THE ABUNDANCES AND DISTRIBUTION OF SOME TRACE ELEMENTS IN SOME SELECTED SOUTH AFRICAN SHALES

by

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1 SUMMARY

The concentrations of fifteen trace elements Be, Ga, Cu, Zn, Co, Ni, V, Cr, Sc, Y, Yb, Zr, Nb, Th and Pb, have been determined in 315 Southern African argillaceous rocks which range in age from the early Precambrian Fig Tree Series to the Triassic Beaufort Series of the Karroo System. Less than two micron clay fractions have been separated from thirty-three of these sediments, and they have been analysed for the same trace elements. The determinations have been carried out by X-ray fluorescence and emission spectrographic analysis. In addition, forty-four selected samples have been analysed for U and Th by gamma-ray spectroscopy. The results obtained for several international rock standards, which were analysed simultaneously, emphasize the high quality of the data of this work.

A literature survey pertaining to the formation of clay minerals has been carried out and from this it is concluded that the general consensus of opinion is that clay minerals are principally formed in the weathering environment and not in the environment of deposition. Consequently, the bulk of the trace element content of clay minerals is incorporated in the weathering environment and trace element data is most useful in providing information concerning the composition of the source rocks and possibly the prevailing climatic conditions during weathering. This is shown particularly for the Fig Tree Series sediments which are considered to have been derived from a source area containing ultrabasic rocks, basic rocks and granites in the proportion 2:3:2 respectively. Chemical weathering is thought to have occurred in a reducing, oxygen-less, primordial atmosphere.

The trace element data and inter-element ratios are used to delineate the amount of variation in the trace element content of the sedimentary sequences studied. Correlation coefficients are used to determine groups of associated elements and an attempt is made, where possible, to correlate the trace element content with mineralogy. Carbonaceous shales from the Northern Ecca Facies of the Karroo System have been studied in most detail. It is shown that, in general, their trace element content is very variable but several elements show an association with the organic content. The development of authigenic iron minerals has not usually played a controlling role in the distribution of trace elements in these carbonaceous shales. Trace element concentrations were not found to vary systematically with height in the succession, but decreases in concentrations were noted along a NW-SE trend line from near the edge of the Northern Ecca basin of sedimentation to the centre of the Natal Trough. Possible reasons for this trend are given. The trace element abundances of the shales dredged from the Agulhas Bank are similar to those of the Bokkeveld Series and Malmesbury Formation shales and they cannot be used to positively adentify to which stratigraphic sequence these shales belong.

The abundances and distribution of the trace elements in the sediments of this work have been discussed individually. A strong coherence has been observed between Ga and Al and a mineralogical control of the Ga/Al ratio has been noted. Chlorite-rich shales tend to have the lowest and kaolinite-rich shales the highest Ga/Al ratios. V and Cr are often correlated with Ti and Al in the non-car-

bonaceous shales, and with Ti and the organic content in the carbonaceous shales. The development of a V and Cr bearing authigenic Ti mineral, possibly anatase, is postulated. This phase is associated with the clay fraction in non-carbonaceous shales and is adsorbed on the coaly plant material of carbonaceous shales. The concentrations of U and Th in most shales are found to be significantly higher than those for similar shales from other parts of the world and the possibility of Southern Africa being a high Th and U province is suggested.

Trace element variations with geological age have been studied in some detail. It was found that Ni and Cr decreased and Zr increased slightly with decrease in the age of the sediment. Yb and Be increased until Malmesbury times and then remained relatively constant. Any systematic variation in the concentrations of the remaining elements was masked by the normal spread of concentrations.

The possibility of using trace elements as indicators of environment of deposition is discussed comprehensively. The trace element concentrations were examined in shales of undoubted marine origin, the Bokkeveld Series, and the undoubted fresh-water origin, the Witteberg Series and parts of the Ecca Series. These shales were also selected because they all contain dominant illite. It was found that V and Cr were enriched in marine and Cu in fresh-water shales. Two axis and triangular plots were constructed of these element/Al against each other and it is shown that a good separation

into marine and fresh-water "fields" is obtained. It is suggested that these elements are potentially useful in paleo-environmental studies but that further research should be directed towards gaining more information on the actual sorption behaviour of these elements in the sedimentary environment.

A few suggestions for further research on South African shales are given.

CONTENTS

VOLUME I

		PAGE
1.	SUMMARY	(i)
2.	INTRODUCTION	1
3.	ANALYTICAL PROCEDURES	4
	3.1 Sample Preparation	4
	3.2 Clay Mineral Separation	6
	3.3 X-ray Diffraction	10
	3.4 Emission Spectrography	12
	3.4.1 Introduction	12
	3.4.2 Method of Analysis	14
	3.4.3 Quality of Data	17
	3.5 X-ray Fluorescence Spectrometry	23
	3.5.1 Introduction	23
	3.5.2 Zinc, Copper and Nickel	25
	3.5.3 Zirconium, Niobium, Yttrium, Thorium and Lead	30
	3.5.4 Chromium	34
	3.5.5 Gallium	35
	3.6 Gamma Spectroscopy - Thorium, Uranium	36
4.	NOTES ON THE ORIGIN AND DISTRIBUTION OF TRACE ELEMENTS IN SHALES	37
5.	THE TRACE ELEMENT GEOCHEMISTRY OF SOUTH AFRICAN SHALES	50
	5.1 Introduction	50
	5.2 The Swaziland System	55
	5.3 The Kheis System	67
	5.4 The Witwatersrand System	68
	5.5 The Sinclair Group	70
	5.6 The Damara System	72
	5.7 The Malmesbury Formation	73
	5.8 The Cango Formation	75

CONTENTS (cont.)

