.7595	25.3607
31	Rashoop	Granophyre	27.7660	25.5327

No.	Site Name	Rock Type	Long. E.	Lat. S.
32	Mpatsetlha	Sandstone	27.7213	25.1136
33	Mpatsetlha	Mudstone	27.7193	25.1154
34	Leeupoort Tin	Felsite	27.7048	24.9141
35	Tooyspruit	Feldspathic sandstone	27.8764	24.8220
36	Kwaggafontein	Greenschist	27.8409	24.8385
37	Rietfontein	Alkali granite (N)	27.5652	24.9192
38	Rietfontein	Alkali granite (N)	27.5860	24.9110
39	Sutelong	Quartzite	27.9500	25.1000
40	Dikebu	Granite (L)	27.9666	25.2000
41	Pretoria Saltpan	Granite (N)	28.0822	25.4063
42	Pretoria Saltpan	Granite (N)	28.0792	25.4054

9.3 Appendix A3. XRF instrumental parameters

DEPARTMENT OF GEOLOGICAL SCIENCES

UNIVERSITY OF CAPE TOWN

INSTRUMENTAL PARAMETERS AND DATA QUALITY FOR ROUTINE MAJOR AND TRACE ELEMENT DETERMINATIONS BY WDXRFS

J P WILLIS

INFORMATION CIRCULAR No. 14

1995

MAJOR ELEMENTS

Nine major elements, Fe, Mn, Ti, Ca, K, P, Si, Al and Mg (with Ni and Cr when Ni and Cr concentrations exceed ~2000 ppm) are determined using fusion disks prepared according to the method of Norrish and Hutton (1969). The disks are analyzed on a Philips PW1480 wavelength dispersive XRF spectrometer with a Mo/Sc x-ray tube. Fe, Mn and Ti are measured with the tube at 100 kV, 25 mA. The other elements are determined with the tube at 40 kV, 65 mA. Peak only measurements are made on the elements Fe through Mg. Sodium is determined using powder briquettes, the x-ray tube at 40 kV, 65 mA, and with backgrounds measured at -2.00 and +2.00°2θ from the peak position. Analytical conditions are given in Table 1.

Fusion disks made up with 100% Johnson Matthey Specpure SiO_2 are used as blanks for all elements except Si. Fusion disks made up from mixtures of Johnson Matthey Specpure Fe_2O_3 and $CaCO_3$ are used as blanks for Si. Intensity data are collected using the Philips X40 software. Matrix corrections are made on the elements Fe through Mg using the de Jongh model in the X40 software. Theoretical alpha coefficients used in the de Jongh model for all other elements on the analyte element are calculated using the Philips on-line ALPHAS programme. Na_2O is not included in the matrix corrections in de Jongh model, and no matrix corrections are made to the sodium intensities.

Table 1. Analytical conditions for determination of major elements using a Philips PW1480 WDXRF spectrometer.

Element/ line	Collimator	Crystal	Detector	PHS LWL	PHS UPL	Counting time (s)	Concentration range *	RMS	No. of standards
FeKα	F	LiF(220)	FL	16	70	150	0 - 17	0.118	14
MnKα	F	LiF(220)	FL	15	70	150	0 - 0.22	0.005	14
TiKα	F	LiF(200)	FL	28	70	150	0 - 2.75	0.020	14
CaKα	F	LiF(200)	FL	36	70	20	0 - 12.5	0.037	14
K Kα	F	LiF(200)	FL	36	70	50	0 - 15.5	0.057	14
P Kα	C	GE(111)	FL	25	75	100	0 - 0.36	0.008	14
SiKα	C	PE(002)	FL	32	74	100	0 - 100	0.408	14
AlKα	C	PE(002)	FL	25	75	80	0 - 17.5	0.136	14
MgKα	F	PX-1	FL	30	74	150	0 - 46	0.095	14
NaKα	F	PX-1	FL	30	78	200	0 - 9	0.189	15

* = all concentrations expressed as wt% oxide

$$RMS = \sqrt{\frac{1}{n - k} \sum \left(Conc_{given} - Conc_{calc}\right)}$$

where

n = no. of standards
k = no. of calibration coefficients, *i.e.* 2, the slope and intercept of the calibration line.
$Conc_{given}$ = recommended concentration for an element in a standard
$Conc_{calc}$ = concentration of an element calculated from the best-fit calibration line

First order calibration lines, with intercept, are calculated using all data points, including blanks. Calibration plots for Fe_2O_3, CaO, SiO_2 and MgO are given in Figures 1 - 4.

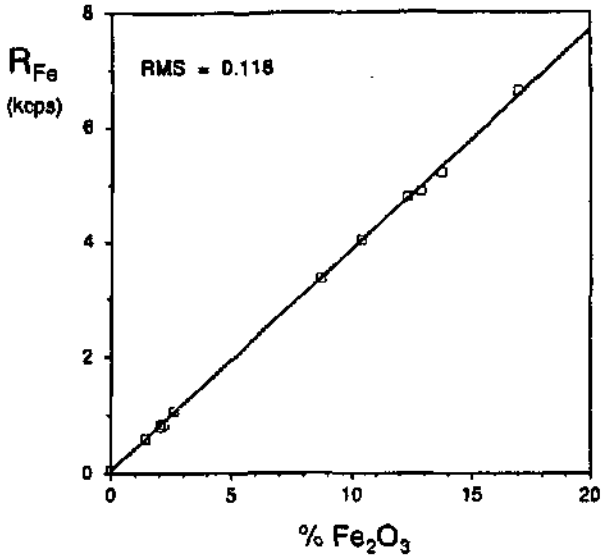


Figure 1. **Calibration plot for Fe_2O_3 using "Norrish" fusion disks.**

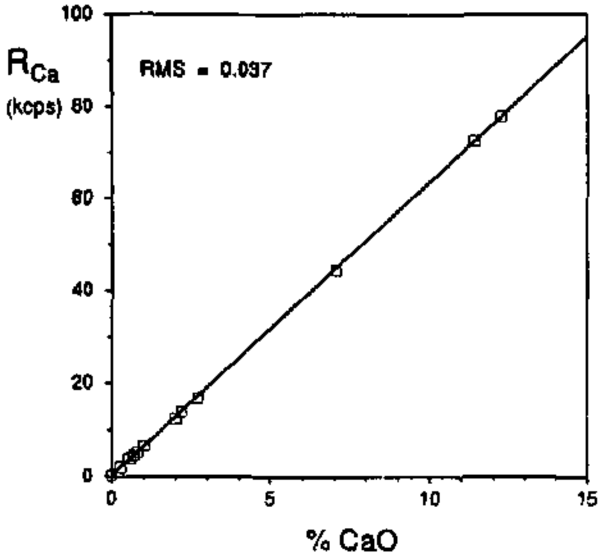


Figure 2. **Calibration plot for CaO using "Norrish" fusion disks.**

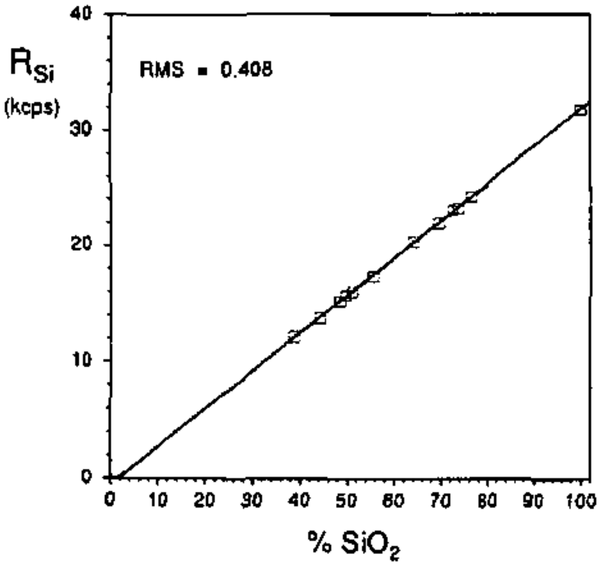


Figure 3. **Calibration plot for SiO_2 using "Norrish" fusion disks.**

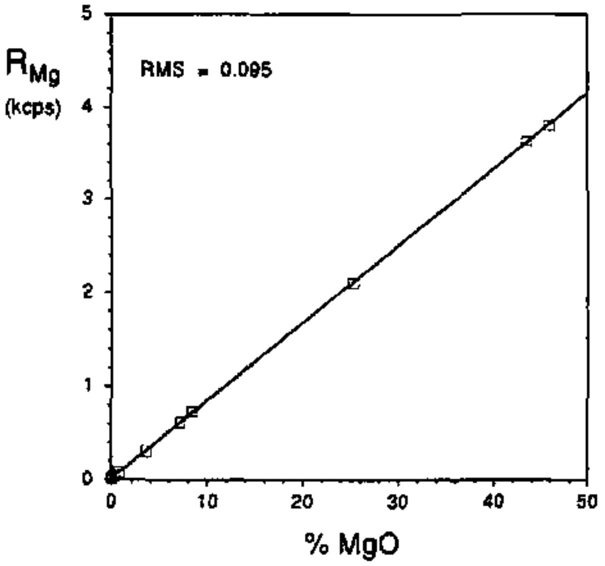


Figure 4. **Calibration plot for MgO using "Norrish" fusion disks.**

TRACE ELEMENTS

Trace elements are determined on powder briquettes using a series of x-ray tubes. Analytical conditions are listed in Tables 2 and 3.

Table 2. X-ray tubes and tube and x-ray path settings for the determination of trace elements using a Siemens SRS303AS and Philips PW1480 WDXRF spectrometer.

Spectrometer	Element/line	X-ray tube		X-ray path
		Target	kV - mA	
SRS303AS	RhKαC	Rh	60 45	Vacuum
SRS303AS	MoKα	Rh	60 45	Vacuum
SRS303AS	NbKα	Rh	60 45	Vacuum
SRS303AS	ZrKα	Rh	60 45	Vacuum
SRS303AS	Y Kα	Rh	60 45	Vacuum
SRS303AS	SrKα	Rh	60 45	Vacuum
SRS303AS	U Lα_1	Rh	60 45	Vacuum
SRS303AS	RbKα	Rh	60 45	Vacuum
SRS303AS	ThLα_1	Rh	60 45	Vacuum
SRS303AS	PbLβ_1	Rh	60 45	Vacuum
PW1480	ZnKα	Au	60 45	Vacuum
PW1480	CuKα	Au	60 45	Vacuum
PW1480	NiKα	Au	60 45	Vacuum
PW1480	CoKα	W	50 55	Vacuum
PW1480	MnKα	W	50 55	Vacuum
PW1480	CrKα	W	50 55	Vacuum
PW1480	V Kα	W	50 55	Vacuum
PW1480	BaLα_1	Cr	50 55	Vacuum
PW1480	ScKα	Cr	50 55	Vacuum

Table 3. Instrumental conditions for determination of trace elements using a Siemens SRS303AS and Philips PW1480 WDXRF spectrometer.

Element /line	Collimator	Crystal	Detector	PHS LWL UPL	Counting time (s)	Background position(s) relative to peak position	Concentration range *
RhKαC	F	LiF(220)	SC	0.6 1.5	200		
MoKα	F	LiF(200)	SC	0.7 1.7	160	-0.8 +0.65	0 - 5.2
NbKα	F	LiF(200)	SC	0.5 1.6	160		0 - 268
ZrKα	F	LiF(200)	SC	0.5 1.6	160		0 - 1210
Y Kα	F	LiF(200)	SC	0.5 1.6	160	-0.61 +0.54	0 - 143
SrKα	F	LiF(200)	SC	0.5 1.6	160	+0.60	0 - 440
U Lα_1	F	LiF(200)	SC	0.5 1.6	160		0 - 15
RbKα	F	LiF(200)	SC	0.5 1.6	160	+0.53	0 - 530
ThLα_1	F	LiF(200)	SC	0.5 1.6	160		0 - 51
PbLβ_1	F	LiF(200)	SC	0.4 1.4	160	+1.27	0 - 40
ZnKα	F	LiF(220)	FS	20 80	200	-1.08 +4.24	0 - 235
CuKα	F	LiF(220)	FS	20 80	200	+4.44	0 - 227
NiKα	F	LiF(220)	FS	20 80	200	+2.52	0 - 630
CoKα	F	LiF(220)	FL	15 75	200	+1.00	0 - 116
MnKα	F	LiF(220)	FL	15 75	200	-2.30 +4.70	0 - 1700
CrKα	F	LiF(220)	FL	15 75	200	-4.10 +2.90	0 - 465
V Kα	F	LiF(220)	FL	13 67	200	+3.40	0 - 640
BaLα_1	F	LiF(200)	FL	25 75	200	-5.20	0 - 2680
ScKα	F	LiF(200)	FL	25 75	200	-2.78	0 - 54

* = all concentrations expressed as part per million (ppm or mg.kg^{-1})

The RhKα Compton peak is used to determine the mass absorption coefficients of the specimens at the RhKαC wavelength (Figure 5) and the calculated values are used to correct for absorption effects on the Mo, Nb, Zr, Y, Sr, U, Rb, Th, Pb, Zn, Cu and Ni analyte wavelengths. Primary and secondary mass absorption coefficients for the Co, Mn, Cr, V, Ba and Sc analyte wavelengths are calculated from major element compositions using the tables of Heinrich (1986). Mass absorption coefficient corrections are made to the net peak intensities, (gross peak intensities corrected for dead time losses, background and spectral overlap), to correct for absorption differences between standards and specimens. No corrections are made for enhancement, which could be small but significant (<~5% relative) for the elements Cr, V, Ba and Sc in certain specimens, depending on their concentrations of Fe, Mn and Ti.

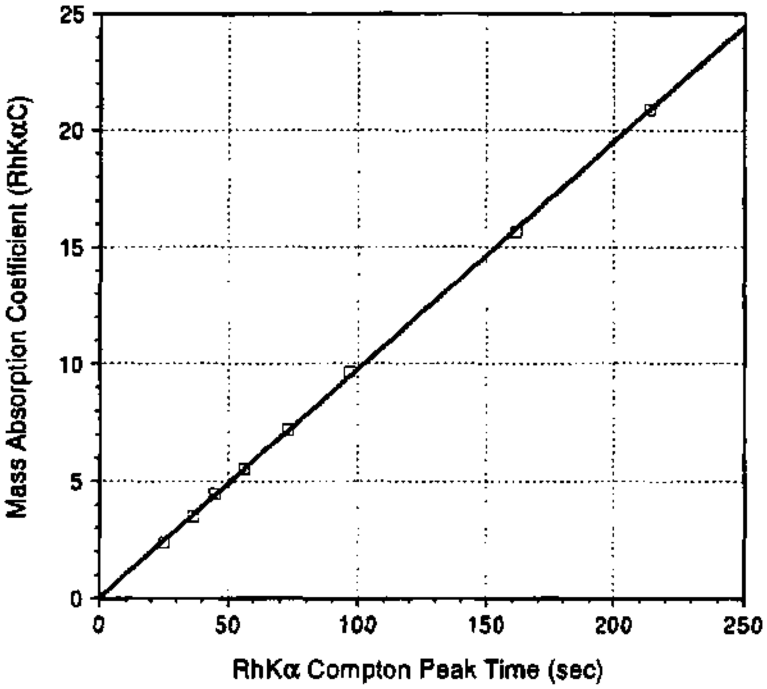


Figure 5. **Calibration line for determination of mass absorption coefficients at the RhKαC wavelength. RhKαC peak time is the time required to accumulate 400 000 counts on the RhKαC peak using the fixed count method.**

Measured intensity data are processed through the computer program TRACE to correct gross peak intensities for background and spectral overlap and to make mass absorption coefficient corrections according to the methods outlined in Duncan *et al.* (1984). First order calibration lines with zero intercept are calculated using six or more international rock standard reference materials (SRMs) for each element. The one standard deviation (1 σ) error due to counting statistics and the lower limit of detection is calculated for each element in each specimen.

Table 4 lists the given and calculated concentrations for selected elements in a number of rock SRMs, which gives an indication of the accuracy of the trace element data. Table 5 lists the one standard deviation counting error and lower limit of detection for each of the elements in an acidic (low Fe, Ca and Mg, high Si) rock and in a mafic (high Fe, Ca and Mg, low Si) rock. Because of the difference in mass absorption coefficients between the two types of specimen the counting error and lower limit of detection will be slightly higher in mafic rock specimens. The two examples given cover the range of mass absorption coefficients found in the majority of geological rock, soil and sediment specimens.

The counting error and lower limit of detection are calculated using the following formulae:

$$1\,\sigma \ \mathit{error}\ (\mathit{in\ ppm}) \ = \ \mathit{Conc} \times \frac{\sqrt{\dfrac{I_p}{T_p} + \dfrac{I_b}{T_b}}}{I_n}$$

and $$LLD\ (in\ ppm) = \frac{6}{m}\sqrt{\frac{I_b}{T_{total}}}$$

where Conc = calculated concentration in ppm
m = net peak / concentration
I_p = gross peak count rate in cps
I_b = background count rate under the peak in cps
I_n = $I_p - I_b$ = true net peak count rate in cps
T_p = counting time for peak in seconds
T_b = total counting time for background in seconds
T_{total} = $T_p + T_b$

N.B. I_b is the calculated background *plus* any corrections for spectral interference, and is equal to $I_p - I_n$.

Table 4. Given and calculated trace element data (all values in ppm) for some rock SRMs.

Element	QLO-1		BHVO-1		W-2		STM-1		BIR-1	
	Given	Calc	Given	Calc	Given	Calc	Given	Calc	Given	Calc
Mo	2.6	3.5	1.0	0.8	(0.6	0.5	5.2	3.1	(0.5	<0.8
Nb	10	11	19	19	7.9	7.4	268	267	0.6	0.9
Zr	185	190	179	181	94	95	1210	1220	16	19
Y	24	25	28	28	24	23	46	47	16	17
Sr	336	329	403	395	194	195	700	689	108	109
U	1.9	2.3	0.4	<1.6	0.5	<1.2	9.1	8.8	0.01	<1.2
Rb	74	71	11	9.7	20	20	118	114	0.3	<0.6
Th	4.5	4.0	1.1	1.8	2.2	2.7	31	31	0.03	<1.5
Pb	20	20	2.6	3.1	9.3	8.5	18	17	3	3.1
Zn	61	61	105	106	77	79	235	242	71	69
Cu	29	25	136	139	103	108	(4.6	2.1	126	132
Ni	(5.8	1.8	121	127	70	72	(3	1.7	166	170
Co	7.2	7.6	45	44	44	43	0.9	<1.9	51	52
Mn	720	690	1300	1290	1260	1240	1700	1600	1320	1280
Cr	(3.2	3.6	289	312	93	100	(4.3	3.2	382	404
V	54	44	317	314	262	257	(8.7	<1.6	313	306
Ba	1370	1430	139	138	182	191	560	589	7.0	10
Sc	8.9	10.3	31.8	33.9	35	36	0.6	0.5	44	39

(n.n = value given for information only

Table 5. **Calculated trace element data, 1 σ counting error and lower limit of detection (all values in ppm) for two rock specimens having different mass absorption coefficients.**

Element	JR-2			JB-1a		
	Calc	1 σ	LLD	Calc	1 σ	LLD
Mo	4.1	0.2	0.6	1.8	0.3	0.7
Nb	19	0.1	0.4	28	0.2	0.5
Zr	87	0.1	0.3	152	0.2	0.4
Y	51	0.2	0.6	24	0.2	0.6
Sr	8.2	0.1	0.4	444	0.3	0.5
U	11	0.3	0.9	2.3	0.4	1.2
Rb	303	0.2	0.4	39	0.2	0.6
Th	34	0.4	1.1	9.8	0.5	1.4
Pb	24	0.5	1.3	7.5	0.6	1.8
Zn	28	0.2	0.6	84	0.4	0.9
Cu	1.1	0.3	0.8	55	0.5	1.1
Ni	1.3	0.3	0.8	139	0.7	1.3
Co	<1.2	0.4	1.2	37	0.9	2.3
Mn	878	1.7	1.2	1100	2.0	1.8
Cr	1.6	0.4	1.3	406	1.5	2.0
V	1.7	0.4	1.2	193	1.4	3.0
Ba	28	0.6	1.5	523	1.8	3.3
Sc	6.0	0.2	0.5	26	0.4	0.9

REFERENCES

Duncan, A R, Erlank, A J and Betton, P J (1984) Analytical techniques and database descriptions. *Spec. Publ. geol. Soc. S. Afr.*, **13**, Appendix 1, 389-395.

Heinrich, K F J (1986) Mass absorption coefficients for electron probe microanalysis. In: *Proc. 11th Int. Congress on X-ray Optics and Microanalysis, London, Canada*, J B Brown and R H Packwood (Eds).

9.4 Appendix A4. Whole rock major element analyses

Concentrations are in weight %, apart from F which is in parts per million. '*n/a*' is not available. (N) is Nebo Granite, (L) is Lebowa Granite. The total for RO6 includes 6.22 wt% SrO.

No.	Site Name	Rock Type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O-	LOI	F	Total
RO1	Bapong	Quartzite	96.85	0.06	0.17	1.15	0.01	0.01	0.14	0.02	0.06	0.10	0.07	0.10	*n/d*	98.7
RO2	Moreteletsi	Monzonite	60.86	0.42	15.05	9.69	0.16	5.88	7.28	1.07	0.28	0.09	0.10	*n/d*	216	100.9
RO3	Green Tweed	Syenite	58.44	1.09	17.17	5.42	0.31	0.73	1.37	8.28	5.52	0.10	0.25	1.36	5310	100.6
RO4	Thabayadiotsa	Syenite	47.76	0.77	15.79	6.25	0.80	0.44	7.03	8.9	5.06	0.06	0.18	4.35	16431	99.0
RO5	Kubu drive Quarry	Syenite	57.31	0.22	16.72	10.38	0.47	0.10	1.15	6.08	4.59	0.04	0.64	1.36	6958	99.8
RO6	Moepo	Fluorite ore	10.67	1.29	2.57	13.55	1.09	1.00	31.60	1.28	0.07	6.94	0.52	14.07	80514	98.9
RO7	N of Pilanesberg	Norite	53.34	0.15	18.58	7.55	0.15	*6.91*	*11.79*	2.67	0.22	*n/d*	0.05	0.11	183	101.5
RO8	Mabeleapodi	Alkali granite	59.16	1.06	14.03	8.64	0.56	0.70	1.95	2.8	7.76	0.10	0.67	1.33	1061	98.9
RO9	Lesung	Norite	52.43	0.22	17.24	7.65	0.16	7.45	13.10	2.38	0.23	0.01	0.08	0.08	153	101.0
RO10	Lesung	Magnetite ore	1.53	14.22	4.10	78.87	0.20	0.07	0.03	*n/d*	0.03	*n/d*	0.34	1.18	*n/d*	100.6
RO11	Modike	Alkali granite (N)	73.88	0.18	12.25	3.33	0.04	0.07	0.62	3.33	5.54	0.04	0.18	0.36	489	99.9
RO12	Suncity-Lesung	Norite	51.99	0.18	18.74	7.37	0.14	6.92	12.93	2.4	0.18	*n/d*	0.12	0.06	221	101.1
RO13	Smaldale Farm	Dolomitic limestone	9.09	*n/d*	0.08	0.75	0.27	19.09	27.65	*n/d*	0.01	*n/d*	0.17	42.38	400	99.5
RO14	Tamboetieshoek	Ironstone	31.91	0.22	4.83	57.46	2.66	0.21	0.91	*n/d*	0.08	0.5	0.13	1.07	168	100.0
RO15	Dwarsberg	Sandstone	94.69	0.10	2.16	1.29	0.01	0.04	0.03	0.08	0.54	*n/d*	0.11	0.49	*n/d*	99.5
RO16	Rampapaanspoort	Norite	53.12	0.32	10.62	11.30	0.18	16.13	7.11	1.65	0.41	0.05	0.05	*n/d*	205	101.0
RO17	*Holfontein*	Garnet-biotite hornfels	61.26	0.86	17.98	10.54	0.12	3.59	0.78	1.74	2.88	0.07	0.09	0.63	774	100.6
RO18	Leboaneng	Ironstone	42.98	0.01	0.11	55.58	0.06	*n/d*	0.04	*n/d*	0.03	0.04	0.13	1.39	*n/d*	100.4
RO19	GaRamoloreng-	Dolomite	0.32	0.01	0.13	1.96	0.87	19.47	30.16	*n/d*	*n/d*	0.13	0.15	45.39	509	98.6
RO20	Makoropeja	Granite (L)	76.21	0.12	11.85	3.43	0.02	0.14	0.24	5.27	1.92	0.07	0.22	0.94	163	100.4
RO21	Northblock 7	Granite (L)	74.78	0.13	11.91	2.85	0.02	0.03	0.45	3.43	5.78	*n/d*	0.14	0.62	2849	100.4

No.	Site Name	Rock Type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O-	LOI	F	Total
RO22	Northblock 10	Granite (L)	74.6	0.16	12.33	3.01	0.01	0.2	0.34	3.52	5.34	*n/d*	0.40	0.57	1924	100.7
RO23	Slipfontein	Quartz pegmatite	98.49	*n/d*	0.04	1.19	0.01	*n/d*	*n/d*	0.05	0.01	*n/d*	0.06	*n/d*	*n/d*	99.9
RO24	Kwarriekraal	Granophyre					0.02	0.06	0.34	3.25	6.76	0.02			950	
RO25	Kenkelbos	Alkali granite (L)	75.32	0.17	11.45	3.33	0.02	0.09	0.81	3.59	4.31	*n/d*	0.24	1.07	2527	100.7
RO26	Blokspruit	Alkali granite (L)	77.58	0.40	4.38	12.95	0.21	0.26	0.14	0.03	1.46	0.03	0.33	0.56	1260	98.5
RO27	Blokspruit	Alkali granite (L)	76.58	0.06	12.00	1.59	0.01	0.08	0.49	2.92	6.00	*n/d*	0.33	0.56	3351	101.0
RO28	Borakalalo	Sandstone	89.23	0.17	6.17	1.08	0.01	0.19	0.03	0.05	1.93	0.02	0.21	0.78	735	99.9
RO29	Sephai	Limestone	6.02	0.05	0.74	0.42	0.03	2.84	47.87	*n/d*	0.08	*n/d*	1.52	39.79	858	99.4
RO30	GaTsogwe	Granite (N)	75.81	0.21	11.35	3.29	0.04	0.10	0.72	3.49	4.95	0.02	0.16	0.32	480	100.5
RO31	Rashoop	Granophyre	74.99	0.22	11.56	3.77	0.04	0.19	0.11	2.91	4.99	0.01	0.48	0.80	127	100.1
RO32	Mpatsetlha	Sandstone	95.76	0.05	1.68	1.34	0.01	0.05	0.03	0.04	0.54	0.01	0.11	0.19	119	99.8
RO33	Mpatsetlha	Mudstone	59.27	0.57	11.99	4.43	0.16	1.55	15.15	1.62	4.29	0.12	0.18	0.81	464	100.2
RO34	Leeupoort Tin	Felsite	73.40	0.48	13.05	2.15	0.04	0.88	0.61	5.44	2.06	0.04	0.18	1.48	2171	100.0
RO35	Tooyspruit	Feldspathic sandstone	89.97	0.05	4.58	0.77	0.01	0.12	0.04	0.10	3.99	0.02	0.17	0.05	373	99.9
RO36	Kwaggafontein	Greenschist	65.81	0.38	10.70	7.48	0.07	5.52	4.55	1.79	2.01	0.08	0.22	1.55	4981	100.7
RO37	Rietfontein	Alkali granite (N)	75.78	0.21	12.19	1.54	0.01	0.05	0.38	3.88	5.62	0.02	0.29	0.39	2570	100.6
RO38	Rietfontein	Alkali granite (N)	73.89	0.19	12.19	3.09	0.04	0.09	0.94	4.01	5.30	0.01	0.09	0.28	2284	100.3
RO39	Sutelong	Quartzite	96.77	0.06	0.88	1.10	0.01	0.01	0.10	0.40	0.37	*n/d*	0.08	0.10	132	99.9
RO40	Dikebu	Granite (L)	76.45	0.20	12.36	1.35	0.01	0.05	0.15	3.56	5.83	0.01	0.23	0.46	520	100.7
RO41	Pretoria Saltpan	Granite (N)	74.15	0.26	12.37	2.25	0.02	0.11	0.19	2.53	6.57	0.01	0.31	1.08	410	99.9
RO42	Pretoria Saltpan	Granite (N)	73.99	0.22	12.05	3.58	0.05	0.13	0.78	3.56	5.30	0.03	0.11	0.48	437	100.3

9.5 Appendix A5. Fluorine-bearing minerals in thin section

The percentage of the four main fluorine-bearing mineral groups was estimated in thin section using an optical microscope. Calculating the maximum F content of each mineral from the chemical formulae in Deer *et al.* (1977) gives the maximum F concentration in the whole rock after multiplication by the appropriate estimated percentages. The actual F concentration is shown for comparison.

No.	Rock Type	%Fluorite	%Apatite	%Mica	%Hornblende	F section (F ppm)	F XRF ppm
1	Quartzite	0	0	0	0	0	40
2	Monzonite	0	0	5	0	7000	162
3	Syenite	1	0.1	5	1	12328	5310
4	Syenite	1	0	0	5	7150	16431
5	Syenite	1	0	0.1	0	4940	6958
6	Fluorite ore	10	0.1	0	0	48058	80514
7	Norite	0	0	0	0	0	183
8	Alkali granite	0	0	0	10	4700	1061
9	Norite	0	0	0	0	0	153
10	Magnetite ore	0	0	0	0	0	-320
11	Alkali granite	0	0	2	0.1	2847	489
12	Norite	0	0	0	0	0	221
13	Dolomitic limestone	0	0	0	0	0	400
14	Ironstone	0	0	0	0	0	168
15	Sandstone	0	0	0	0	0	24
16	Norite	0	0	0	0	0	205
17	Garnet-biotite hornfels	0	0	20	0	28000	774
18	Ironstone	0	0	0	0	0	-318
19	Dolomite	0	0	0	0	0	509
20	Granite	0	0		0	0	216
21	Granite	0	0	2	0	2800	2849
22	Granite	0	0	5	0	7000	1924
23	Quartz	0	0	0	0	0	39
24	Granophyre	0	0	2	0	2800	949
25	Alkali granite	0.1	0	1	0	1880	2527
26	Alkali granite	0	0	0	0	0	1260

No.	Rock Type	%Fluorite	%Apatite	%Mica	%Hornblende	F section (F ppm)	F XRF ppm
27	Alkali granite	1	0.1	0	0	4858	3351
28	Sandstone	0	0	0	0	0	735
29	Limestone	0	0	0	0	0	858
30	Granite	0	0	0.1	3	1550	480
31	Granophyre	0	0	0.1	2	1080	127
32	Sandstone	0	0	0	0	0	119
33	Mudstone	10	0	0	0	48000	464
34	Felsite	0	0	0	0	0	2171
35	Feldspathic sandstone	0	0	0.1	0	140	373
36	Greenschist	0	0	0	0	0	4981
37	Alkali granite	1	0	0.1	0	4940	2570
38	Alkali granite	1	0	0	0	4800	2284
39	Sandstone	0	0	0	0	0	132
40	Granite	0	0	0	0	0	520
41	Granite	0	0	0.1	0	140	410
42	Granite	0.1	0	1	3	3290	437

9.6 Appendix A6. Electron microprobe analyses of minerals from rock types in the study area

Concentrations in weight percent, LLD is the mean lower limit of detection, ***n/d*** is not detected and K-flsp is potassium feldspar.

Table A6.1 Analyses of mica and amphiboles from miscellaneous rock types in the field area.

Sample No.	**Mineral**	**F**	**Na_2O**	**K_2O**	**SiO_2**	**TiO_2**	**Al_2O_3**	**Cr_2O**	**FeO**	**MnO**	**MgO**	**CaO**	**Total**
	LLD:	**0.17**	**0.04**	**0.03**	**0.06**	**0.04**	**0.05**	**0.05**	**0.09**	**0.08**	**0.03**	**0.03**	
RO3	Amph	2.69	4.11	1.32	45.39	2.79	6.46	*n/d*	14.04	1.02	12.82	10.10	100.74
RO3	Amph	2.38	4.24	1.39	45.66	2.55	6.16	*n/d*	15.71	1.06	12.10	9.62	100.87
RO3	Amph	*n/d*	11.65	*n/d*	51.65	3.04	0.98	*n/d*	27.12	0.46	0.60	2.98	98.48
RO3	Amph	1.33	8.71	2.28	50.72	1.30	1.12	*n/d*	24.69	4.00	4.65	0.36	99.16
RO3	Amph	2.47	3.95	1.36	44.47	3.09	6.85	*n/d*	13.74	1.01	12.47	10.33	99.74
RO4	Amph	*n/d*	3.92	*n/d*	47.67	0.58	1.35	*n/d*	25.67	1.71	2.05	16.61	99.56
RO4	Mica	*n/d*	12.97	5.76	43.55	*n/d*	32.83	*n/d*	1.82	*n/d*	*n/d*	0.30	97.23
RO4	Amph	*n/d*	4.56	*n/d*	50.23	0.22	0.45	*n/d*	23.43	1.60	3.10	16.10	99.69
RO8	K-Flsp	*n/d*	0.30	15.79	65.19	*n/d*	17.05	*n/d*	1.22	0.35	*n/d*	0.53	100.43
RO11	Mica	*n/d*	0.10	8.62	33.14	3.33	13.15	*n/d*	35.76	0.36	0.32	*n/d*	94.78
RO11	Mica	*n/d*	0.10	8.10	32.83	3.42	13.72	*n/d*	35.97	0.30	0.38	0.06	94.88
RO11	Mica	*n/d*	0.10	8.25	33.43	3.59	12.96	*n/d*	35.71	0.33	0.55	0.23	95.15
RO11	Mica	*n/d*	0.11	6.43	33.94	2.57	14.01	*n/d*	34.71	0.20	0.77	0.18	92.92
RO11	Mica	*n/d*	*n/d*	7.93	33.73	3.16	12.69	*n/d*	36.90	0.36	0.67	0.2	95.64
RO11	Mica	*n/d*	0.07	8.04	32.76	3.35	13.24	*n/d*	36.59	0.21	0.20	0.06	94.52
RO11	Amph	0.45	2.01	1.41	38.79	1.55	8.92	*n/d*	33.25	0.55	0.50	10.46	97.89

Sample No.	Mineral	F	Na_2O	K_2O	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Total
	LLD:	0.17	0.04	0.03	0.06	0.04	0.05	0.05	0.09	0.08	0.03	0.03	
RO11	Amph	0.65	2.01	1.45	39.27	1.69	8.80	*n/d*	33.63	0.58	0.55	10.61	99.24
RO11	Amph	0.72	2.07	1.36	39.41	1.66	8.48	*n/d*	34.19	0.46	0.54	10.41	99.30
RO11	Mica	*n d*	0.30	7.05	32.81	2.68	12.97	*n/d*	35.27	0.26	1.10	0.15	92.59
RO11	Mica	*n d*	*n d*	7.99	33.15	3.22	12.50	*n/d*	35.21	0.25	0.76	0.72	93.80
RO22	Amph	0.30	0.17	3.20	37.95	0.30	23.07	*n/d*	20.71	0.14	4.07	0.19	90.10
RO24	Mica?	1.27	0.05	*n d*	44.14	*n/d*	38.45	*n/d*	1.48	*n/d*	0.05	0.30	85.74
RO24	Mica?	1.36	0.06	*n d*	43.36	*n/d*	39.31	*n/d*	0.74	*n/d*	0.04	0.31	85.18
RO24	Mica?	*n d*	*n d*	*n d*	42.20	*n/d*	23.63	0.84	7.27	0.28	18.76	4.10	97.08
RO25	Amph	*n d*	0.13	3.64	23.98	*n/d*	13.60	*n/d*	42.77	*n/d*	0.84	0.15	85.11
RO25	Mica	*n d*	0.12	4.83	29.89	*n/d*	14.78	*n/d*	33.1	*n/d*	1.11	0.15	83.98
RO25	Amph	0.19	0.17	2.92	20.80	0.29	15.96	*n/d*	46.23	*n/d*	0.91	0.17	87.64
RO25	Mica	*n d*	0.13	3.73	32.48	0.20	18.93	*n/d*	32.13	*n/d*	0.98	0.17	88.75
RO30	Mica	*n d*	*n d*	8.33	33.44	2.51	11.63	*n/d*	38.58	*n/d*	1.22	*n/d*	95.71
RO30	Mica	*n d*	*n d*	8.12	34.14	2.50	11.40	*n/d*	37.19	0.14	1.17	*n/d*	94.66
RO30	Mica	*n d*	0.10	7.45	33.68	2.02	12.01	*n/d*	36.47	*n/d*	1.22	0.11	93.06
RO30	Mica	*n d*	0.13	7.40	33.26	2.02	11.66	*n/d*	36.75	*n/d*	1.24	0.16	92.62
RO30	Mica	*n d*	0.08	7.91	34.09	2.01	12.03	*n/d*	36.81	0.14	1.26	0.08	94.41
RO30	Mica	*n d*	*n d*	7.95	34.03	1.44	11.43	*n/d*	39.53	*n/d*	0.83	*n/d*	95.21
RO30	Mica	*n d*	*n d*	7.87	35.11	1.39	13.37	*n/d*	35.56	*n/d*	0.67	0.06	94.03
RO30	Mica	*n d*	0.11	7.64	35.73	2.54	12.78	*n/d*	33.95	*n/d*	0.6	0.05	93.4

Sample No.	Mineral	F	Na_2O	K_2O	SiO_2	TiO_2	Al_2O_3	Cr_2O	FeO	MnO	MgO	CaO	Total
	LLD:	0.17	0.04	0.03	0.06	0.04	0.05	0.05	0.09	0.08	0.03	0.03	
RO42	Mica	*n/d*	0.1	6.89	31.94	0.7	12.86	*n/d*	36.42	*n/d*	0.56	0.06	89.53
RO42	Mica	*n/d*	0.22	4.97	35.54	0.29	15.57	*n/d*	30.28	*n/d*	0.57	0.11	87.55

Table A6.2 Analyses of Mica in sample RO17, including the analysis of Cl.

	F	Cl	Na	K	Si	Ti	Al	Cr	Fe	Mn	Mg	Ca	Total
LLD:	0.17		0.04	0.02	0.06	0.04	0.05	0.05	0.09	0.08	0.03	0.03	
	n/d	0.16	0.16	9.24	35.33	4.62	17.72	0.14	22.71	*n/d*	8.00	*n/d*	98.08
	n/d	0.13	0.12	9.19	35.29	4.55	18.08	0.14	22.66	*n/d*	8.13	*n/d*	98.29
	n/d	0.15	0.12	9.25	34.73	4.76	17.84	0.12	22.39	*n/d*	7.94	*n/d*	97.3
	0.35	0.16	0.08	9.53	35.25	4.32	18.66	0.14	21.7	*n/d*	7.98	*n/d*	98.17

Table A6.3 Analyses of carbonate minerals in sample RO6 (Pilanesberg).

Mineral	$CaCO_3$	$FeCO_3$	$MgCO_3$	$MnCO_3$	$SiCO_3$	$SrCO_3$	$BaCO_3$	Total
LLD:	0.01	0.22	0.20	0.20	0.13	0.16	0.14	
Cal	93.61	*n/d*	*n/d*	*n/d*	*n/d*	4.29	*n/d*	97.9
Cal	95.24	1.37	*n/d*	1.26	*n/d*	0.64	*n/d*	98.51

Mineral	**$CaCO_3$**	**$FeCO_3$**	**$MgCO_3$**	**$MnCO_3$**	**$SiCO_3$**	**$SrCO_3$**	**$BaCO_3$**	**Total**
LLD:	**0.01**	**0.22**	**0.20**	**0.20**	**0.13**	**0.16**	**0.14**	
Cal	91.95	*n/d*	*n/d*	*n/d*	*n/d*	6.00	*n/d*	97.95
Cal	91.46	*n/d*	*n/d*	*n/d*	*n/d*	7.28	*n/d*	98.74
Cal	90.64	*n/d*	*n/d*	*n/d*	*n/d*	8.01	*n/d*	98.65
Cal	91.85	*n/d*	*n/d*	*n/d*	*n/d*	7.49	*n/d*	99.34
Cal	91.63	*n/d*	*n/d*	*n/d*	*n/d*	7.07	*n/d*	98.7
Cal	91.99	*n/d*	*n/d*	*n/d*	*n/d*	7.24	*n/d*	99.23
Cal	86.80	*n/d*	*n/d*	*n/d*	*n/d*	11.10	*n/d*	97.9
Cal	99.10	1.15	*n/d*	1.28	*n/d*	0.28	*n/d*	101.81
Cal	95.67	1.40	*n/d*	2.06	*n/d*	0.51	*n/d*	99.64
Cal	94.97	1.25	*n/d*	1.94	*n/d*	0.60	*n/d*	98.76
Cal	95.94	1.58	*n/d*	1.99	*n/d*	0.51	*n/d*	100.02
Mean	**93.14**	**0.52**	**0.0**	**0.66**	**0.0**	**4.69**	**0.0**	**99.01**
Stron	14.60	*n/d*	*n/d*	*n/d*	*n/d*	87.58	*n/d*	102.18
Stron	14.53	*n/d*	*n/d*	*n/d*	*n/d*	87.27	*n/d*	101.8
Stron	7.15	*n/d*	*n/d*	*n/d*	*n/d*	95.12	*n/d*	102.27
Mean	**12.09**	**0.00**	**0.00**	**0.00**	**0.00**	**89.99**	**0.00**	**102.08**
Mixed	56.83	19.59	13.28	7.56	0.70	0.93	*n/d*	98.89
Mixed	54.34	27.06	11.9	7.06	0.27	0.32	*n/d*	100.95
Mixed	51.82	17.21	17.79	9.90	1.69	0.60	*n/d*	99.01
Mean	**54.33**	**21.29**	**14.32**	**8.17**	**0.89**	**0.62**	**0.00**	**99.62**

Table A6.4 Analysis of apatites from sample RO6 (Pilanesberg). Cl, FeO, MnO and MgO were not present above the detection limit (0.026 wt% for Cl and approximately 0.08 wt% for the others). H_2O estimated assuming F + OH = 2.0 in structural formula.

P_2O_5	CaO	SrO	F	Subtotal	O=F	H_2O	Total
39.91	51.72	2.94	3.35	97.92	1.41	0.11	96.62
39.93	50.54	4.55	3.08	98.10	1.30	0.23	97.03
39.21	49.70	6.78	3.60	99.29	1.52	0	99.29
39.89	51.47	3.94	2.60	97.90	1.09	0.47	97.28
40.02	49.64	6.76	2.64	97.82	1.11	0.45	98.40
40.07	51.61	2.59	3.55	97.82	1.49	0.01	96.34
39.82	51.13	5.77	2.67	99.39	1.12	0.44	98.71
39.72	50.87	4.71	2.93	98.23	1.23	0.31	97.31
40.40	51.46	3.63	2.45	97.94	1.03	0.55	97.46
40.18	50.68	5.30	2.47	98.63	1.04	0.54	98.13

9.7 Appendix A7. Cation, anion, total alkalinity, pH, and TDS values for groundwater samples collected in this study

Major ion analyses of groundwaters. Concentrations in mg/ℓ. Abbreviations: "TDS" = total dissolved solids; "T.alk" = total alkalinity, in mg/ℓ $CaCO_3$. Site i.d. is derived from the 1:50 000 map reference, followed by a sequential number, starting at 10001.

Site id	**Site no., name, description**	**pH**	**TDS**	**Ca^{2+}**	**Mg^{2+}**	**K^+**	**Na^+**	**NO_3^-**	**Cl^-**	**F^-**	**SO_4^{2-}**	**T.Alk**
2526BD10001	1: Bapong, self help garden	6.80	108	8	20	0.7	2	2	1	0.4	4.0	96
2526BD10002	2: Bapong, southern end	6.29	268	31	99	1.5	9	195	35	0.07	6.0	49
2526BD10003	3: Bapong, northern end	5.34	120	11	33	1.4	4	9	6	0.03	4.0	85
2526BB10001	7: Mabeeskraal, middle of village	7.00	82	9	8	1.5	9	2	2	0.03	4.0	66
2526BB10002	8: Mabeeskraal, Marula Park	7.39	270	31	44	2.3	14	50	8	0.04	7.0	168
2526BB10003	9: Mabeeskraal, Mami's house, zone 4	7.15	183	19	23	1.7	17	15	4	0.04	5.0	131
2526BD10004	10: Maologane	7.31	540	74	38	1.8	125	53	99	3.02	14.3	259
2526BD10005	11: Maologane, Joyce's yard	6.93	901	138	50	8.2	204	140	152	2.97	27.6	409
2526BD10006	12: Maologane, Private Yard	9.09	2300	2	2	18.6	1205	2	748	35.3	103.8	775
2526BD10007	13: Maologane, Private yard	6.77	991	87	49	6.0	218	147	256	3.55	39.8	329
2526BD10008	14: Maologane, private yard	6.86	1440	288	111	4.8	289	91	601	1.75	67.0	342
2526BD10009	15: Maologane, Private yard	7.33	*n/a*	1	1	6.9	380	0	72	33.6	18.6	451
2526BD10010	16: Maologane, Dikeme middle school	7.35	612	66	39	1.8	172	17	107	2.72	31.2	354
2526BB10004	17: Raborife, Mr Raborife's yard	6.78	878	31	670	0.4	3	230	114	5.39	66.6	348
2526BB10005	18: Raborife, private	7.47	891	31	652	2.0	4	306	132	0.03	61.0	312
2526BB10006	19: Mmorogong (Tlhatlhaganyane)	7.26	411	60	85	0.7	52	19	7	3.51	3.7	318
2526BB10007	20: Mmorogong, Christoff's yard	7.31	411	67	80	0.5	59	21	11	3.3	22.7	323
2526BB10008	21: Mmorogong, Tapson's yard	7.24	417	51	75	0.7	58	8	7	3.07	20.5	311

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2526BB10009	22: Mmorogong, Johanna's yard	7.09	789	89	44	0.4	258	81	136	3.84	49.2	384
2526BB10010	23: Mmorogong, Witness' yard	7.35	409	73	69	0.6	53	18	8	2.39	4.7	305
2526BB10011	24: Mmorogong, animal gear	7.14	444	61	30	0.0	83	12	12	2.99	7.2	311
2526BB10012	25: Mmorogong, owner absent	7.02	361	75	22	0.5	65	18	8	2.98	22.6	256
2526BB10013	26: Mmorogong, Joseph's yard	7.14	324	51	19	0.0	60	6	11	3.68	4.9	219
2526BB10014	27: Mmorogong, Mthembu's yard	7.15	321	50	18	0.0	51	18	8	3.54	9.7	213
2526BB10015	28: Mmorogong, Sekgwelea's yard	7.10	342	10	2	0.0	8	8	6	3.62	4.7	262
2526BB10016	29: Mmorogong, Master's yard	7.05	373	70	20	0.0	66	1	7	3.2	23.3	274
2526BB10017	30: Mmorogong, Public H/P	7.06	381	72	21	0.6	62	13	26	3.18	12.2	244
2526BB10018	31: Tlhatlhaganyane, Animal gear east	6.95	461	83	74	0.8	49	6	6	4.02	5.7	342
2526BB10019	32: Tlhatlhaganyane	7.38	550	21	265	1.4	8	87	13	0.33	33.2	342
2526BB10020	33: Tlhatlhaganyane	7.20	429	23	172	0.6	5	2	8	0.2	4.8	359
2526BB10021	34: Tlhatlhaganyane, Early learning C	9.75	1060	1	3	5.6	504	16	290	58.4	98.8	360
2527AC10001	35: Ledig, Lena's yard	7.59	253	36	18	2.3	46	28	7	1.93	2.9	146
2527AC10002	36: Ledig, Lydia's yard	7.52	252	11	4	1.5	60	8	22	2.05	4.3	85
2527AC10003	37: Ledig, Pilanesberg seepage spring	7.63	135	60	8	7.6	80	98	50	1.63	10.1	158
2527AC10004	38: Ledig, Esky's yard	7.12	369	46	17	3.0	35	17	6	0.95	2.6	158
2527AC10005	39: Ledig, public	7.29	231	26	5	3.2	71	2	8	2.93	4.6	158
2527AC10006	40: Ledig, Nicholas's yard	6.94	235	30	17	2.5	76	14	8	3.68	2.8	207
2527AC10007	41: Ledig, Joan's yard	7.24	298	15	4	1.8	57	17	9	1.7	6.5	91
2527AC10008	42: Ledig, Phineas's yard	7.20	176	28	5	1.9	66	44	18	1.55	7.6	128
2527AC10009	43: Ledig, Jacob's yard	7.02	249	14	2	3.5	56	1	7	1.54	2.9	122

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527AC10010	44: Ledig, Alexander's yard	7.28	179	15	5	3.3	46	5	6	1.92	3.2	109
2527AC10011	45: Ledig, Zulu section	7.30	156	9	2	2.1	53	4	5	2.26	2.5	109
2527AC10012	46: Ledig, public	7.05	169	26	6	1.1	31	4	6	0.38	5.1	128
2527AC10013	47: Ledig, Onika's yard	6.84	174	11	3	2.3	41	7	5	0.55	3.3	103
2527AC10014	48: Ledig, Katherine's yard	7.12	148	22	5	3.1	57	62	21	2.84	5.4	115
2527AC10015	49: Ledig, Moses' yard	7.16	234	16	4	1.2	38	16	7	1.37	3.1	109
2527AC10016	50: Ledig, Dorothy's yard	7.05	177	40	16	1.1	30	36	18	2.39	10.7	103
2526BB10022	51: Makoshong, northern	7.27	231	21	34	0.7	9	29	6	0.28	7.3	207
2526BB10023	52: Makoshong	7.29	415	38	48	0.8	13	45	30	0.32	16.6	237
2526BB10024	53: Makoshong, next to shop	7.44	285	13	23	0.2	7	13	9	0.35	8.3	189
2526BB10025	54: Makoshong	7.63	192	14	26	0.8	15	21	3	0.24	5.5	128
2526BD10011	55: Mahobieskraal	6.87	48	6	7	0.8	2	1	2	0.08	0.5	33
2526BD10012	56: Mahobieskraal, vegetable garden	7.59	131	16	18	1.5	10	2	3	0.11	2.3	97
2526BB10026	57: Motlhabe, south east	8.14	495	22	143	1.2	27	24	10	0.73	9.2	342
2526BB10027	58: Motlhabe	7.28	515	3	114	1.6	22	79	27	0.24	16.6	280
2526BB10028	59: Motlhabe	7.13	384	52	79	3.5	15	129	24	0.12	19.1	178
2526BB10029	60: Motlhabe	7.09	196	39	15	1.6	15	20	10	0.15	8.4	122
2526BB10030	61: Motlhabe	7.78	470	33	118	2.1	13	26	13	0.11	6.7	329
2526BB10031	62: Ntswana le Metsing	7.72	581	10	171	0.3	14	25	18	0.18	9.8	408
2526BB10032	63: Motlhabe	7.60	542	0	165	0.3	15	32	8	0.14	24.9	408
2427CC10001	64: Sefikile	7.53	571	88	53	1.4	78	32	78	0.23	30.0	329
2526BB10033	65: Makgope Mine	7.82	520	3	145	0.0	12	7	10	0.13	2.1	402

Site id	**Site no., name, description**	**pH**	**TDS**	**Ca^{2+}**	**Mg^{2+}**	**K$^+$**	**Na$^+$**	**NO$_3^-$**	**Cl$^-$**	**F$^-$**	**SO$_4^{2-}$**	**T.Alk**
2526BB10034	66: Makgope mine, domestic supply	7.81	499	4	174	0.5	13	10	6	0.16	2.6	360
2526BB10035	67: Witkleifontein grazing	7.71	478	14	155	0.6	18	29	23	0.34	*n/a*	364
2527AC10017	69: Southeast of Pilanesberg	6.90	248	17	8	0.9	23	2	4	1.93	0.8	73
2527AC10018	70: Southeast of Pilanesberg	7.22	135	53	53	0.8	29	6	7	0.15	9.6	250
2427CC10002	71: Sefikile	6.72	382	11	47	3.1	29	6	26	0.19	22.7	244
2527AA10001	72: Sefikile	6.79	505	423	308	0.0	423	34	50	0.81	32.7	299
2427CC10003	73: Tsweneng, south	7.15	396	60	60	0.8	14	1	0	0.26	0.0	292
2527AA10002	74: Leswaaneng spring	10.36	2010	15	7	25.1	1038	1	928	69.4	167.2	262
2527AA10003	75: Salty spring	10.41	1860	4	2	24.0	870	1	803	67	148.3	286
2527AA10004	76: Lesetlheng, outside chief's house	7.88	356	36	5	3.7	96	45	24	4.77	3.4	195
2527AA10005	77: Ramatshaba	7.63	524	336	197	0.4	511	111	58	2.82	37.0	262
2527AA10006	78: Ramatshaba	7.52	366	26	13	3.8	94	99	28	3.71	1.2	238
2527AA10007	79: Ramatshaba	8.88	219	5	2	1.1	83	0	96	3.85	9.6	49
2527AA10008	80: Ramatshaba	7.66	604	71	56	2.6	153	108	28	0.81	71.2	323
2527AA10009	81: north of Pilanesberg	7.44	404	26	39	1.5	81	32	7	1.45	15.7	268
2527AA10010	82: north of Pilanesberg	7.99	186	37	12	1.7	13	16	6	0.52	2.0	128
2527AA10011	83: north of Pilanesberg	8.78	305	17	3	1.5	93	0	162	0.83	30.9	43
2527AC10019	84: Chaneng, next to Agricor	7.36	337	0	88	2.7	87	32	6	0.17	9.0	384
2527AC10020	87: Robega A (Boshkoppie farm)	7.29	530	15	2	3.2	9	10	10	2.23	22.6	64
2527AD10001	88: Tsitsing	7.07	261	40	13	1.5	90	0	61	5.8	3.9	250
2527AD10004	92: Tsitsing	7.22	532	7	1	4.7	14	0	3	5.51	1.8	37
2527CB10001	93: KwaSeretube	7.23	605	1632	693	121.5	134	5459	1460	0.09	1745	268

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527CB10002	94: KwaSeretube	7.35	474	31	38	0.1	5	7	3	0.06	3.6	158
2527CB10003	95: Bospoort Dam	10.50	419	88	53	1.4	78	32	78	0.23	30.0	329
2527CB10005	97: Swartkoppies, Mev Engelbrechts fa	7.40	456	26	43	0.7	6	27	3	0.05	2.5	140
2527CB10006	98: Tlapa, grazing lands	7.35	456	31	48	0.4	7	19	3	0.04	3.8	238
2527CB10007	99: Tlapa, grazing lands	7.39	423	129	63	1.1	30	21	8	0.04	9.6	244
2527CB10008	100: Tlapa, arable field	7.46	642	138	91	0.0	48	164	74	0.1	91.7	305
2527CB10010	102: Tlapa	7.11	460	31	6	1.8	70	0	36	5.37	9.6	152
2527CB10011	103: Maumong	7.44	833	79	41	0.7	63	30	47	0.2	54.1	232
2527CB10012	104: Lekgaloug	7.42	233	21	3	1.6	50	0	31	9.1	24.8	73
2527CB10013	105: Rankelanyane	7.48	537	30	4	0.7	25	3	4	0.91	2.4	104
2527CB10014	106: Lekjaneng	7.52	329	43	9	0.8	54	7	28	3	7.0	170
2527CB10015	107: Malejaneng	7.42	392	40	30	1.3	36	53	16	0.57	32.4	195
2527CB10016	108: Thekwane, kraal	7.37	348	70	32	1.0	45	0	68	0.5	66.1	195
2527DA10001	109: Bapong oustad	6.79	5530	84	72	9.2	155	2	271	0.22	385.1	49
2527DA10002	110: Bapong, roberts yard	7.58	192	85	60	0.0	59	30	24	2.82	2.8	85
2527DA10003	111: Bapong	7.53	571	60	13	1.5	32	5	6	1.63	6.6	158
2527DA10005	113: Bapong, Legalawong sub village	7.50	159	162	67	1.8	87	580	219	0.15	77.4	104
2527DA10006	114: Modderspruit	7.41	208	94	53	12.8	113	3	142	0.46	343.7	152
2527DA10007	115: Modderspruit	7.38	216	81	49	0.2	32	112	30	0.15	13.6	232
2527DA10008	116: Seqwelane	7.22	561	63	61	0.7	43	227	51	0.1	38.8	232
2527DA10009	117: Makolokwe, western end	7.12	649	69	99	0.6	24	189	62	0.09	73.0	195
2527DA10010	118: Bethanie farm	7.13	197	105	80	0.1	32	242	81	0.08	137.8	274

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527DA10011	119: Bethanie cattle post	7.66	237	88	54	0.1	38	66	41	0.09	41.1	256
2527BC10001	120: Wilgevonden east cattle post	7.50	195	21	12	3.8	23	14	5	0.93	1.5	85
2527DA10012	121: Bethanie, south east	7.23	421	130	77	0.5	77	103	109	0.11	289.6	262
2527DA10013	122: Bethanie, outside church	8.29	186	72	61	0.1	23	8	81	0.1	154.6	287
2527DA10014	123: Waaikraal farm	6.94	148	118	107	1.1	75	257	177	0.2	392.6	268
2527DA10015	124: Modikwe	7.38	237	147	125	0.0	23	38	70	0.13	160.0	280
2527DA10016	125: Modikwe, south	6.95	350	82	64	0.0	54	2	86	0.12	147.7	216
2527DA10017	126: Modikwe	7.18	421	72	90	0.0	130	182	179	0.14	521.2	250
2527DA10018	127: Gwatlhe River	9.69	747	37	9	1.9	22	0	17	0.66	3.3	116
2527DA10019	128: Modikwe, school	6.95	178	30	7	1.4	22	37	9	0.85	2.3	79
2527DA10020	130: Modikwe, west	7.27	237	11	4	3.3	23	0	4	1.57	1.1	79
2527DA10021	131: Berseba	6.97	343	34	8	2.2	71	49	38	1.94	12.7	91
2527DA10022	132: Bethanie	6.50	875	77	18	2.1	51	197	95	0.24	4.3	91
2527DA10023	133: Krokodile Riv, Hartebeespoort fm	7.76	644	14	10	2.3	46	11	3	0.15	2.5	122
2527BD10001	134: Maboloka, Bafokeng section	7.32	351	45	9	1.8	25	1	5	1.94	3.6	140
2527BD10002	135: Maboloka, Taung section	7.12	255	11	2	1.7	14	5	4	0.55	0.3	61
2527BD10003	136: Maboloka, Solomon middle school	7.30	341	62	5	1.9	24	122	29	1	3.0	67
2527BD10004	137: Maboloka, Phuthanang Primry schl	6.72	180	26	3	2.2	18	74	17	0.27	1.8	128
2527BD10005	138: Maboloka grazing	7.10	469	33	16	6.3	335	17	378	0.38	41.1	225
2527BD10006	139: Maboloka, Tumo primary school	6.87	350	55	12	2.2	52	0	42	0.97	9.6	171
2527BD10007	140: Maboloka	6.73	374	287	59	9.0	222	14	754	0.43	20.6	262
2527BD10008	141: Letlhakaneng	6.81	258	62	14	4.9	262	1	224	0.95	57.6	292

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527BD10009	142: Letlhakaneng	7.28	723	43	15	3.0	101	9	63	0.79	48.6	189
2527BD10010	143: Letlhakaneng	7.20	964	105	26	5.2	247	106	143	0.79	60.1	354
2527BD10012	145: Rietgat grazing	6.90	378	114	28	7.3	197	15	318	0.57	22.9	244
2527BD10013	146: Rietgat grazing	7.34	274	43	11	3.7	49	20	48	0.63	43.8	231
2527BD10014	147: Waterval grazing	6.79	134	32	10	4.8	317	0	362	5.72	50.4	183
2527BD10015	148: Waterval grazing	6.83	177	241	60	11.0	343	3	970	0.6	37.2	171
2527BD10016	149: Waterval (Tsogwe)	6.37	147	35	12	18.6	102	14	68	0.62	64.2	213
2527BD10017	150: Tsogwe	6.54	232	149	79	12.2	177	2	162	0.41	14.8	281
2527BD10018	151: Tsogwe, Tsogwe School	6.00	147	30	56	12.2	249	8	275	0.09	40.3	274
2527BD10019	152: Kgomokgomo (Rooiwal)	7.71	854	90	43	7.5	137	0	46	0.44	19.9	341
2527BD10020	153: Kgomokgomo	7.31	302	97	69	8.3	138	0	141	0.36	10.7	207
2527BD10021	154: Legonyane	7.02	1370	81	50	3.3	110	41	64	0.76	47.7	189
2527BD10022	155: Legonyane	7.65	805	82	34	4.7	76	15	68	0.81	38.5	213
2527BD10023	156: Legonyane, outskirts	7.68	399	71	71	3.7	110	36	83	0.55	50.7	244
2527BD10024	157: Leganyane, lethabong primary scl	7.17	785	14	6	0.0	610	0	357	8.42	29.1	244
2527BD10025	158: Legonyane	7.22	460	106	37	14.8	369	0	242	5.19	29.0	250
2527BD10026	159: Legonyane	7.46	827	86	68	27.8	260	1	331	0.5	44.6	256
2527BD10027	162: Jericho	7.42	359	11	47	12.4	243	0	69	0.44	58.8	488
2527BD10028	163: Madinyane, Ramogatla	7.64	831	53	26	14.3	463	38	97	0.7	69.2	402
2527BD10029	164: Madinyane	7.12	1710	67	136	61.6	793	93	280	0.73	150.0	305
2527BB10003	166: Bultfontein grazing	7.52	1100	13	6	1.2	35	0	5	6.26	9.5	79
2527BB10004	167: Jonathan, next to cemetary	7.21	1100	19	4	1.8	20	0	4	4.26	2.6	61

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527BB10005	168: GaHabedi grazing	7.73	588	32	6	2.8	21	0	2	4.91	4.3	85
2527BB10006	169: Zoutpansleegte grazing	7.01	650	15	9	2.3	68	0	17	7.95	11.5	122
2527BB10007	170: GaHabedi	6.84	313	33	6	3.5	55	1	17	4.76	5.2	122
2527BB10008	171: Sephai grazing	7.23	454	29	26	8.2	135	0	21	4.81	4.5	213
2527BB10009	172: Sephai	7.15	514	37	5	2.0	39	0	8	4.88	3.9	164
2527BB10010	173: Sephai	7.35	552	46	6	1.7	49	0	9	4.17	4.9	226
2527BB10011	174: Sephai	6.83	386	61	18	7.2	153	1	110	4.88	20.0	122
2527DB10001	175: Mmakau, Tshwara section	7.31	422	41	47	3.8	37	2	12	0.26	2.6	244
2527DB10002	176: Tshwara	7.30	573	172	122	16.2	223	12	563	0.53	282.2	378
2527DB10003	177: Mmakau, Mongopeng section	7.16	529	33	57	8.6	106	12	92	0.96	32.8	500
2527DB10004	178: Mmakau, Polonia Section	7.31	639	14	4	2.3	11	27	5	0.09	0.0	49
2527DB10005	179: Mmakau	7.24	459	13	5	3.3	14	41	5	0.06	0.0	43
2527DB10006	180: Mmakau, Tetele subvillage	7.39	674	33	10	2.9	308	0	301	6.08	111.8	189
2527DB10007	181: Mmakau, Switch subvillage	7.28	565	87	36	1.0	29	52	14	0.14	9.3	205
2527DB10008	182: Mothuthlung	7.31	904	139	22	4.7	83	3	63	2.04	15.1	183
2527DB10009	183: Mothuthlung, Switch subvillage	7.23	572	37	9	4.6	36	0	30	1.17	11.9	97
2527DB10010	184: btwn Rankotia and Ntswaphelong	7.61	527	7	3	2.8	315	0	54	17.8	27.6	317
2527DB10011	185: Vametco mine	7.26	920	14	12	7.1	49	6461	24	0.98	2.2	299
2527DB10012	186: Lerulaneng	7.31	217	88	9	6.1	18	96	33	0.13	1.7	171
2527DB10013	187: Lerulaneng	7.04	153	13	22	3.7	164	0	121	3.01	17.4	268
2527DB10014	188: Lerulaneng	7.13	98	42	17	3.0	32	60	23	2.33	2.6	110
2427DD10001	189: Paarlkraal farm	7.09	138	23	7	1.3	29	1	4	4.22	4.1	85

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2427DD10002	190: Paarlkraal grazing	6.69	111	22	4	1.6	22	1	3	4.58	4.9	73
2527BB10012	191: Doornfontein grazing	6.67	132	44	24	3.7	79	96	62	2.18	9.5	134
2527BA10001	192: Doornfontein grazing	6.84	149	45	14	1.4	93	0	66	4.89	4.7	180
2527BB10014	195: Ruigterpoort grazing	6.70	115	26	3	2.0	92	39	55	6.39	9.8	128
2527BB10015	196: Blokspruit grazing	6.83	147	19	3	2.0	21	5	7	2.92	1.9	171
2527BB10016	197: Blokspruit grazing	7.05	204	34	4	1.5	67	0	57	4.65	9.7	171
2527BA10003	198: Die mont van Blokspruit	7.22	145	20	5	1.9	69	104	318	1.08	112.0	420
2527BA10004	199: Die mont van Blokspruit	7.72	290	50	71	3.8	81	79	254	0.96	159.6	277
2527BA10005	200: Kenkelbos	7.00	189	25	26	3.4	149	26	206	2.06	185.9	225
2527BA10006	201: Kwarriekraal	6.66	68	62	164	6.5	209	142	1412	0.61	632.7	308
2527BD10030	202: Tolwane River	8.32	291	57	29	16.7	297	64	163	0.93	94.6	427
2527BD10031	203: Shakung	7.33	591	35	27	3.4	117	276	516	1.55	423.9	274
2527BD10032	204: Shakung	7.25	790	46	15	5.8	32	49	16	0.34	1.3	85
2527BD10033	205: Shakung	7.35	422	120	35	7.6	80	36	17	0.59	3.0	122
2527BD10034	206: Shakung	7.51	486	119	80	0.0	41	110	40	0.11	29.4	341
2527BD10035	207: Moiletswane	6.93	400	64	47	0.0	45	35	21	0.06	46.7	274
2527BD10036	208: Moiletswane	7.29	376	3	3	0.7	8	3	156	0.14	107.0	92
2527BD10037	209: Moiletswane	7.00	492	97	68	0.3	36	39	49	0.08	43.0	268
2527BD10038	210: Dipompong	8.54	769	70	58	0.3	42	151	20	0.06	39.4	226
2527BD10039	211: Dipompong	7.35	644	64	62	0.0	27	0	12	0.08	13.0	311
2527BD10040	212: Makgabetlwane	7.25	837	122	155	5.8	59	186	45	0.06	86.7	403
2527BD10041	213: Makgabetlwane	7.19	660	58	70	1.0	42	23	20	0.09	0.0	317

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527BD10042	214: Rabosula, outside Kalkbank Pr.sc	7.39	785	101	89	0.0	49	281	150	0.08	63.5	262
2527BD10043	215: Rabosula	7.19	951	40	24	0.0	22	14	11	0.06	15.1	134
2527BD10044	216: Rabosula	7.39	850	101	70	0.0	46	85	30	0.06	35.7	305
2527BD10045	217: Botshabelo (Vyeboschlaagte no.1)	7.06	1530	74	44	0.0	27	99	29	0.07	52.4	250
2528AC10001	218: Klippan	7.39	356	152	170	28.4	317	1	1000	1.52	20.3	342
2527BD10046	219: Winterveld	6.72	171	95	53	0.0	22	30	7	0.14	n/a	311
2527BD10047	220: Winterveld	6.73	216	54	56	0.1	26	1	7	0.12	9.1	268
2528AC10003	222: Winterveld, Matlwareng primary s	6.84	245	57	90	20.5	230	1	273	2.11	1.6	329
2527DB10015	223: Kgabaletsane	7.88	212	36	14	1.6	45	0	5	3	3.0	183
2527DB10016	224: Kgabaletsane	7.23	403	40	54	6.0	35	56	31	0.17	8.2	305
2527DB10017	225: Kgabaletsane	7.19	95	67	36	3.1	37	2	16	0.17	3.8	305
2528CA10001	226: Hebron	10.36	227	n/a	n/a	n/a	n/a	n/a	n/a	8.24	n/a	128
2528CA10002	227: Hebron	7.09	227	26	20	6.9	49	54	33	0.63	64.9	85
2528CA10003	228: Hebron	7.57	136	9	4	9.4	36	n/a	n/a	0.19	n/a	85
2528CA10004	229: Hebron	6.42	145	n/a	n/a	n/a	n/a	n/a	n/a	0.14	n/a	30
2527BB10017	232: Tamootielaagte	7.34	192	75	29	1.8	81	19	137	2.45	64.4	144
2527BB10018	233: Tambootielaagte	7.05	248	13	1	6.1	260	0	280	8.82	10.7	114
2527BB10019	234: Tambootielaagte	4.66	169	33	7	2.0	37	4	10	3.4	5.9	114
2427DD10003	236: Waterval	6.90	170	28	9	1.8	54	0	5	4.33	3.4	157
2527BB10021	237: Waterval	7.22	226	13	7	4.1	33	24	15	4.73	6.2	72
2527BB10023	239: Lebitloane	7.13	317	47	5	1.4	34	0	7	2.15	9.1	128
2527BB10024	240: Lebitloane	6.75	335	54	12	2.4	91	16	64	2.07	17.4	170

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2528AC10006	242: Stinkwater, Mr Teledi's farm	8.07	527	26	15	5.5	114	28	141	1.94	26.9	187
2528AC10007	243: Stinkwater, next to Namo Prm Scl	6.79	272	56	128	21.4	643	0	803	1.38	386.9	421
2528AC10008	244: Stinkwater	6.81	315	17	24	4.2	190	1	215	2.97	42.4	256
2528AC10009	245: Mogogelo	7.24	560	25	20	4.4	6	57	52	0.11	5.5	91
2528AC10010	246: Dilopye	6.65	277	19	26	3.0	18	26	14	0.14	4.2	152
2528AC10011	247: Suurman	7.35	274	6	53	6.4	164	34	77	0.78	24.0	370
2528AA10001	248: Makekeng (Syferkuil)	7.35	359	12	5	2.6	26	11	15	0.1	0.4	91
2528AC10012	249: Syferkuil	7.07	493	19	44	1.6	95	51	137	0.39	11.8	262
2528AC10013	250: Syferkuil A grazing	7.62	347	13	7	2.4	5	0	4	0.79	0.3	287
2528AC10014	251: Syferkuil grazing	6.80	108	26	20	6.9	49	54	33	0.63	64.9	85
2528AC10015	252: Mathiebiestad, Senteng Prm schl	6.86	3350	184	157	33.8	1450	279	1181	3.83	1955.6	433
2528AC10016	253: Mathiebiestad, Lepomo Prm schl	6.31	2940	43	48	21.5	348	36	1465	0.52	1066.1	280
2528AC10017	254: Mathiebiestad, Regodile ELC	7.12	1760	74	180	34.2	452	29	681	2.98	323.4	433
2528AC10018	255: Mathiebiestad, south	6.90	1590	57	100	10.3	415	87	644	4.2	76.8	402
2528AC10019	256: Mathiebiestad	7.32	1170	733	254	39.4	601	8	493	4.76	28.1	262
2528AC10020	257: Mathiebiestad, Ramogoga ELC	7.40	643	39	37	18.0	184	0	104	3.16	28.8	341
2528AC10021	258: Mathiebiestad, Mahobotle Prm sch	6.95	1880	152	170	28.4	317	1	1000	1.52	20.3	342
2528AC10022	259: Mathiebiestad	7.29	960	46	60	19.4	274	47	247	2.48	40.6	390
2528AC10023	260: Mathiebiestad	7.51	1100	57	90	20.5	230	1	273	2.11	1.6	329
2528AA10002	261: Potoane (Goedgewacht)	7.36	1440	184	157	33.8	1450	279	1181	3.83	1955.6	433
2528AA10003	262: Mathiebiestad, Geodgewaagd 2	7.21	646	43	48	21.5	348	36	1465	0.52	1066.1	280
2528AA10004	263: Slagboom grazing	7.56	86	74	180	34.2	452	29	681	2.98	323.4	433

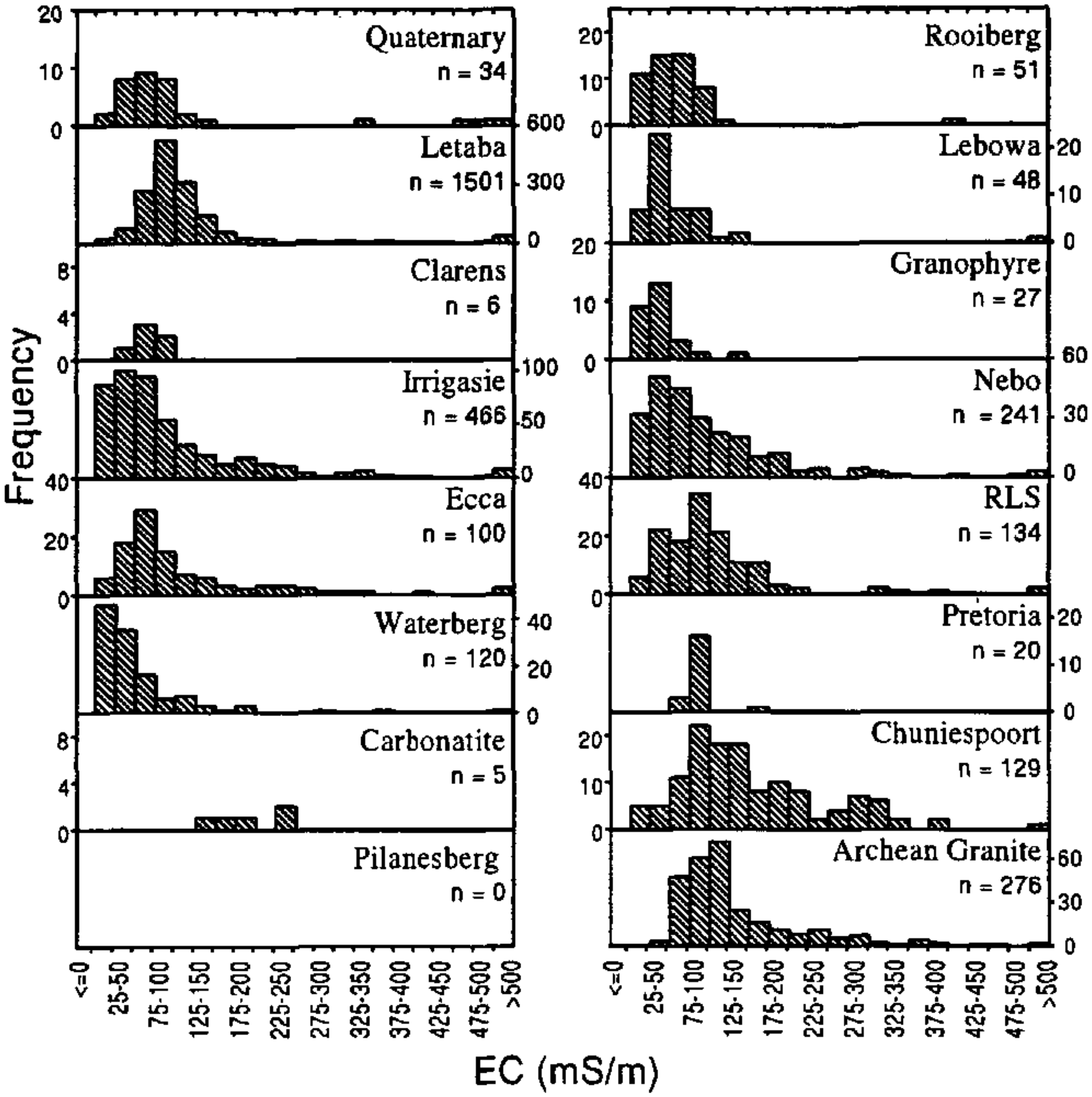
Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2528AA10005	264: Slagboom	7.11	100	57	100	10.3	415	87	644	4.2	76.8	402
2527BB10025	265: Bollantlokwe	7.53	508	60	10	0.8	36	59	24	0.51	3.4	128
2528AA10006	266: Bedwang grazing	8.19	802	733	254	39.4	601	8	493	4.76	28.1	262
2527BB10026	267: Tholwe	7.94	284	66	17	1.1	66	15	39	0.68	19.5	213
2527BB10027	268: De Grens trust	6.65	107	35	8	2.5	30	43	16	0.35	1.7	98
2527BB10028	269: De Grens private	7.77	251	112	23	3.4	45	4	120	1.07	74.6	183
2428DD10001	270: Lefiswane	6.85	94	8	3	5.0	13	27	19	0.08	0.2	92
2428DD10002	271: Lefiso	6.37	81	12	5	3.6	12	34	24	0.07	0.1	24
2428DD10003	272: Lefiso	7.75	200	19	7	2.5	26	6	9	0.07	1.3	134
2528BA10001	275: Rooikoppies grazing	7.16	1890	56	128	21.4	643	0	803	1.38	386.9	421
2528BB10001	276: Ramantsho, primary school	6.66	145	13	7	2.4	5	0	4	0.79	0.3	287
2528BA10002	277: Rooifontein grazing	7.27	711	17	24	4.2	190	1	215	2.97	42.4	256
2528BA10003	278: Semohlase	7.14	240	25	20	4.4	6	57	52	0.11	5.5	91
2428DC10001	279: Semohlase grazing?	7.17	470	69	39	2.4	74	153	40	0.31	34.1	207
2428DC10002	280: Goedviralles	6.95	986	92	106	3.5	103	144	313	0.2	135.6	274
2528BA10004	281: Bultfontein grazing	7.02	238	19	26	3.0	18	26	14	0.14	4.2	152
2528BA10005	282: Bultfontein grazing	7.29	647	6	53	6.4	164	34	77	0.78	24.0	370
2528BA10006	283: Bultfontein grazing	7.32	562	19	44	1.6	95	51	137	0.39	11.8	262
2528AB10001	284: Klippan grazing	7.08	389	39	37	18.0	184	0	104	3.16	28.8	341
2527AA10013	287: Quarantine Camp	10.55	997	6	0	16.9	807	4	481	65.9	246.2	258
2527AA10014	288: Letswaaneng spring auger hole, L	10.33	1950	14	5	3.3	14	7	9	0.44	15.5	53
2527BB10029	291: Jonathan Camp, Borakalalo Park	7.43	476	73	14	3.4	48	65	50	0.55	10.2	158

Site id	Site no., name, description	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	Cl^-	F^-	SO_4^{2-}	T.Alk
2527BB10031	292: Makoropeja	8.24	682	47	18	4.0	40	43	41	0.77	10.5	116
2527BB10032	293: Tlolwe Base, Borakalalo	7.38	192	105	26	5.1	169	0	276	1.69	50.8	201
2527BA10007	294: Blokspruit base, Borakalalo	7.54	342	28	11	6.4	44	0	83	0.35	49.3	94
2527BB10033	295: Moretele Camp, Borakalalo Park	8.05	576	111	31	6.5	273	33	371	2.04	56.7	288
2527BB10034	298: Bultfontein	6.61	169	67	12	2.8	78	45	81	1.04	16.3	152
2527BB10035	299: Klipvoor Primary school	6.05	78	21	5	1.2	29	0	8	2.41	12.7	176
2527BA10008	300: Slipfontein fluorite mine	6.61	181	35	77	9.6	317	72	360	1.29	182.6	292
2527AC10023	302: Mankwe river at Mankwe bridge	7.87	73	29	5	2.6	22	0	2	5.28	2.1	91
2527AA10015	303: Blinkwater, Pilanesberg	7.49	72	35	5	2.5	41	4	7	3.88	8.0	123
2527AA10016	304: Pilanesberg centre	6.97	196	60	43	1.9	18	238	8	0.73	9.8	274
2526BD10013	306: Pilanesberg, Green Tweed	7.10	263	27	6	2.8	79	27	49	2.97	22.9	142
2527BA10009	307: Nooitgedacht farm	7.02	845	41	74	1.4	168	86	131	1.34	167.0	360
2527BA10010	308: Nooitgedacht, Wolvaardts	7.16	744	28	7	2.5	37	0	30	4.9	0.0	143
2527AB10001	309: Nooitgedacht, cattle	7.25	421	45	16	3.0	51	11	7	2.25	3.6	170
2527BA10011	310: Nooitgedacht, Van nickerk	7.66	545	20	4	1.8	50	5	22	3.11	92.3	173
2527BA10012	311: Nooitgedacht, Eloff's	7.26	2170	45	6	1.8	38	0	22	2.79	8.4	169
2527BA10014	313: Pienaars river, Buffelspoort	8.16	259	85	55	1.3	53	16	9	1.22	20.9	322
2527BA10015	314: Buffelspoort, Fred de la poorts'	7.18	1540	74	18	9.4	379	0	555	4.04	47.3	226
2527BA10016	315: Buffelspoort, Standers	7.22	974	160	57	13.4	156	2	577	2.18	139.3	330
2527BA10017	316: Kwarriekraal	7.25	241	37	10	3.8	171	0	173	4.67	147.7	153
2527BA10018	317: Mooimeisjiesfontein	7.35	326	66	12	3.9	138	16	237	3.38	113.1	209
2527BA10019	318: Slipfontein, fanigalo	7.99	280	49	10	4.4	59	88	46	3.88	11.5	113

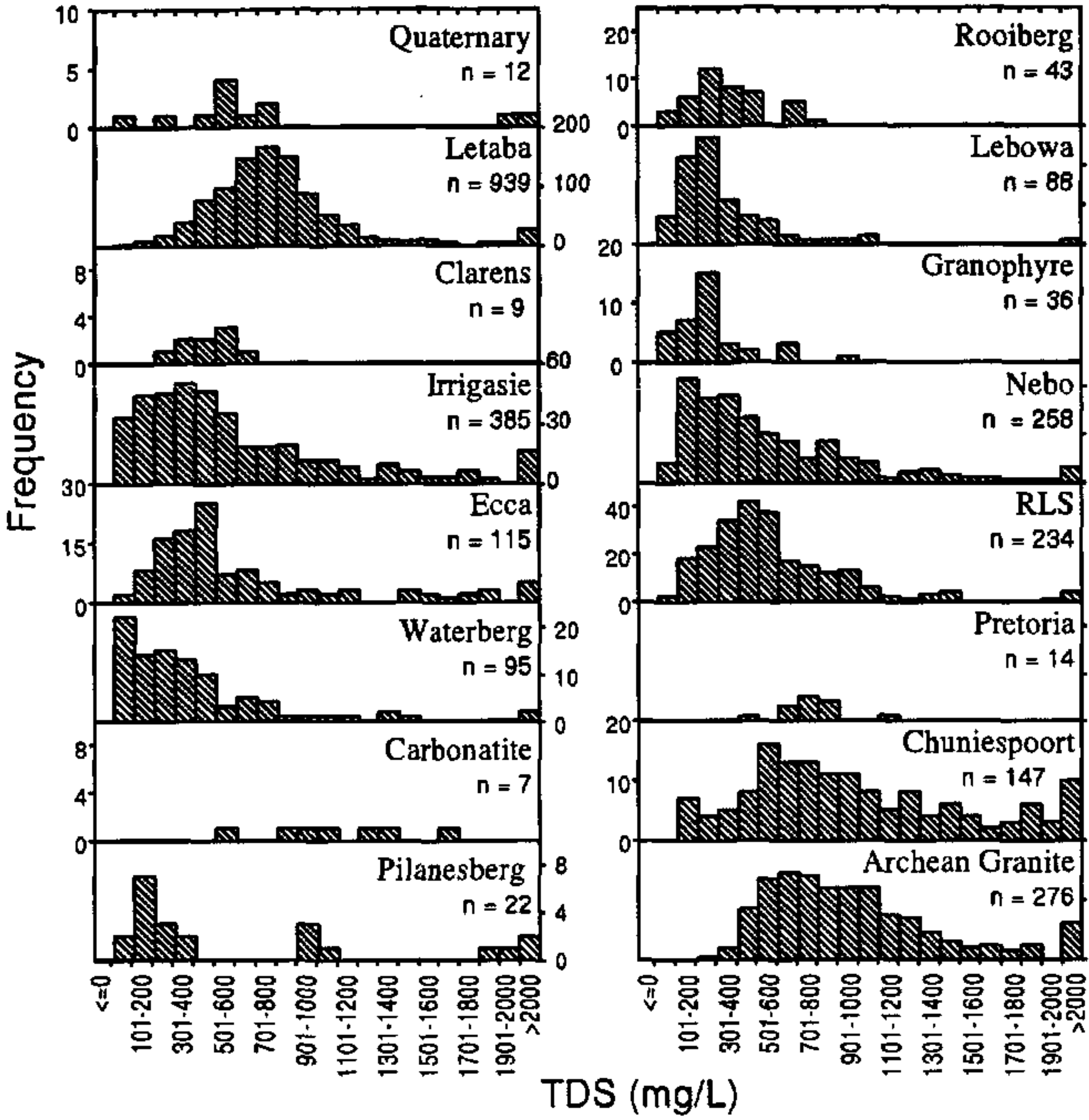
Site id	**Site no., name, description**	**pH**	**TDS**	**Ca^{2+}**	**Mg^{2+}**	**K^+**	**Na^+**	**NO_3^-**	**Cl^-**	**F^-**	**SO_4^{2-}**	**T.Alk**
2427DC10001	319: *Mooimeisjiesfontein, spruit*	7.54	234	32	6	5.4	16	5	51	0.89	80.4	82
2427DC10002	320: Rietfontein	7.75	804	28	7	2.2	291	1	18	5.62	1.3	350
2427DC10003	321: Weihoek	7.83	517	16	3	2.4	175	0	94	11.2	12.5	143
2427DC10004	322: Driefontein game farm	7.11	457	24	9	1.5	133	4	117	8.99	20.3	143
2427DC10005	323: Koperfontein, Shikari game camp	9.41	504	6	2	3.7	178	0	153	11.6	15.4	131
2427DC10006	324: Driefontein	7.60	225	34	6	1.9	38	0	11	3.98	7.1	120
2427DD10004	325: Hartbeesfontein	6.54	135	13	3	1.4	24	11	11	4.01	2.8	71
2427DD10005	326: Rietdal	7.00	240	17	8	1.3	36	4	15	4.01	10.1	157
2427DD10006	327: Morgenzon	7.38	234	54	5	2.5	22	0	11	3.77	4.6	143
2427DD10007	328: Kromdraai	7.10	175	26	5	0.5	27	19	17	3.36	2.7	82
2427DD10008	329: Kromdraai, plot 142	6.91	558	50	13	1.8	49	0	31	4.34	13.2	184
2427DD10009	330: Kromdraai, plot 304	7.29	215	41	6	1.1	29	0	8	3.41	2.7	139
2427DD10010	331: Kromdraai, plot 48	7.29	253	54	7	0.6	39	1	8	3.83	3.9	165
2427DC10007	332: Hardekoolbult	7.21	454	58	13	2.0	104	21	73	4.11	18.2	172
2527BA10020	333: Kruidfontein, dam draining hills	7.04	168	115	47	7.2	32	4	4	0.39	10.8	330
2527BA10021	334: Kruidfontein	7.08	502	77	44	6.8	56	93	22	0.33	20.4	300
2528AC10024	335: Pretoria Saltpan, old artesian	8.21	2680	9	2	9.7	1052	0	1544	7.59	0.0	259
2528AC10025	337: Soutpan	7.02	200	17	3	2.7	31	14	6	1.11	0.0	75
2528AC10026	338: Soutpan, Mr Mon's	7.00	558	26	15	5.5	114	28	141	1.94	26.9	187

9.8 Appendix A8. Histograms of analyte concentrations in groundwaters from 16 major rock types in the study area

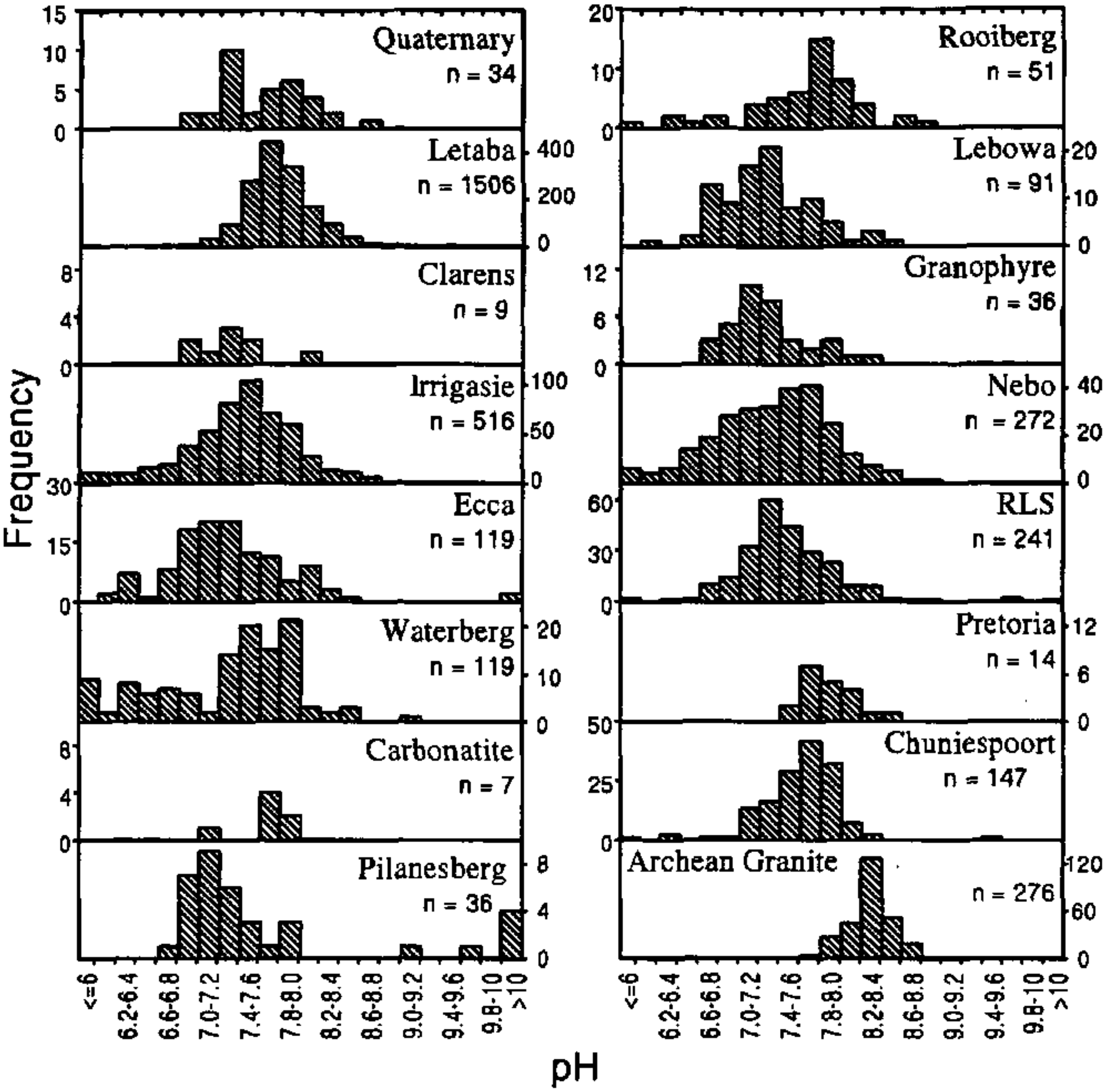
9.8.1 Electrical Conductivity



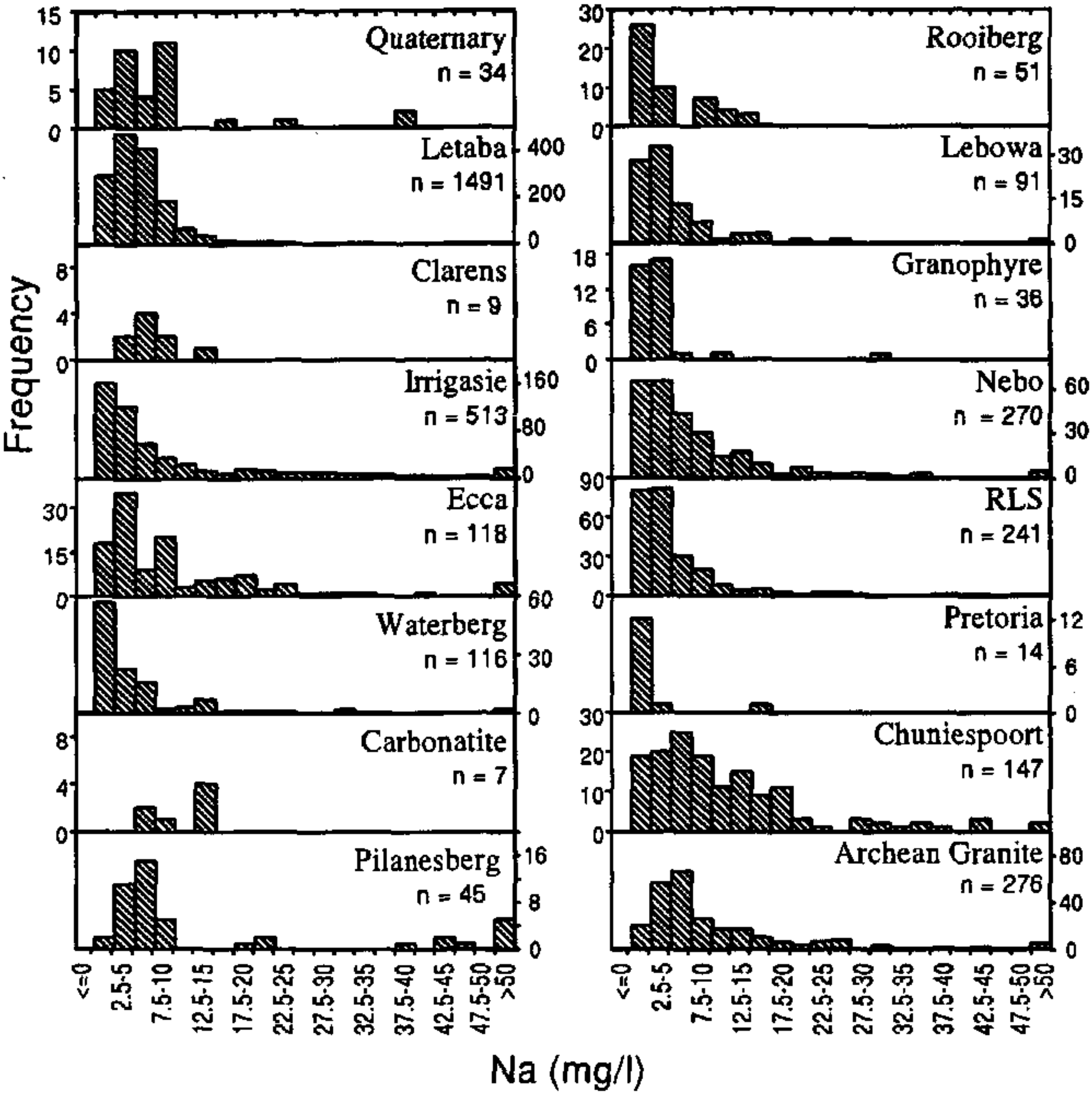
9.8.2 Total Dissolved Solids



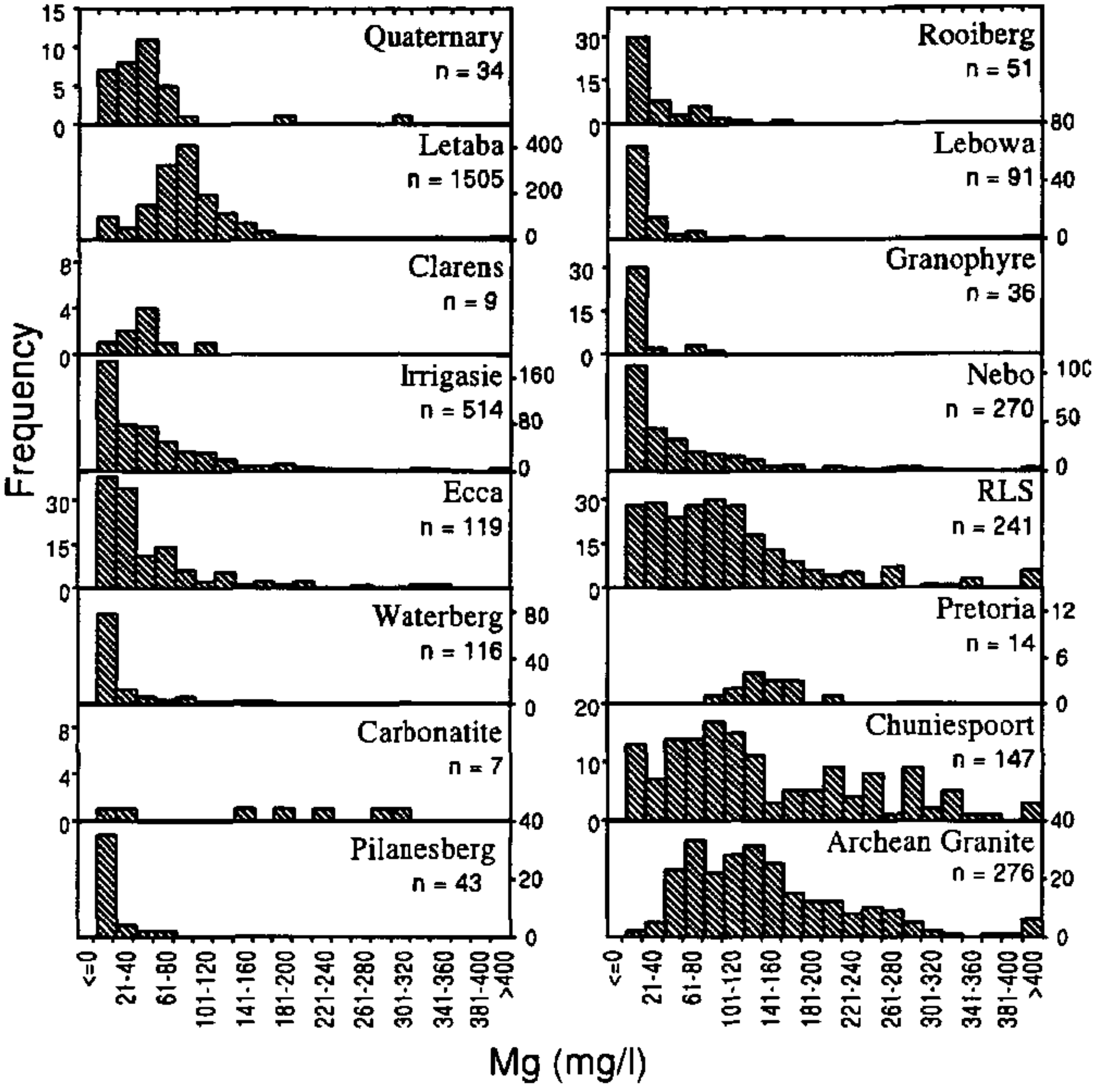
9.8.3 pH


Frequency
pH
Quaternary
n = 34
Letaba
n = 1506
Clarens
n = 9
Irrigasie
n = 516
Ecca
n = 119
Waterberg
n = 119
Carbonatite
n = 7
Pilanesberg
n = 36
Rooiberg
n = 51
Lebowa
n = 91
Granophyre
n = 36
Nebo
n = 272
RLS
n = 241
Pretoria
n = 14
Chuniespoort
n = 147
Archean Granite
n = 276
<=6
6.2-6.4
6.6-6.8
7.0-7.2
7.4-7.6
7.8-8.0
8.2-8.4
8.6-8.8
9.0-9.2
9.4-9.6
9.8-10
>10

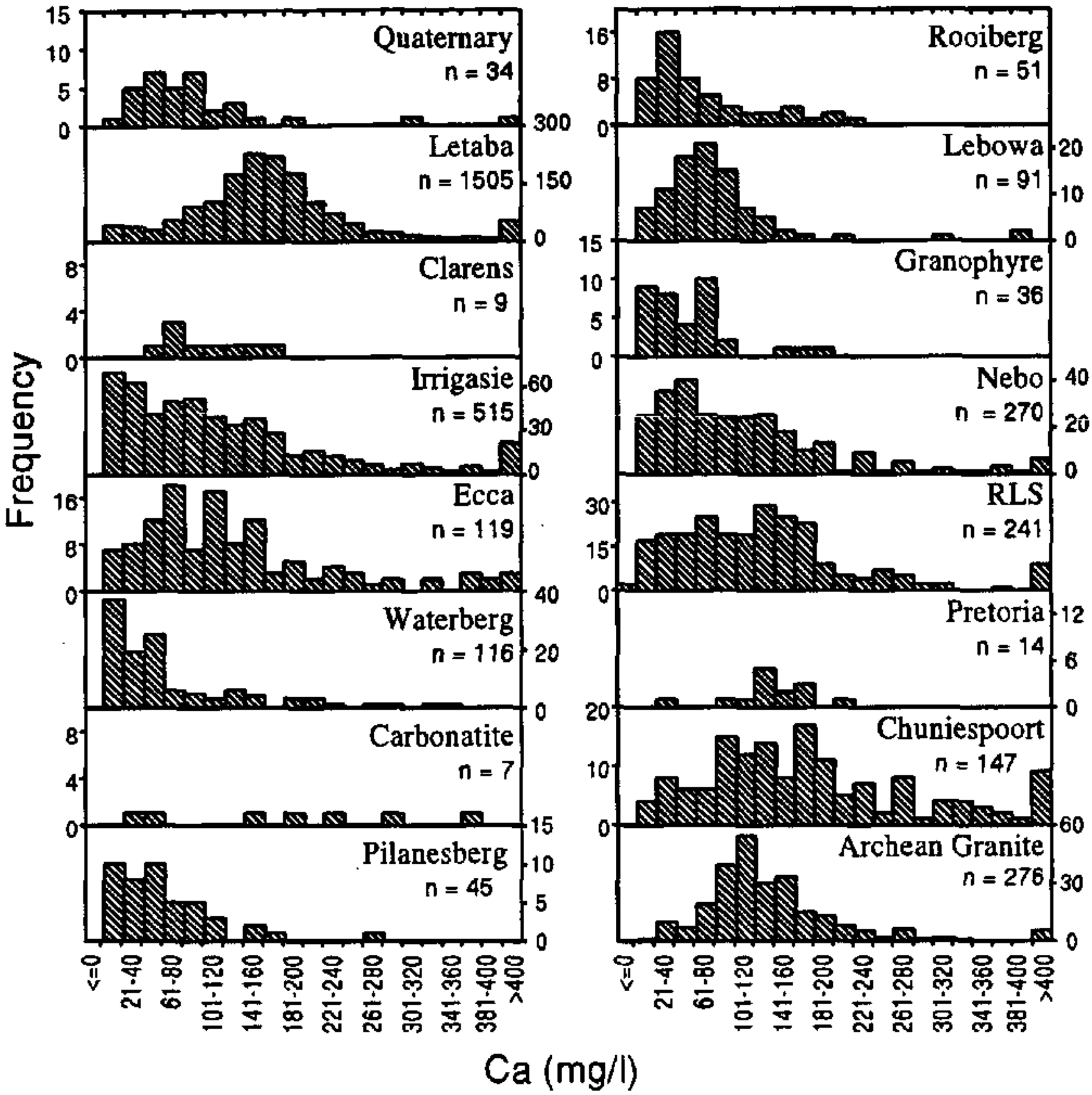
9.8.4 Sodium


Frequency
Quaternary
n = 34
Letaba
n = 1491
Clarens
n = 9
Irrigasie
n = 513
Ecca
n = 118
Waterberg
n = 116
Carbonatite
n = 7
Pilanesberg
n = 45
Rooiberg
n = 51
Lebowa
n = 91
Granophyre
n = 36
Nebo
n = 270
RLS
n = 241
Pretoria
n = 14
Chuniespoort
n = 147
Archean Granite
n = 276
<=0
2.5-5
7.5-10
12.5-15
17.5-20
22.5-25
27.5-30
32.5-35
37.5-40
42.5-45
47.5-50
>50
Na (mg/l)

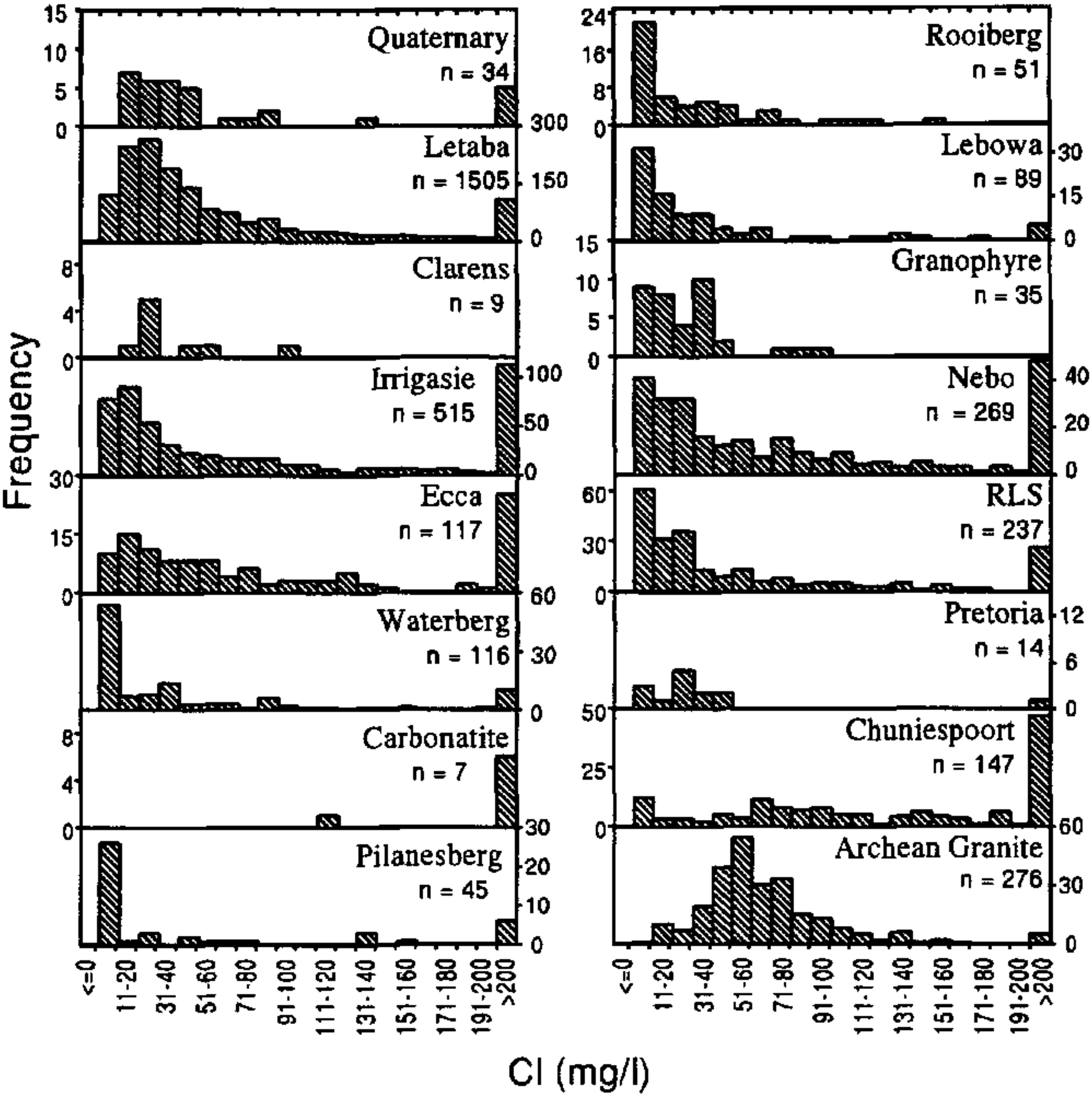
9.8.5 Magnesium



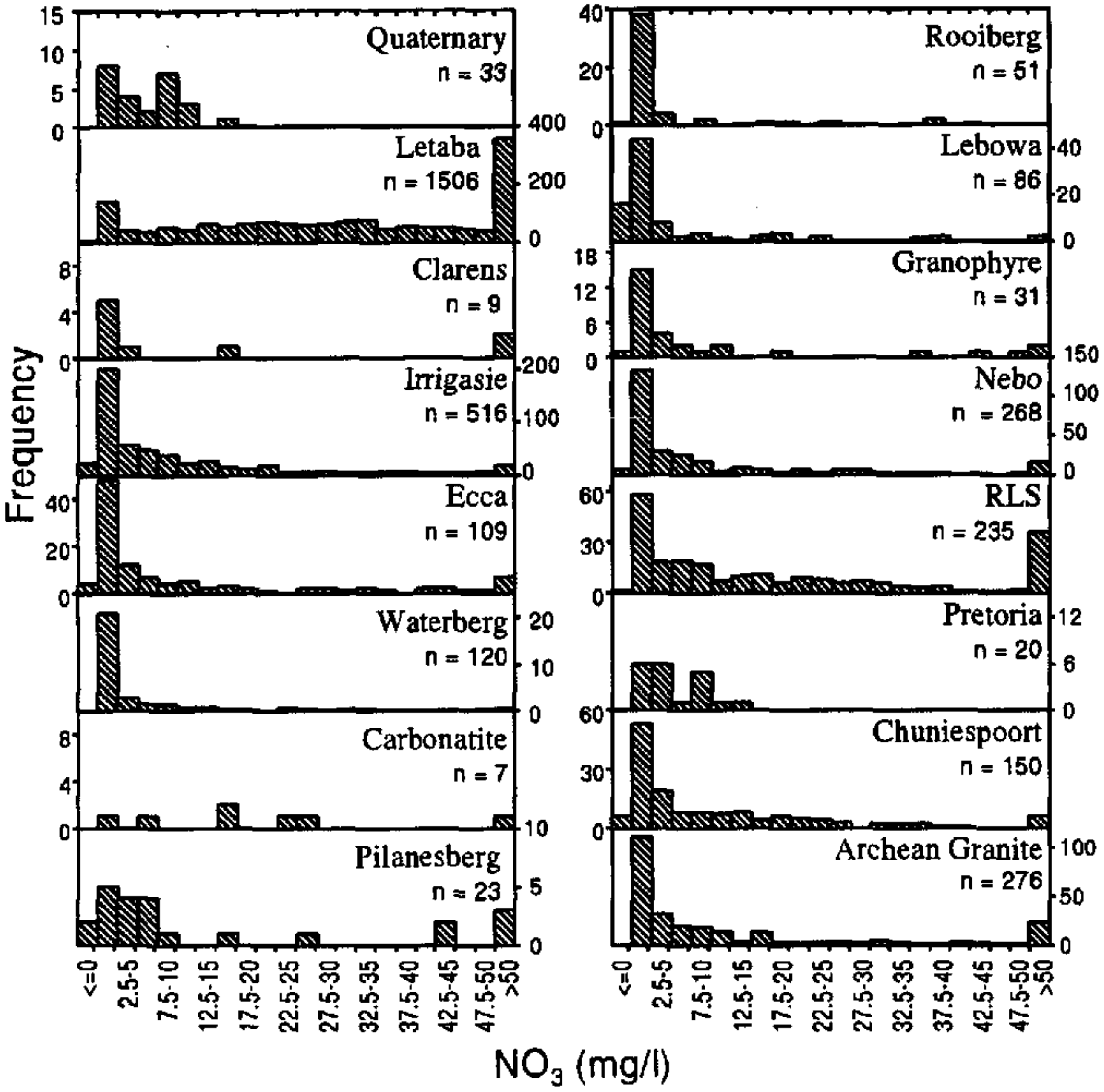
9.8.6 Calcium


Quaternary
n = 34
Letaba
n = 1505
Clarens
n = 9
Irrigasie
n = 515
Ecca
n = 119
Waterberg
n = 116
Carbonatite
n = 7
Pilanesberg
n = 45
Rooiberg
n = 51
Lebowa
n = 91
Granophyre
n = 36
Nebo
n = 270
RLS
n = 241
Pretoria
n = 14
Chuniespoort
n = 147
Archean Granite
n = 276
Frequency
Ca (mg/l)
<=0
21-40
61-80
101-120
141-160
181-200
221-240
261-280
301-320
341-360
381-400
>400
0
5
10
15
300
150
8
4
16
60
30
40
20
12
6

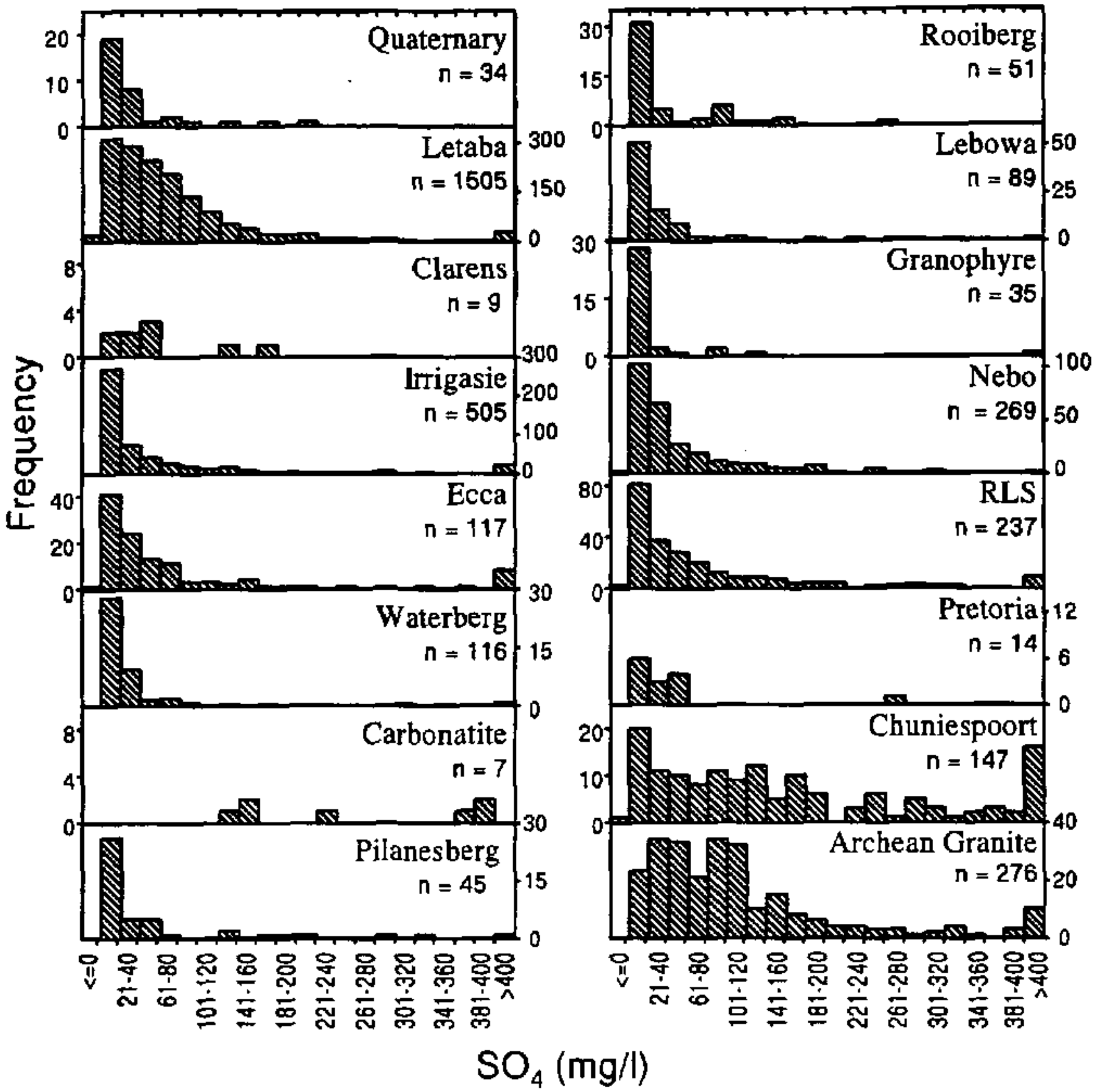
9.8.7 Chloride



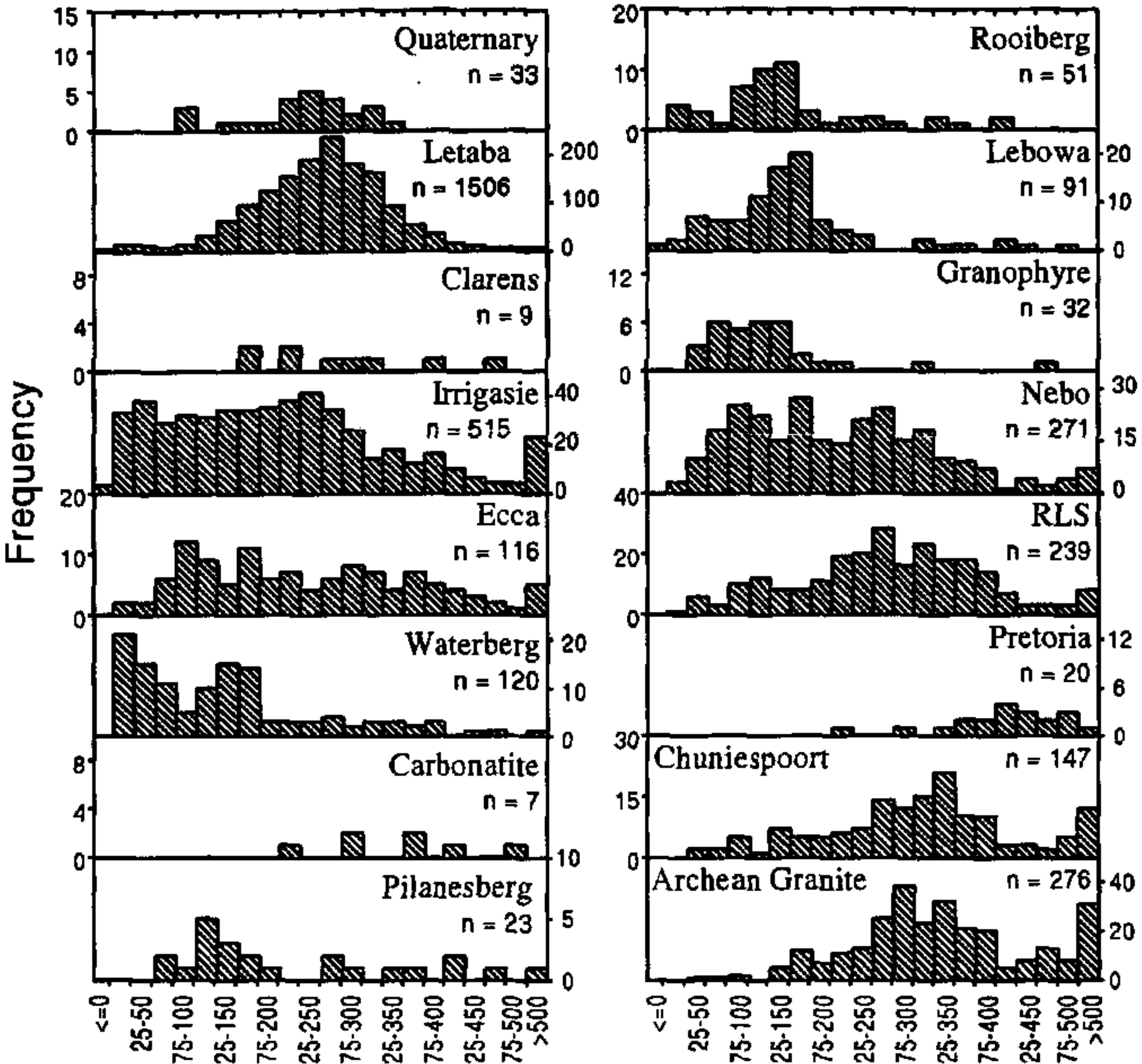
9.8.8 Nitrate


Frequency
NO$_3$ (mg/l)
Quaternary
n = 33
Letaba
n = 1506
Clarens
n = 9
Irrigasie
n = 516
Ecca
n = 109
Waterberg
n = 120
Carbonatite
n = 7
Pilanesberg
n = 23
Rooiberg
n = 51
Lebowa
n = 86
Granophyre
n = 31
Nebo
n = 268
RLS
n = 235
Pretoria
n = 20
Chuniespoort
n = 150
Archean Granite
n = 276
<=0
2.5-5
7.5-10
12.5-15
17.5-20
22.5-25
27.5-30
32.5-35
37.5-40
42.5-45
47.5-50
>50

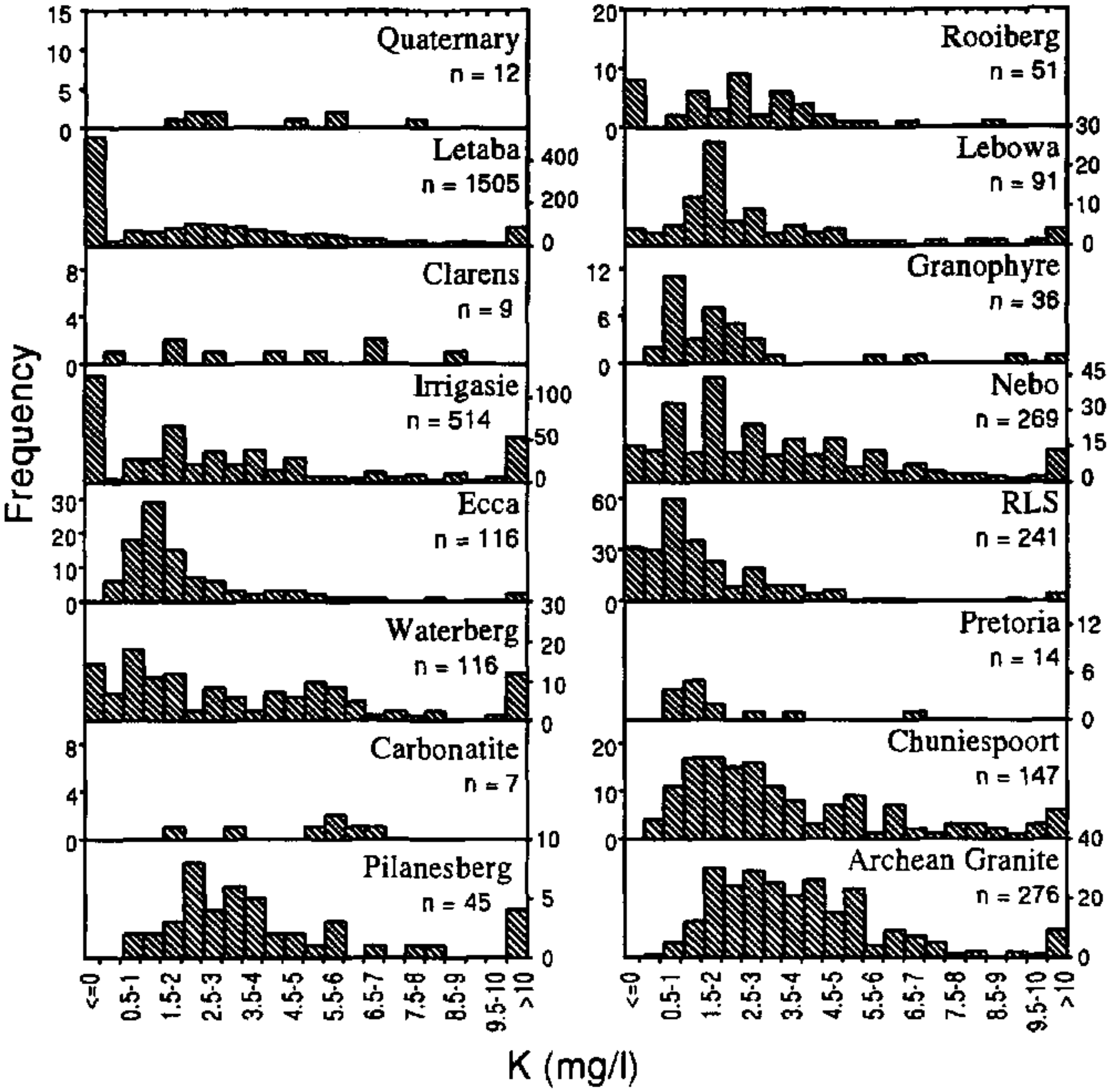
9.8.9 Sulphate



9.8.10 Total Alkalinity



9.8.11 Potassium



9.9 Appendix A9. Trace element analyses of acidified groundwater samples

Performed by Dr. A. Bartha of the Bophuthatswana Geological Survey using ICP-AES. All concentrations are in mg/ℓ.

Site	**As**	**Mo**	**Al**	**Sr**	**Ba**	**Ni**	**Cr**	**V**	**Zn**	**Cu**	**Li**	**Cd**	**Co**	**Pb**
LLD:	0.012	0.004	0.0015	0.00002	0.00007	0.006	0.004	0.004	0.009	0.002	0.0006	0.0015	0.005	0.014
1	0.003	0.002	0.000	0.033	0.019	0.000	0.004	0.002	0.009	0.001	0.000	0.000	0.001	0.006
7	0.003	0.001	0.001	0.054	0.021	0.001	0.001	0.001	0.036	0.002	0.007	0.000	0.002	0.002
12	0.021	0.049	0.017	0.081	0.001	0.000	0.000	0.001	0.870	0.002	0.014	0.000	0.004	0.000
17	0.004	0.004	0.007	0.139	0.024	0.007	0.001	0.007	7.429	0.014	0.000	0.001	0.006	0.001
21	0.002	0.002	0.049	1.960	0.002	0.000	0.000	0.009	1.790	0.010	0.003	0.000	0.001	0.000
27	0.003	0.007	0.118	1.684	0.001	0.000	0.000	0.000	0.050	0.004	0.003	0.000	0.000	0.002
32	0.002	0.006	0.005	0.323	0.042	0.000	0.071	0.075	0.209	0.005	0.000	0.000	0.000	0.000
37	0.001	0.000	4.416	1.610	0.047	0.001	0.001	0.003	0.033	0.001	0.002	0.000	0.003	0.001
43	0.002	0.010	0.041	1.227	0.022	0.000	0.000	0.000	16.960	0.001	0.008	0.000	0.001	0.007
48	0.002	0.002	0.001	0.748	0.008	0.000	0.000	0.001	1.875	0.001	0.002	0.000	0.002	0.000
60	0.003	0.006	0.030	0.179	0.011	0.001	0.002	0.001	3.727	0.007	0.005	0.000	0.009	0.000
63	0.002	0.002	0.001	0.091	0.005	0.000	0.051	0.014	0.202	0.001	0.000	0.000	0.006	0.000
65	0.002	0.004	0.006	0.074	0.016	0.000	0.013	0.025	0.023	0.003	0.001	0.000	0.004	0.000
69	0.002	0.001	0.000	1.116	0.003	0.000	0.001	0.003	1.110	0.007	0.000	0.000	0.003	0.000
72	0.002	0.004	0.039	0.573	0.009	0.000	0.001	0.041	0.106	0.008	0.000	0.001	0.004	0.000
74	0.005	0.046	0.162	0.121	0.007	0.001	0.000	0.013	0.005	0.001	0.000	0.000	0.001	0.000
80	0.002	0.002	0.050	0.534	0.007	0.000	0.001	0.009	0.138	0.004	0.000	0.000	0.002	0.000
86	0.001	0.001	0.033	0.225	0.102	0.000	0.013	0.006	0.225	0.003	0.013	0.000	0.002	0.000

Site	As	Mo	Al	Sr	Ba	Ni	Cr	V	Zn	Cu	Li	Cd	Co	Pb
LLD:	**0.012**	**0.004**	**0.0015**	**0.00002**	**0.00007**	**0.006**	**0.004**	**0.004**	**0.009**	**0.002**	**0.0006**	**0.0015**	**0.005**	**0.014**
91	0.002	0.000	0.086	0.398	0.041	0.000	0.001	0.051	0.061	0.000	0.001	0.000	0.006	0.000
97	0.001	0.000	0.010	0.530	0.017	0.000	0.000	0.020	0.758	0.003	0.000	0.000	0.000	0.000
103	0.002	0.000	0.154	0.525	0.017	0.000	0.000	0.020	0.758	0.004	0.000	0.000	0.003	0.000
108	0.002	0.000	0.064	0.231	0.006	0.000	0.000	0.048	0.140	0.000	0.000	0.000	0.003	0.017
109	0.001	0.001	0.707	11.000	0.104	0.002	0.002	0.001	5.650	0.000	0.001	0.002	0.004	0.000
114	0.002	0.002	0.009	0.103	0.016	0.000	0.000	0.004	0.061	0.009	0.001	0.001	0.000	0.000
119	0.003	0.003	0.018	0.249	0.052	0.000	0.000	0.000	0.148	0.005	0.099	0.001	0.000	0.021
125	0.003	0.001	0.012	0.360	0.037	0.000	0.000	0.000	0.177	0.011	0.004	0.000	0.001	0.000
131	0.001	0.000	0.018	0.281	0.015	0.000	0.001	0.028	0.294	0.009	0.003	0.000	0.000	0.013
132	0.001	0.001	0.000	0.408	0.002	0.000	0.000	0.000	0.416	0.007	0.042	0.001	0.002	0.034
134	0.002	0.004	0.015	0.588	0.270	0.003	0.001	0.000	0.099	0.011	0.065	0.000	0.000	0.016
143	0.001	0.000	0.016	1.146	0.095	0.000	0.000	0.000	0.292	0.000	0.116	0.001	0.001	0.022
148	0.002	0.008	0.021	0.079	0.023	0.001	0.000	0.000	0.908	0.009	0.005	0.000	0.003	0.024
152	0.002	0.002	0.009	0.594	0.207	0.000	0.000	0.000	0.320	0.030	0.092	0.000	0.002	0.029
155	0.002	0.009	0.168	0.754	0.128	0.000	0.002	0.000	1.287	0.016	0.069	0.001	0.000	0.016
161	0.002	0.004	0.026	0.184	0.034	0.001	0.006	0.000	4.287	0.001	0.029	0.003	0.003	0.010
163	0.001	0.003	0.027	0.874	0.024	0.000	0.000	0.000	0.897	0.009	0.106	0.001	0.000	0.015
166	0.004	0.008	0.007	0.970	0.126	0.000	0.000	0.000	0.030	0.005	0.236	0.001	0.000	0.030
172	0.001	0.000	0.011	0.707	0.038	0.000	0.000	0.030	0.766	0.000	0.017	0.002	0.000	0.042
178	0.002	0.003	0.007	0.416	0.011	0.002	0.000	0.007	0.768	0.004	0.004	0.000	0.001	0.000
182	0.001	0.000	0.024	0.735	0.064	0.000	0.003	0.060	0.811	0.012	0.005	0.001	0.006	0.009

Site	As	Mo	Al	Sr	Ba	Ni	Cr	V	Zn	Cu	Li	Cd	Co	Pb
LLD:	**0.012**	**0.004**	**0.0015**	**0.00002**	**0.00007**	**0.006**	**0.004**	**0.004**	**0.009**	**0.002**	**0.0006**	**0.0015**	**0.005**	**0.014**
185	0.007	0.001	0.027	0.768	0.078	0.000	0.000	0.063	0.022	0.004	0.005	0.000	0.000	0.008
192	0.006	1.000	0.018	0.052	0.014	0.000	0.000	0.000	0.373	0.006	0.006	0.000	0.001	0.020
201	0.003	0.003	0.091	0.017	0.040	0.003	0.000	0.000	1.800	0.022	0.004	0.004	0.002	0.035
205	0.002	0.005	0.014	1.143	0.448	0.001	0.000	0.000	0.709	0.005	0.047	0.007	0.000	0.004
215	0.002	0.001	0.013	1.667	0.051	0.000	0.000	0.014	0.529	0.002	0.029	0.001	0.000	0.014
219	0.001	0.002	0.012	0.108	0.007	0.002	0.000	0.000	1.886	0.000	0.007	0.000	0.000	0.005
224	0.001	0.000	0.001	0.150	0.017	0.000	0.009	0.000	7.663	0.009	0.008	0.001	0.001	0.023
229	0.001	0.002	0.329	0.039	0.073	0.000	0.000	0.000	0.141	0.009	0.002	0.000	0.000	0.018
230	0.187	0.023	0.047	0.094	0.068	0.005	0.000	0.038	0.052	0.017	0.004	0.000	0.000	0.000
233	0.012	0.004	0.012	0.090	0.030	0.001	0.000	0.000	0.437	0.011	0.008	0.002	0.003	0.014
236	0.006	0.002	0.011	0.051	0.001	0.001	0.000	0.000	0.250	0.013	0.007	0.000	0.002	0.000
251	0.002	0.001	0.007	0.053	0.088	0.000	0.000	0.000	0.117	0.005	0.002	0.001	0.001	0.047
255	-0.001	0.000	0.001	1.903	0.133	0.001	0.002	0.000	0.187	0.006	0.090	0.002	0.006	0.013
262	0.001	0.000	0.025	0.991	0.128	0.002	0.004	0.001	3.248	0.005	0.031	0.001	0.000	0.005
271	0.002	0.000	0.045	0.053	0.231	0.000	0.005	0.000	6.809	0.003	0.002	0.002	0.006	0.021
275	0.002	0.000	0.024	3.851	0.103	0.001	0.002	0.000	2.819	0.000	0.133	0.002	0.001	0.029
280	0.002	0.000	0.000	0.605	0.028	0.000	0.001	0.051	0.089	0.006	0.005	0.000	0.000	0.000
282	0.002	0.000	0.025	1.004	0.152	0.002	0.000	0.003	0.134	0.006	0.054	0.001	0.000	0.021

9.10 Appendix A10. Iodide concentrations in selected groundwater samples

Concentration in μg/l. For sample site details refer to Appendix A.1. Iodide analysed by J. Paiker, South African Institute for Medical Research.

Site No.	Iodide	Site No.	Iodide	Site No.	Iodide
1	0	103	0	182	1.6
12	96	108	0	185	12.2
17	63	109	91	192	2.3
21	0	114	0	201	6.3
27	0	119	0	205	85
32	0	125	0	215	220
37	0	131	0	219	1.0
43	0	132	3.0	224	7.2
60	0	17?	63	229	3.2
63	0	142	83	230	641
65	61	152	0	236	2.5
69	0	155	95	251	0
72	0	161	15.0	255	188
74	70	163	82	262	64
80	0	166	94	271	0
91	58	172	4.2	275	86
97	185	178	2.2	280	0

9.11 Appendix A11. Sampling protocol for collection of water samples

A protocol for water sampling was formulated before fieldwork commenced and was adhered to as much as possible. The sampling protocol comprised the following steps:

1) Check that water can be obtained from the borehole (wind is blowing, machinery in working order and permission has been obtained from farmer, owner or local chief).
2) Note the date, time, type and state of equipment, size and state of the borehole apron, possible sources of contamination (e.g. kraals, pit latrines, industries, dams, oil soaks), topographic setting, surrounding rocks/soil type and (if available) depth of borehole and water level.
3) If the borehole has been frequently used recently (i.e. wind has been blowing for several days or a frequently used village handpump) take the samples immediately. If it is not frequently used, pump until no change in emerging water temperature and colour occurs.
4) Carry out the field tests (see below).
5) Rinse the 'trace metal' and 'major ion' sample bottles with groundwater. Filter approximately 400 ml of groundwater, using 0.45 µm Teflon filter papers. Although Teflon is a fluorinated compound, its extreme inertness ensured that no contamination of the samples took place. Fill 2 × 100 ml 'major ion' bottles with unfiltered sample and 2 × 100 ml 'trace element' bottles with filtered sample. Where bacterial contamination is suspected, or when cloudy or coloured samples are obtained, filter the sample for the 'major ion' bottles.
6) Add 5 drops of 1 M nitric acid to the 'trace element' bottles. Check with universal indicator paper that the pH is below 2; if not add another 5 drops of acid and repeat. Seal the tops tightly.
7) Mark the site and sample number with an indelible marking pen on the top and the sides of the bottles. Note in the field notebook the sample and site number, whilst marking the site number on the 1:50000 map.
8) Pack all equipment securely. Scan the site for any equipment and rubbish.

The samples were stored in the dark and at approximately 4°C whenever possible, but the large number of samples and duplicates meant that not all bottles could be accommodated in refrigerated storage. Visual inspection at the time of major ion analysis at the University of Cape Town showed that almost all of the samples were identical in appearance to the original: no precipitation of minerals or growth of bacteria or algae had taken place.

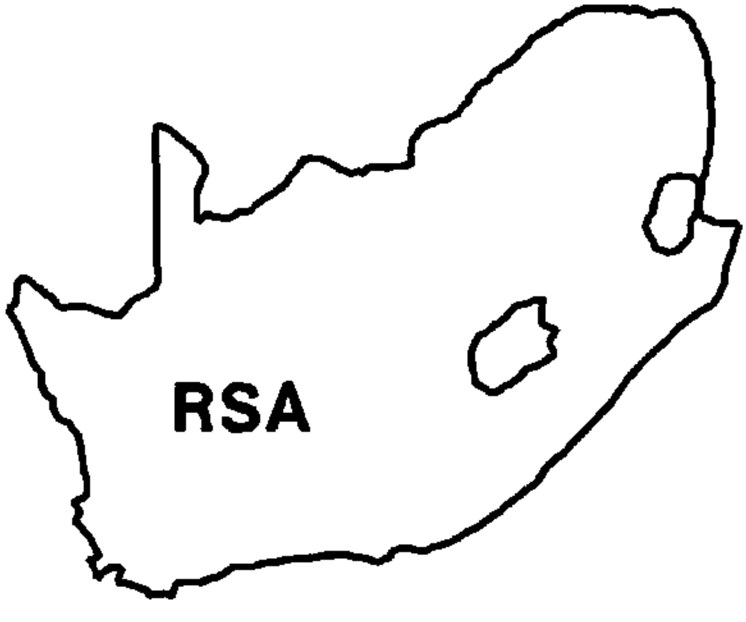
Sample site details are listed in Appendix A1.

9.12 Appendix A12. Workshop on Fluoride and Fluorosis

ABSTRACT VOLUME

Fluoride
and
Fluorosis

The status of South African Research



ABSTRACT VOLUME

of a workshop on

Fluoride and Fluorosis: The Status of South African Research

held at

Manyane Centre, Pilanesberg National Park, North West Province

10th and 11th August 1995

Prepared by L P McCaffrey

Department of Geological Sciences, University of Cape Town

PROGRAMME

THURSDAY 10th AUGUST

Workshop chaired by J.P. Willis, Dept. of Geological Sciences, University of Cape Town.

08h00-09h00 Registration

09h00-09h15 Introductory remarks: **L.P. McCaffrey**

09h15-10h00 Keynote Speaker, **Ron Fuge** (University of Wales, Aberystwyth): The Geochemistry of Fluorine.

10h00-10h30 What would be the Maximum Concentration of Fluoride in Water that will not cause Dental Fluorosis. **J.B. du Plessis** (Department of Stomatology, MEDUNSA)

10h30-10h45 Tea

Fluoride in the natural environment:

10h45-11h15 Distribution and Origin of High Fluoride Groundwater in the Western Bushveld Area. **L.P. McCaffrey** (Department of Geological Sciences, University of Cape Town)

11h15-11h45 Distribution of Fluoride in Groundwater of the Northern Springbok Flats. **M. Fayazi** (Department of Water Affairs and Forestry)

11h45-12h15 Soil and Plant Responses to Irrigation with a Fluoride-rich Waste Water. **M. Ginster and M. Fey** (SASOL)

12h15-12h30 Discussion
12h30-13h30 Lunch

Fluorosis in humans and animals:

13h30-14h00 Dental Fluorosis with Varying Levels of Fluoride in Drinking Water. **M.I. Rudolph, M. Molefe and U.M.E. Chikte** (Department of Community Dentistry, University of the Witwatersrand)

14h00-14h30 A New Approach to define the Target Water Quality Range for Fluoride in the Drinking Water for Livestock. **J.A. Meyer, N.H. Casey & C.B. Coetzee** (Department of Animal and Wildlife Sciences, University of Pretoria)

14h30-15h00 Psychological Effects of Dental Fluorosis. **B. Mothusi** (Department of Health, North West Province)

15h00-15h15 Tea

The politics of fluoride and defluoridation:

15h45-15h43 Water Quality and the Reconstruction and Development Programme. **F. van Zyl and S. Hartley** (Department of Water Affairs and Forestry)

15h4S-16h15 Perceptions regarding Knowledge, Purpose and Desirability of Water Fluoridation in South Africa. **U.M.E. Chikte and A. Josie-Perez** (Department of Community Dentistry, Univ. of the Witwatersrand)

16h15-16h45 Water defluoridation. **J. Schoeman and M. Lebone** (Watertek,CSIR)

16h45-17h15 Discussion

17h15-17h20 Closing remarks: **J.P. Willis**

FRIDAY 11th AUGUST

08h00-13h00 Field trip, visiting sites of geochemical, geological, and hydrogeochemical interest around the Pilanesberg National Park in an open-topped vehicle. Guidebook is supplied, warm clothing essential.

CONTENTS

9.12.1 Abstracts

Distribution of Fluoride in Groundwater of the Northern Springbok Flats

M. Fayazi
Directorate Geohydrology, Department of Water Affairs and Forestry
Private Bag X313, Pretoria, 0001

The regional groundwater study of the Northern Springbok Flats is based on the field hydrocensus of 1986 and compiled from geohydrological data of 3201 boreholes, including a number of springs/seepages and coal exploration boreholes. The Northern Springbok Flats is mainly underlain by Karoo Sequence of sediments and lavas. It begins with up to 100m of shale and sandstone (Ecca Group), followed by up to 151m of mudstones and siltstones (Irrigasie Sediments). These are overlain by sandstones from the Clarens Formation (183m) and finally are capped by basalts of the Letaba Formation (659m). The Karoo Sequence rests uncomfortably on rocks of the Bushveld Igneous Complex, the Rooiberg Group and sediments of the Waterberg Group. Three major groundwater sampling programmes have been undertaken in the area in 1972, 1982/83 and 1991 (this paper). During these sampling programmes attempts were made to sample groundwater from the same boreholes. A relatively high fluoride level was recorded and a peak value of 25,4 mg/L has been recorded on the farm Minerva 628 KS.

Spatial analysis shows that groundwater with a fluoride content greater than 1,0 mg/L is situated in an area underlain by the Karoo sedimentary rocks (especially the Irrigasie mudstones and Ecca shales). The fluoride level in groundwater from the basaltic aquifer is generally less than 1,5 mg/L. An analysis of temporal variation showed that: (i) about 60% of the samples showed an increase in fluoride level between 1972 and 1982/83; (ii) about 65% of the samples showed an increase in fluoride level between 1972 and 1991; (iii) an equal change (50% increase and 50% decrease) in fluoride concentration occurred between 1982/83 and 1991 and (iv) no general trend exists over any period of sampling.

It can be concluded that high fluoride groundwater is found in areas underlain by Karoo sediments. In sedimentary rocks, the fluoride is usually hosted in fluorite, micas, amphiboles, apatite and clay. Fluoride in groundwater may originate from the most common fluoride-bearing mineral, i.e. fluorite (CaF_2). Fluorite is known to occur in the granites of the Bushveld Complex which surround the basins of the Springbok Flats. During arid erosional episodes, weathered products derived from granitic rocks containing fluorite were carried into the basin of deposition and have accumulated locally in the Karoo sediments which later resulted in an enrichment of fluoride in the groundwater. In general, the fluoride level in groundwater from the Northern Springbok Flats is strongly controlled by the geochemistry of the rock in which groundwater is encountered.

1

Distribution and Origin of High Fluoride Groundwater in the Western Bushveld Area

LP. McCaffrey
Department of Geological Sciences, University of Cape Town

The study area covers approximately 30000 km^2, primarily in the eastern districts of the former Republic of Bophuthatswana, and is roughly coincidental with the western lobe of the Bushveld Igneous Complex (BIC). The area is known to have endemic dental fluorosis. Skeletal fluorosis occurs sporadically to the north of the study area.

Three hundred groundwater samples have been analysed for fluoride (F) concentration using High Pressure Ion Chromatography and a Fluoride Ion Selective Electrode. Fluoride concentrations from the Bophuthatswana Department of Water Affairs' computer data base have been amalgamated with the current data set and geological information to produce maps of F concentration in groundwater. High F groundwater is found inside the Pilanesberg Alkaline Igneous Complex (mean = 3.7 mg/L) and very high F concentrations (mean = 57 mg/L) are found around the perimeter. High F concentrations in groundwater are also found in the Nebo Granite and the mineralised Lebowa Granite. The groundwater of the basic portion of the BIC is almost uniformly low in F.

Currently no fluorine producing or consuming industries are present, very little subaerial deposition of F salts is thought to occur and clear lithological control suggest that the cause of most high F concentrations in groundwater is due to dissolution of F bearing minerals in bedrock and soil. Microscopic study of thin sections of common rock types from the area shows that fluorite, mica and hornblende are the most common F bearing minerals. Fluorite is found in sub-economic concentrations in the Pilanesberg and as disseminations in the Lebowa and Nebo Granites. The total F concentration in rock and soil (determined by X-Ray Fluorescence) is very high in the Lebowa Granite (rock mean = 1570 ppm, soil mean = 300 ppm, n = 8) and Pilanesberg (whole rock mean = 27000 ppm, soil mean = 3100 ppm, n = 4), although more general sampling of the latter rock type by previous workers gave a mean F concentration of 5000 ppm.

2

Soil and Plant Responses to Irrigation with a Fluoride-rich Waste Water

M. Ginster and M.V. Fey[1]
Sastech Research and Development, P 0 Box 1, Sasolburg, 9570
[1]Dept. of Geological Sciences, Univ. of Cape Town, Rondebosch, 7700

By irrigating grass pastures, Sasol has been disposing of an effluent containing potentially sufficient concentrations of fluoride (F) to inhibit plant growth. Pre-treating the effluent with gypsum prior to irrigation was found to be effective for reducing the F concentrations to tolerable levels and for improving the sodium adsorption ratio (SAR) of the effluent for irrigation purposes. Effluent F concentrations were reduced by gypsum treatment from ± 160 mg/L to ± 40 mg/L. Soil chemical and plant growth studies were conducted with a solution simulating the concentration of F in the effluent. Two contrasting soil types obtained from the irrigation sites were used: (i) a vertic black clay (Rensburg topsoil) with 50% (mainly smectitic) clay, 1.7% organic C, pH(KCl) of 7,0 and CEC (cation exchange capacity) of 41 $\text{cmol}_c\ \text{kg}^{-1}$, and (ii) an acidic sandy clay loam (Swartland topsoil) with 30% (mainly kaolinitic) clay, 2% organic C, pH(KCl) of 4.2 and CEC of 14 $\text{cmol}_c\ \text{kg}^{-1}$. Analysis of foliar F in Tall Fescue grass grown under irrigation with F solutions indicated that F uptake from the Swartland soil responded strongly to increasing applied quantities of F. From the Rensburg soil there was no significant foliar accumulation of F in response to increased F application. The Swartland soil was found to have a smaller F retention capacity than the Rensburg soil. The Swartland soil's acidity is sufficiently high for Al to occupy a significant portion of the exchangeable cation suite, and it is suggested that soluble Al-F complexes may have contributed to bioavailability of F, with pH, Ca status, and the type and content of clay being other possible contributing factors. Lime application to maintain a near-neutral pH may be required to minimize F mobility.

3

What would be the Maximum Concentration of Fluoride in Water that will not cause Dental Fluorosis?

J.B. Du Plessis
Department of Stomatological Studies, MEDUNSA

Dental fluorosis is a sign of chronic fluoride poisoning in children under six to seven years of age. Unfortunately this is only seen years after the damage, which is irreversible, has been done. Because fluoride in the water is the main source of fluoride to the human being, it is necessary to know the maximum concentration in the water that will not cause dental fluorosis. The fluoride content of the water supply to the Orange Free State (OFS) Goldfields varies between 0,4 and 0,9 ppm with a mean value of 0,54 ppm. A survey to determine the prevalence of dental fluorosis in the Black and White population groups in this area was conducted during 1992. The results showed that the White population had significantly more dental fluorosis than the Black population. When comparing the results of this study with the results from other studies in the USA it can be extrapolated that the maximum safe concentration of fluoride in the water for the OFS goldfields is 0,7 ppm.

Dental Fluorosis with Varying Levels of Fluoride in Drinking Water.

M.J. Rudolph, M. Molefe, and U.M.E. Chikte
Department of Community Dentistry, University of the Witwatersrand

Several studies have investigated the varying levels of naturally occurring fluoride in water and the resulting effect of fluorosis.

The purposes of this study were to determine the prevalence and compare levels of dental fluorosis in children and adults from 4 villages with a range of fluoride in water from 0.1 to 7-8 ppm. At each of the 4 villages, 30 individuals in age ranges 6-7, 12-13 and 35-55 were randomly selected. Dean's and TSIF fluorosis indices were used. Statistical analysis was done using the U-test of Mann Whitney and the Kruskal Wallis test. The highest severity using Dean's Index for 6-7 year olds was found at Village 4 (7- 8 ppm), as expected, with 28 per cent of subjects recording severe fluorosis and 41 per cent moderate. Early signs of questionable fluorosis were identified even in a few subjects exposed to recommended safe levels (0.4 - 0.9 ppm) and very low levels of fluoride in the drinking water. Similar findings of severe fluorosis were also found for the 12 year olds and adult group in the villages with high fluoride content (3-6 ppm and 7-8 ppm). Every subject at the two villages with high fluoride levels showed some degree of fluorosis. Using the TSIF for labial and palatal surfaces of permanent anterior teeth for 6-7 year olds, no canine teeth exhibited signs of fluorosis. The prevalence of fluorosis was higher in the maxillary central incisors than the lateral incisors. The labial surfaces were more affected than the palatal surfaces. Signs of fluorosis on canine teeth were seen on the 12-13 year old and adult groups. The differences between the percentage of subjects with fluorosis and the severity of fluorosis was highly significant between villages 1 and 2 and villages 3 and 4. Questionable fluorosis was shown on 3 subjects even at safe levels of fluoride in the water. This finding raises the question of safe levels of fluoride in water. Subjects exposed to water containing high levels of fluoride manifested with severe fluorosis which is a public health problem.

A New Approach to define the Target Water Quality Range for Fluoride in the Drinking Water for Livestock

J.A. Meyer, N.H. Casey & C.B. Coetzee
Department of Animal and Wildlife Sciences, University of Pretoria

An assessment of water samples from non hydrogauging water stations from the Northern Transvaal, North West and Northern Cape provinces for potentially hazardous water quality constituents revealed fluoride (F), total dissolved solids, chloride, sulphate and nitrate to have the highest incidence of potential toxicity.

Biological trials were conducted investigating the effects of F on sheep, cattle and poultry. In the first trial with South African Mutton Merino (SAMM) wethers, F at 5 levels (<1, 6, 10, 14 and 20 mg F/L) in the drinking water had no significant adverse effect ($P<0.05$) on growth or health over the 20 - 45 kg growth phase. Thyroid gland weight increased significantly with increasing F levels. No clinical signs of fluorosis were observed and no histopathological lesions were found.

Similar results were found in a second trial with 15 mg F/L using SAMM wethers and 20 mg F/L using Bonsmara steers over the growth phase from weaned to market weight. In both these trials a saline water treatment appeared to have a beneficial effect in terms of carcass masses as compared to control and F treatments. In the steers a saline water treatment had a significant negative correlation with metacarpal bone F concentration.

The effect of F in the drinking water over a 49 day growth phase of Ross Broiler hens to a level of 20 mg/L had a positive effect on weight gain and feed intake and no adverse effects on growth or health to slaughter weight. No significant differences were found between treatments (0-20 mg F/L) regarding performance parameters over a 19-74 week laying period in Silver Hy-line layers.

Further research on different categories of exposure, weaning practices and placental transfer are currently underway. The results thus far indicate that the Target Water Quality Guideline Range for toxic water quality constituents is best defined in terms of a water quality index system based primarily on exposure time and ingestion (mg/head/day) factors.

6

Psychological Effects of Dental Fluorosis

B. Mothusi
Department of Health, North West Province

Dental fluorosis is one of the major dental problems affecting the local inhabitants of the North West Province, especially those in the Pilanesberg, Odi and Moretele regions.

The economic development in the Pilanesberg has attracted many people, who flock to seek employment. This affects the other family members, as members of the family born in areas with low fluoride content have normal white teeth, while those born in the abovementioned regions have fluorosed (brown-stained) teeth.

The aims and objectives of the paper are to strike a balance between fluoridation and de-fluoridation, and to show that fluorosed teeth have some effect on the self-esteem of the local people, especially adolescents. Most of the reviewed papers identify the effects of fluoride in cavity reduction, but few indicate the effect of excessive amounts and none the psychological trauma caused by it.

The psychological effect in terms of the unsightly, brown-stained teeth has induced the adolescents, with fluorosed teeth, to demand that these teeth be extracted and replaced with dentures. Thus it is imperative that when we advocate water fluoridation, we should at the same time consider those regions with a high amount of fluoride causing dental fluorosis/brown-stained teeth.

When all is said and done, water fluoridation is the answer to tooth decay (dental caries) and it should be supported.

7

Water Quality and the Reconstruction and Development Programme

F. van Zyl and S. Hartley
Department of Water Affairs and Forestry

The fundamental principle of good government is to ensure all its citizens have access to quality of life.

Access to a supply of clean water is one of the key contributors to this fundamental principle. In order to enact this statement it is therefore essential to determine what is clean water. This paper discusses the philosophy of what is water quality, what is acceptable and the implications of accepting certain basic criteria and standards. Specific reference is made to the incorporation of water quality in the Water Supply and Sanitation actions being implemented. Fluoride is one of the primary constituents that will be specifically addressed.

8

Perceptions regarding Knowledge, Purpose and Desirability of Water Fluoridation in South Africa

U.M.E. Chikte and A. Josie-Perez
Department of Community Dentistry, University of Witwatersrand

The implementation of water fluoridation, defined as the controlled adjustment of fluoride concentration in the drinking water to an optimum amount, is influenced by social, political, environmental and economic factors.

This paper reports on a national survey in South Mrica (n=2229) designed to assess public perceptions with regard to the knowledge, purpose and desirability of water fluoridation.

Most of the respondents (66.4%) have not heard or read about water fluoridation. The sources of information for those who have heard or read about water fluoridation (23.9%) are the community (33.1%), radio (22.3%), newspapers (19.2%) and television (17.2%). In response to the question on the purpose of water fluoridation, most of the respondents (41.1%) said that fluorides purify water, while 25% said it protects teeth. In response to the question, "Do you think fluoride should be added to water if it can reduce tooth decay?", 62.2% of the respondents said "Yes", while 13.5% said "No".

The lack of accurate knowledge about water fluoridation amongst the public needs to be addressed.

Water Defluoridation

J.J. Schoeman and M.L. Lebone
Watertek, CSIR

Different water defluoridation methods and case studies for water defluoridation will be presented. The following defluoridation methods will be discussed: (a) Methods based upon the addition of chemicals to cause precipitation or co-precipitation during coagulation; (b) Methods based upon ion-exchange or adsorption; and (c) Methods based upon membrane separation.

Case studies regarding treatment of groundwater (4 to 20 mg/L F) with the activated alumina defluoridation and reverse osmosis processes will be presented. The economics of these processes for water defluoridation will also be considered. Both the activated alumina and reverse osmosis processes can be effectively applied for water defluoridation. Fluoride concentration levels in groundwater varying between 4 and 20 mg/L can be reduced to less than 1 mg/L with both these processes.

10

9.12.2 List of delegates

List of Delegates:

Name	Institution	Telephone	Fax
Barnard, H.C., Mr	Geohydrology, Department of Water Affairs and Forestry	(012) 328-6397	(012) 299-2692
Carrim, M., Dr	North West Province Fluoride Committee		
Chikte, U., Dr	Dept. of Community Dentistry, Witwatersrand Univ.	(011) 339-2044	(011) 407-8665
De Araujo, R., Dr	Dept. of Community Dentistry, MEDUNSA	(012) 529-4871	
Du Plessis, M., Mr	Water Research Commission	(012) 331-2565	(012) 330-0340
Du Plessis, J.B., Dr	Department of Stomatological Studies, MEDUNSA	(012) 529-4876	(012) 529-4871
Fayazi, M., Mr	Geohydrology, Department of Water Affairs and Forestry	(012) 326-1780	(012) 299-3348
Fuge, R., Dr	University of Wales, Aberystwyth		
Ginster, M., Mr	Sastech (Research and Development)	(016) 708-2826	(016)708-2931
Gugushe, Dr	Department of Community Dentistry, MEDUNSA	(012) 529-4871	
Hanke, L, Mr	AEC	(012) 316-5138	(012) 316-6201
Ismail, A., Mrs	Environmental Health, Gtr. Jhb. Trans. Metrop. Council	(011) 403-1069	
Knesl, O., Mr	Department of Geological Sciences, U.C.T.	(021) 650-2917	(021) 650-3783
Landley, P.	AEC	(012) 316-5138	(012) 316-5874
Lebone, M., Mrs	Watertek, CSIR	(012) 841-2842	(012) 841-4785
Levin, M., Dr	Geospecialists	(012) 315-9515	(012) 315-9400
Mothusi, Badu, Mr	Department of Health, North West Province	(0140) 84-2727	
McCaffrey, L., Mr	Department of Geological sciences, U.C.T.	(021) 650-2912	(021) 650-3783
Meyer, J., Mr	Dept. of Animal and Wildlife Sciences, Univ. of Pretoria	(012) 420-0200	(012) 420-3290
Molefe, M., Mr	*North West Province Fluoride Committee*		
Montroedi, Dr.	North West Province Fluoride Committee		
Nel, R, Mrs	North West Province Fluoride Committee		
Reid, C, Ms	Jones and Wagner	(011) 803-1456	(011) 803-1455
Rudolph, M., Prof.	Dept. of Community Dentistry, Witwatersrand Univ.	(011) 339-2044	(011) 407-8659
Schoeman, J., Dr.	Watertek, CSIR	(012) 841-4785	(012) 841-2270
Thipampeng, I., Ms	North West Province Fluoride Committee		
Trollip, E, Mrs	North West Province Fluoride Committee		
Walton, D., Ms	AEC	(012) 316-5738	(012) 316-6352
Waygood, C., Dr.	Jones and Wagner	(011) 803-1436	
Wieckers, H., Dr.	Stewart Scott Consultants	(011) 803-1456	
Willis, J., Prof.	Department of Geological Sciences, U.C.T.	(021) 650-2908	(021) 650-3783
van Zyl, F., Mr	Water Quality, Department of Water Affairs and Forestry	(012) 323-4472	(012) 299-2251
Ubbink, H., Dr	North West Province Fluoride Committee		

9.12.3 Paper by B. Mothusi, "Psychological Effects of Dental Fluorosis"

PSYCHOLOGICAL EFFECTS OF DENTAL FLUOROSIS

Badu Mothusi
Department of Health, North West Province

INTRODUCTION

It is significant to me, that the first Fluoride and Fluorosis workshop is held in the North West Province, not because I am from the Province, not because I am the Head of the Oral Health Services but simply because it is ideal, it is appropriate and North West Province has unfortunately the richest deposits of fluoride in the country (McCaffrey, 1994) .

Dental fluorosis is one of the major dental problems affecting the people in the North-West Province, especially those in the Pilanesburg, Odi and Moretele regions (Zietsman 1988).

People in these regions are hard hit by brown-stained, that is mottled teeth due to an excessive amount of fluoride in their drinking water.

The development in this area has attracted a lot of people, e.g. The Pilanesberg National Park which is the fourth largest park in South Africa (North-West Parks Board, 1992).

The area also boasts of a complex of hotels, sporting and entertainment facilities that rise out of rugged African bushes like an oasis (North West Parks Board, 1992).

These magnificent developments brought changes to the life style of the people in the region. What used to be normally brown-stained accepted teeth are now considered as abnormal and unwanted teeth.

The developments in the area have attracted many people, who flock to Pilanesberg to seek employment. This affects the surrounding family members, as members of the family born in areas with low fluoride content have normal white teeth and while those born in these areas have fluorosed (brown-stained) teeth.

In this region there is a high demand for these fluorosed teeth to be removed and replaced with dentures. It would appear that having such teeth reduces the possibility that people might positively appraise themselves and/or might be positively appraised by others.

AIMS

The aims of the paper are:

To show that fluorosed teeth have some effects on the self esteem of the people especially adolescents;
To place de-fluoridation high on the priority list in areas where there is naturally high amount of fluoride the drinking water.

According to the figures from the Department of Water Affairs, the Mankwe region, i.e. the Sun City Area, and Moretele Region (Hammanskraal) have exceptionally high amounts of fluoride, some areas had up to 13 parts per million parts fluoride in the water.

Some of the bore-holes in the area had to be closed because of the high amount of fluoride and unfortunately some of the these bore holes were in the school-yards.

OBJECTIVES

I believe in water fluoridation, I support fluoridation, I am an advocate of water fluoridation, a member of the National Task Team and we are preaching the Gospel of Water Fluoridation.

But I believe that as long as we preach water fluoridation, we should at the same time talk about water de-fluoridation in areas with high contents of fluoride especially in the North West Province.

We need to strike a balance betweeen fluoridation and de-fluoridation. We need to adjust the level of fluoride in our drinking water.

FLUOROSED TEETH

Fluorosis is a mottling of teeth which in some cases can be unsightly, especially in this part of our country, Pilanesberg. It occurs especially when the levels of fluoride are too high.

Slide 1

Horowitz (1986) defines dental fluorosis as a hypoplasia or hypo-mineralisation of tooth enamel, due to the ingestion of excess amount of fluoride during the period when teeth are developing.

Leverett (1986) studied prevalence of dental fluorosis in fluoridated and non fluoridated communities. In this area it proved that properly adjusted fluoride does not result in dental fluorosis that has reached an objectionable level.

PSYCHOLOGICAL EFFECTS

Most of the information available to date describes effects of excessive amount of fluoride on the teeth.

Most of the reviewed papers indicate the effects of fluoride in caries reduction, but few indicate the harmful effect of excessive amount of fluoride and none the psychological trauma caused by it.

SELF-CONCEPT / SELF ESTEEM

Self concept and self esteem will be used interchangeable in this paper to refer to the image that each person has about himself.

Rungasamy (1979) talks about the incomprehensibility of trying to define self-esteem. He says the more one tries to grasp it the more it seems elusive. Like mercury, it slips and slides eluding the fingers of the mind. In other words self-esteem is not something tangible and static, on the contrary self esteem is a dynamic mental picture that the person has about himself.

Burns (1984) says that the mouth and face are the focal points of a tremendous number of emotional conflicts and that dentofacial deformities can constitute a source of emotional suffering varying from embarrassment to mental anguish.

Slide 2

Hall points out that people do not want to receive unfavourable information about themselves, for example to be informed about bad teeth as this will make them feel inferior and worthless, resulting in low self-esteem.

Slide 2

According to Penrod (1983), self esteem affects people's behaviour and the way they present themselves to others. He continues to say that people with low self esteem assume that other people will not like them. Such people anticipate rejection at every encounter with others and they are awkward and fearful in social situations.

Goldstein (1976) says that an individual sense of what is beautiful influences how he desires to present himself to others, and that a desire to look well is no longer taken as a sign of vanity in a socially, economicallyand sexually competitive world. A pleasing appearance is literally a necessity. The physical aspect of one's self concept is stressed here within the social context in which one lives.

Slide 3

Vrey (quoted in Molefe,1985) states that "if personality is the radiant force emitted from the core of the person, then self-concept is the lens focussing this force on personality traits". Molefe (1985) continues to say that positive or high self-esteem induces one to wear a happy face wherever one goes. He says the importance of acquiring a positive self-concept lies in the fact that it helps to promote self-actualisation provided the person is given essential educational help.

FACE

According to Patter (1985), the face is the most frequently used component in the physical attractiveness research. The face is interesting, enduring and informative. He says that consistent use of the face in evaluating physical attractiveness is justified, because of its unique and powerful properties which appear to make it omnipotent and omnipresent. Thus people with fluorosed teeth keep on shielding their mouth thus hiding their faces.

Slide 4

According to Rubenstein (1983) "Abraham Lincoln once stated in a campaign speech that, based on the appearance of his face, no one ever expected him to be president". Handsome/good looking people are perceived to be leaders.

THE EFFECTS OF FACIAL APPEARANCE IN EMPLOYMENT

Signal and Aronson (1969) suggest that it is more rewarding to please a physically attractive person than one who is not attractive. Waters(1985) suggests that attractive applicants are more favourably perceived than unattractive applicants. Attractive applicants are attributed greater overall employment potential than unattractive applicants. He found that physical appearance plays an important role in the hiring process on all skills levels.

This is so true, as from to day observe Sun city receptionists.

FACIAL APPEARANCE IN ADVERTISING

In 1982 Joseph stated that advertisers believe that the beautiful are also credible, and that physically attractive sources can contribute to a communication's effectiveness.

Slide 5

Observe all our News presenters and People used for/in advertising.

Slide 6
Slide 7
Slide 8

CONCLUSION

The psychological effect in terms of unsightly brown stained teeth has induced the adolescents with fluorosed teeth to demand that these teeth be extracted and replaced with dentures.

Slide 9

Their demand suggests that the unsightly brown teeth negatively affects their appearance and their self concept.

Slide 10

Thus it is imperative that when we advocate water fluoridation, we should at the same time consider areas with high amount of fluoride causing dental fluorosisl brown teeth.

When all is said and done water fluoridation is the answer to tooth decay (dental caries) and it should be supported.

REFERENCES

Burns, R.B. and Dobson, C.B. (1984). Introduction to Psychology. Langaster. M.T.P Press.

Goldstein, R.E. (1976). Esthecs in Dentistry, Esteem in children with special educational needs: Philadelphia. J.L Lippincot.

Hall, J. (19850. Psychology for nurses and health visitors: London. MacMillian.

Horowitz, H.S. (1986). Indexes for measuring dental fluorosis. Journal of Public Health Dentistry, vol 46 179-182.

Joseph, W. (1982). The credibility of physically attractive communications. A review. Journal of Advertising 11, 15-25.

McCaffrey, L.P. (1994). The Geohydrology of the Pilanesburg. Unpbl M.Sc. Diss. Wits.

Leverett, D. (1986). Prevalence of dental fluorosis in fluoridated and non fluoridated communities, a preliminary investigation. Journal of Public Health Dentistry, 46, 184-187.

Molefe, R.D. (1987). The meaning of self -concept for the academic achievement of Tswana teacher-trainees. M.Sc. thesis. Univ. of Pretoria.

Patter, G.L. (1985). The physical attractiveness phenomena. New York. Plenum Press.

Rubenstein, C. (1983). The face psychology today.

Rungasamy, P. (1979). A study of the levels of depression in the physically ill. University of Dublin, Trinity College.

Penrod, S. (1983). Social psychology. Prentice Hall. Englewood Cliffs.

Signal, H. and Aronson, E. (1969). Liking for and evaluation as a function of her physical attractive partner on person perception. Journal of Personlity and Social Psychology, 31,410-414.

Waters, J. (1985). Cosmetic and the Job Market. In Graham J. and Kligman I.S. *Psychology of cosmetic treatment*. New York. Pergamon.

Zietsman, S (1991). Spatial Variation of fluorosis and fluoride content of water in an endemic area of Bophuthatswana. Journal of the Dental Association of South Africa, 46, 11-15.

9.12.4 Paper by J.B. du Plessis, "What would be the maximum concentration of fluoride in water that will not cause dental fluorosis?"

WHAT WOULD BE THE MAXIMUM CONCENTRATION OF FLUORIDE IN WATER THAT WILL NOT CAUSE DENTAL FLUOROSIS?

Dr J B du Plessis
Department of Stomatological Studies, MEDUNSA

The optimum concentration of fluoride in the drinking water of any community is that concentration which will give the maximum protection against dental caries, without causing aesthetically unacceptable dental fluorosis.

During the nineteen thirties this concentration was epidemiologically determined to be 1 ppm for countries with a temperate to cold climate. This concentration was also found to be influenced by other factors, of which the annual average daily maximum air temperature was the most important, because this is the main factor determining the amount of water consumed by the individuals in that area.

On the basis of this evidence the MacKenzie commission of 1966 recommended that the optimum concentration of fluoride in the drinking water for Soll.th Africa should be 0,8 ppm.

Since the ear ly nineteen seventies, various fluoride supplements appeared on the market. Of these fluoridated tooth pastes and fluoride tablets which had to be taken on a daily basis, had the greatest impact on the amount of fluorides consumed by its users. Thus in most countries where water fluoridation is implemented today, the optimum concentration was lowered to vary between 0,5 and 0,8 ppm, depending on the climate.

The best way to determine the optimum concentration of fluoride in the water for South Africa would be to study the epidemiological evidence that we have from areas with varying concentrations of fluoride in its water, as it was done in the USA, Europe and other countries. We have data from the metropolitan areas along our coastline where the fluoride concentration in the water is 0,05 ppm or less. This can be compared to the PWV area which had a fluoride concentration of 0,32 ppm, Bloemfontein with 0,35 ppm and the Free State Gold Fields with 0,55 ppm. We must note however that this last 0,55 ppm is the long time average of the fluoride content, and that it does vary from 0,2 to 0,9 ppm. Due to the particular circumstances these variations may occur over very short periods. According to Burt et al. (1992) it is the long time average that gives protection against dental caries, while Meyers (1978) maintained that it is the high spikes in the fluoride concentration which are mainly responsible for dental fluorosis .

The caries experience of the Black children in these various areas show the dramatic effect of fluoride in preventing dental caries. In the primary dentition of the 6 year old children there is a 51% reduction from the coastal areas to the Free State Gold fields. In the permanent dentition of the 12 year old children the reduction is 84% and in the 15 year old children it is 85%. These results compare very favourably with the best results obtained by water fluoridation prior to the introduction of other fluoride supplements as was reported by Murray and Rugg-Gunn in 1982.

In the White children the pattern of protection against caries compares favourably to what was reported by Newbrun (1989) from water fluoridation studies after the introduction of fluoride supplements. We see a 6% reduction in the caries experience in the primary dentition of 6 year old children, 27% in the permanent dentition of the 12 year old children and 31% in the 15 year old children.

The exact prevalence of dental fluorosis in the coastal areas, the PWV and Bloemfontein is not known. However the prevalence of dental fluorosis on the labial surfaces of the upper central incisors was determined in the Free State Gold Fields. Comparing 15 year old Black and White children it is clear that the White children had much more fluorosis (31% versus 17%).

In the 12 year old children this difference is even bigger (43% versus 17%). This indicates that the white children consumed more fluoride than their Black compatriots, despite the fact that both groups used the same water supply.

If we look at the fluorosis prevalence in 12 and 15 year old black children we can see that there is virtually no difference between the two age groups, indicating that they consumed the same amount of fluoride during the time when the labial surfaces of the upper central incisors were formed.

In the White children there is a big difference between the two age groups. This is particularly so for scores 3 and 4, which are mild and moderate fluorosis. It is clear that the 12 year old group consumed more fluorides than the 15 year old age group. As these examinations were done during 1992, it means, according to Evans and Stamm (1991), that the 12 year old children consumed more fluorides during 1982, when their central incisors were susceptible to fluorosis (22-26 months of age) than the 15 year old children during 1979 when their teeth were affected. This fits in with the pattern of increasing use of fluoride supplements, as it became available during the late 1970s and early 1980s.

Comparing the fluorosis prevalence in the Free State Gold Fields with the latest reports of fluorosis from optimally fluoridated areas in the USA as reported by the Centers for Disease Control in 1991, it is obvious that the White children in the Free State Gold Fields consume more fluorides than the children from the USA, while the Black children had about the same prevalence of fluorosis.

In another study in the USA Driscoll (1986) came to the same conclusions. He also found that in optimally fluoridated areas, a fluorosis prevalence of about 14% can be expected. It must be remembered that most of this kind of very mild and mild fluorosis is aesthetically acceptable.

Thus local epidemiological evidence and the literature from abroad indicates that both Black and White children in the Free State Gold Fields get maximum protection against dental caries. What remains to be explained is why the White children showed an unacceptable high prevalence of dental fluorosis and the Black children not.

Ophaug et al. (1980) did a large dietary study and determined the amount of fluoride in the diet of children using optimally fluoridated water. They found that an average 2 year old child weighing 12,5 kg consumed 0.61 mg fluoride per day. This is equal to an average of 0.049 mg with a range of 0,04 to 0,06 mg per kg of body weight per day.

Pendrys and Stamm (1990) determined that the average 2 year old child, using fluoridated tooth paste swallows about 0.3 mg of fluoride per day. This is equal to 0.024 mg per kg of body weight.

Burt (1991) calculated that the optimum amount of fluoride for a child is 0,05 to 0,07 mg per kg of body weight. If the fluoride intake is between 0,071 and 0,089 mg per kg body weight, it can be regarded as borderline safe, and a small percentage of children will develop mild fluorosis. A diet containing more than 0,09 mg per kg body weight per day during tooth formation will definitely give rise to dental fluorosis with a significant percentage developing moderate and severe fluorosis.

If we now stick to our previous conclusion that the Black children in the Free State Gold Fields get maximum protection against dental caries and show no signs of problems with dental fluorosis, we must then assume that their diet provided about 0,05 mg of fluoride per kg of body weight when the labial surfaces of their upper central incisors were formed during the years 1979 and 1982. This is within the optimum range of fluoride intake as determined by Burt. At that stage they had little or no access to fluoride supplements. Thus it can be concluded that this was their total fluoride intake which they got almost totally from the water containing 0,55 ppm fluoride. On the other hand the white children already had access to fluoridated tooth pastes and other fluoride supplements. Using only the fluoride from tooth paste it can be calculated that the White children consumed approximately 0,074 mg per kg of body weight. This places them in the lower range of the border line dosage of fluoride, and one would not expect to find serious problems with dental fluorosis. Only a few cases of very mild and mild fluorosis might occur.

Using these calculations as a basis it can now further be calculated that if the fluoride content of the water should rise to 0,7 ppm the Black children would have consumed 0.062 mg per kg body weight which is still within the optimum range. On the other hand their White compatriots would have consumed 0.086 mg per kg of body weight. This is at the upper limit of the marginal range and should still not give rise to cases of moderate to severe dental fluorosis.

As was said earlier, the fluoride content of the water in the Free State Gold Fields often rises to as high as 0,9 ppm. In such a case the Black children would have consumed 0.08 mg per kg of body weight, which is still in the marginal range, and only some cases of very mild and mild fluorosis will be seen. In the white children however the consumption of fluoride would have been 0,104 mg per kg of body weight, which places them in the dangerous range where cases of moderate and severe fluorosis will be seen.

Because the results of these calculations fit in so well with what was found during the survey in the Free State Gold Fields it can be concluded that the optimum concentration of fluoride in the drinking water for the Free State Gold Fields and other comparable areas is 0,55 ppm. At the same time it can be concluded that the maximum fluoride content of the drinking water that will not give rise to aesthetically unacceptable dental fluorosis in the Free State Gold Fields and other comparable areas is 0,7 ppm.

REFERENCES

Angelillo, IF, Romano, F, Fortunato, L & Montanaro, D (1990) Prevalence of dental caries and enamel defects in children living in areas with different water fluoride concentrations. Community Dental Health, 7, 229-236.

Brunelle, JA & Carlos, JP (1990) Recent trends in dental caries in U.S. children and the effect of Water fluoridation. Journal of Dental Research, 69, 723-727.

Burt, BA (1992) The changing patterns of systemic fluoride intake. Journal of Dental Research, 71, 1228-1237.

Burt, BA, Ekland, SA & Lewis, DW (1992) Dentistry, Dental Practice, and the Community. 4th ed., Ch. 12, pp 157-158 Philadelphia: W.B. Saunders.

Centers for Disease Control. (1991) Morbidity and Mortality Weekly Report Recommendations and Reports: Public Health Service Report on Fluoride Benefits and Risks, Vol 40, No RR-7 pp 1-8. Atlanta: Department of Health and Human Services, USA.

Clark, DC (1994) Trends in prevalence of dental fluorosis in North America. Community Dentistry and Oral Epidemiology, 22, 148-152.

Dreyer, AG & Grobler, SR (1984) Die fluoried gehalte in die drinkwater van Suid-Afrika en Suidwes-Afrika. Journal of the Dental Association of South Africa, 39, 793-797.

Du Plessis, JB, Carstens, IL, Rossouw, LM & Olivier, I (1994) The Dental caries status of the urban population in the major metropolitan areas of South Africa. In National Oral Health Survey, South Africa 1988-89, Ed.: van Wyk, PJ, pp 24-32 Pretoria: Department of National Health and Population Development.

Du Plessis, JB, Louw, AJ & van der Merwe, CA (1994) Calibration of examiners for the National Oral Health survey: Caries and periodontal diseases. In National Oral Health Survey, South Africa 1988-89, Ed: van Wyk PJ, pp 15-23 Pretoria: Department of National Health and Population Development.

Du Plessis, JB, van Rooyen, JJC, Naude, DA and van der Merwe, CA (1995) Water fluoridation in South Africa: Will it be effective? Journal of the Dental Association of South Africa.

Evans, RW & Stamm, JW (1991) An epidemiologic estimate of the critical period during which human central incisors are most susceptible to fluorosis. Journal of Public Health Dentistry, 51, 251-259.

Feyerskov, O, Manji, F & Baelum, V (1990) The nature and mechanisms of dental fluorosis in man. Journal of Dental Research, 69, 692-700.

Glass, RL (1982) The first international conference on the declining prevalence of dental caries. Journal of Dental Research, 61, 1301-1383.

Grobler, SR & Dreyer, AG (1988) Variations in the fluoride levels of drinking water in South Africa. South African Medical Journal, 73, 217-219.

Horowitz, HS (1990) The future of water fluoridation and other systemic fluorides. Journal of Dental Research, 69, 760-764.

Levy, SM (1994) Review of fluoride exposures and ingestion. Community Dentistry and Oral Epidemiology, 22, 173-180.

Lewis, DW & Banting, DW (1994) Water fluoridation: current effectiveness and dental fluorosis. Community Dentistry and Oral Epidemiology, 22, 153-158.

MacKenzie, WJ (1966) Report of the Commission of inquiry into Fluoridation. Ch VII, pp 113-115. Pretoria: The Government Printer.

Meyers, HM (1978) Fluorides and dental fluorosis. Monographs in Oral Science, 7 pp 1-74 Basel: S Karger.

Murray, JJ, Breckon, JA, Reynolds, PJ & Nunn, JH (1991) The effect of residence and social class on dental caries experience in 15-16-year-old children living in three towns (natural fluoride, adjusted fluoride and low fluoride) in the north east of England. British Dental Journal, 171, 319-322.

Murray, JJ & Rugg-Gunn, AJ (1982) Fluorides in caries prevention. Ch II pp 31-43 and Ch IV pp 58-63 London: Wright.

Newbrun, E (1989) Effectiveness of water fluoridation. Journal of Public Health Dentistry, 49, 279-289.

Nicholson, K & Duff, EJ (1981) Fluoride determination in water. Analytical Letters, 14, 493-517.

Ophaug, RH, Singer, L & Harland, BF (1980) Estimated fluoride intake of average two year old children in four dietary regions of the United States. Journal of Dental Research, 59, 777-781

Pendrys, DG & Stamm, JW (1990) Relationship of total fluoride intake to beneficial effects and enamel fluorosis. Journal of Dental Research, 69, 529-538.

Riordan, PJ and Banks, JA (1991) Dental fluorosis and fluoride exposure in Western Australia. Journal of Dental Research, 70, 1022-1028.

Segretto, VA, Collins, EM, Camann, D & Smith, CT (1984) A current study of mottled enamel in Texas. Journal of the American Dental Association, 108, 56-59.

South African Weather Bureau. (1986) Klimaat statistiek. WB 40. Pretoria: SA Weather Bureau.

Speirs, RL (1981) Fluorides: Systemic balance and cariostatic mechanisms. In Dental Caries. Aetiology, Pathology and Prevention, Ed: Silverstone, LM, Johnson, NW Hardie, JM & Williams, RAD. Ch 10, pp 239-248. Hong Kong, Macmillan.

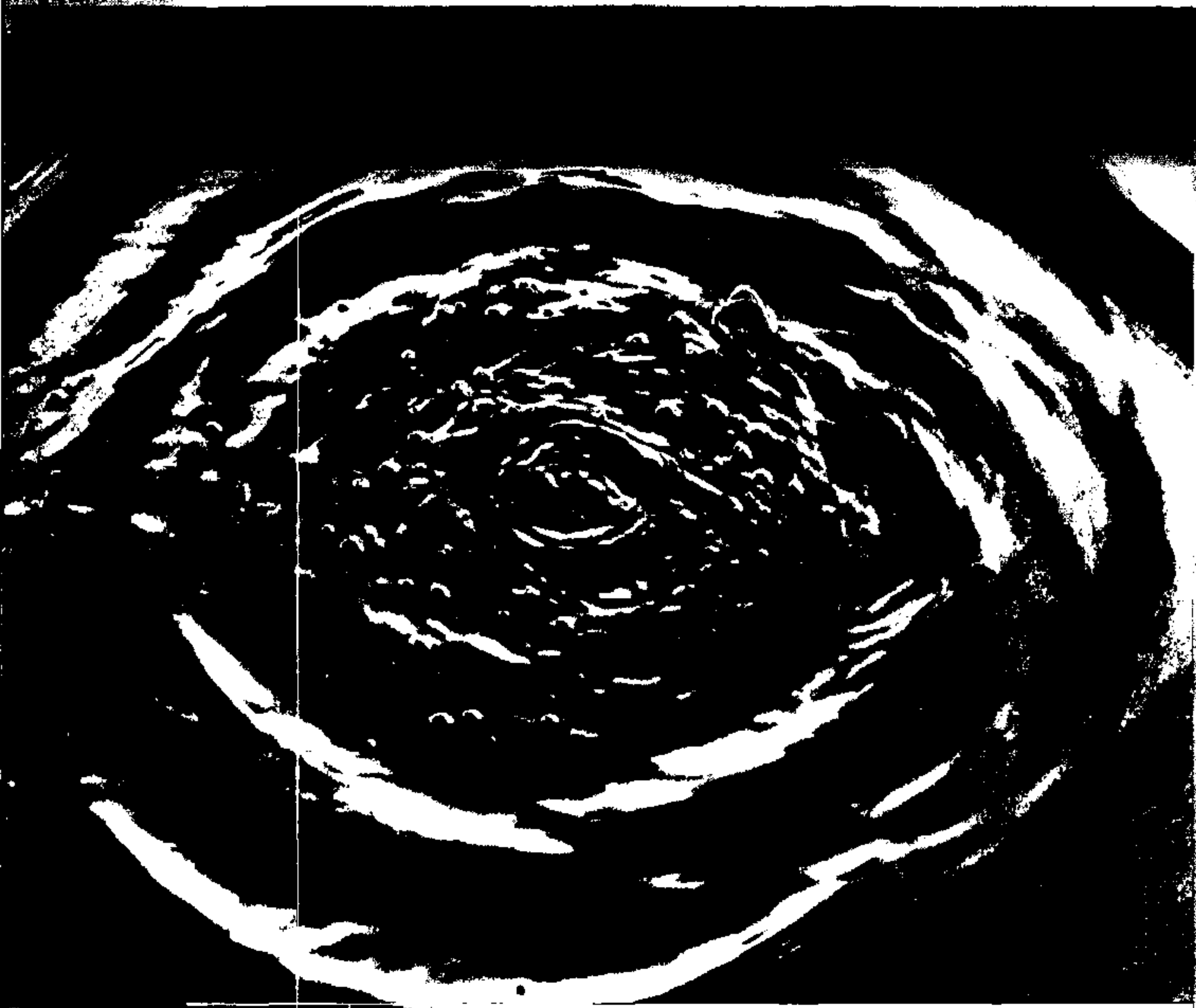
Szpunar, SM & Burt, BA (1988) Dental caries, fluorosis, and fluoride exposure in Michigan schoolchildren. Journal of Dental Research, 67, 802-806.

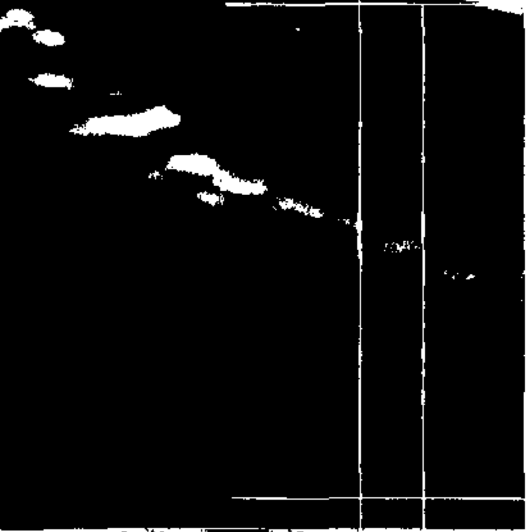
Van Wyk, PJ (1994) Study methodology. National Oral Health Survey, South Africa 1988-1989, pp 4-12. Pretoria. Department of National Health and Population Development.

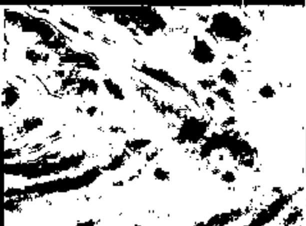
WHO. (1987) Oral health surveys: Basic Methods. 3rd ed. Geneva. World Health Organisation.

WHO. (1994) Fluorides and oral health. WHO Technical Report Series, 846, pp 16-19. Geneva: World Health Organisation.

Woolfolk, MW, Faja, BW & Bagramian, RA (1989) Relation of sources of systemic fluoride to prevalence of dental fluorosis. Journal of Public Health Dentistry, 49, 78-82.







Water Research Commission

PO Box 824, Pretoria, 0001, South Africa

Tel: +27 12 330 0340, Fax: +27 12 331 2565

Web: http://www.wrc.org.za