		PAGE
5.9	The Nama System	76
	5.9.1 Kuibis Series	76
	5.9.2 Schwarzkalk Series	78
	5.9.3 Schwarzrand Series	78
	5.9.4 Fish River Series	79
5.10	The Cape System	79
	5.10.1 Bokkeveld Series	79
	5.10.2 Witteberg Series	85
5.11	The Karroo System	88
	5.11.1 Dwyka Series	88
	5.11.2 Northern Ecca Facies	91
	5.11.2.1 Introduction	91
	5.11.2.2 Borehole Bh 134 and A Series Boreholes, Eastern Transvaal	93
	5.11.2.3 GB Series Boreholes, Northern Transvaal	100
	5.11.2.4 Dannhauser Boreholes, Central Natal	103
	5.11.2.5 Somkele Borehole, Northern Zululand	104
	5.11.2.6 Boreholes from the Vierfontein and Bothaville Districts, Western Transvaal	108
	5.11.2.7 Lower Ecca Shales	109
	5.11.3 Central Ecca Facies	110
	5.11.4 Southern Ecca Facies	111
	5.11.5 Western Ecca Facies	112
	5.11.6 Beaufort Series	114
5.12	Shales dredged from the Agulhas Bank	115
6.	SOME OBSERVATIONS ON THE DISTRIBUTION OF TRACE ELEMENTS IN SOUTH AFRICAN SHALES	118
6.1	Introduction	118
6.2	Beryllium	118
6.3	Gallium	123
6.4	Copper, Zinc, Lead	128
6.5	Cobalt, Nickel	137
6.6	Vanadium, Chromium	144
6.7	Uranium, Thorium	150

CONTENTS (cont.)

		PAGE
6.8	Zirconium	160
6.9	Niobium	164
6.10	Scandium, Yttrium, Ytterbium	168
7.	SOME OBSERVATIONS ON THE VARIATION OF TRACE ELEMENT CONTENT WITH GEOLOGICAL AGE	177
8.	THE USE OF TRACE ELEMENTS AS INDICATORS OF ENVIRONMENT OF DEPOSITION	183
9.	SUGGESTIONS FOR FUTURE RESEARCH ON SOUTH AFRICAN SHALES	196
10.	ACKNOWLEDGEMENTS	198
11.	REFERENCES	200

VOLUME II

APPENDIX 1	SAMPLE DESCRIPTIONS AND LOCALITIES
APPENDIX 2	ELEMENT CONCENTRATIONS AND SOME INTER-ELEMENT RATIOS
APPENDIX 3	TABLES AS REFERRED TO IN VOLUME I
APPENDIX 4	FIGURES AS REFERRED TO IN VOLUME I
APPENDIX 5	COMPUTER PROGRAM FOR ZINC, COPPER AND NICKEL DETERMINATIONS

2. INTRODUCTION

A glance at a geological map of southern Africa will immediately reveal that much of it is covered by sedimentary rocks. These vary from the schistose and dolomitic sequences of the Damara System in the north-west of the area and the sandstone thicknesses of the Cape System in the south and south-east of the area to the tremendously thick and extensive shale horizons of the Karroo System in the central part of the area and the conglomerates and dolomites of the Transvaal System in the north of the area. Now in general, the extent of geological knowledge of any area is usually dependent upon its economic significance, and the detailed knowledge of any formation is normally related to its economic mineralisation. Consequently the various members of the South African stratigraphic column have not been equally studied geologically. Although structural and mineralogical studies of coarse-grained sedimentary rocks and structural studies of fine-grained sedimentary rocks have been undertaken, virtually no mineralogical and geochemical data have been accumulated for fine-grained sedimentary rocks in this country.

Consequently this work was undertaken with the object of collecting information on the mineralogy and major and trace element geochemistry of shales occurring in southern Africa. Particular attention is devoted to the Karroo System, as it blankets most of the Republic of South Africa, and within it the Ecca Series, as this series contains the bulk of the shales found in southern Africa. However, most of the more important shale-containing representatives of the South African stratigraphic column are included in this study.
The sequences analysed range in age from

the 3000 m.y. Precambrian Fig Tree Series to the relatively young lower Triassic sediments of the Beaufort Series of the Karroo System.

The work was started in 1965 under the auspices of the Anglo American Corporation of South Africa when a Research Unit was established in the Geochemistry Department, University of Cape Town. The author joined the Unit in 1966. Since that time aspects of the work have been completed by research workers in the Unit and have been written up in the form of theses. Nel (1968) studied the distribution of boron in the shales, Marchant (1970) examined trace metals in organic separates of the shales and Danchin (1970) related the major element composition of the shales to the nature of the depositional environment of the sediments and also to the chemical nature of their provenance areas. As this whole project was a geochemical and not a geological one, no detailed petrographic studies have been carried out on the samples. Sample classification has been based on X-ray diffraction studies and many samples containing only minor amounts of clay minerals were rejected for analysis purposes. In general only samples consisting predominantly of clay minerals and broadly classified as shales, have been included in this study.

This work is essentially a study of the trace element content of the shales and of the separated clay fraction ($< 2\,\mu$) of a selected suite of shales. An attempt is made to relate the trace element content to the mineralogy of the shales, and to investigate the possibility of using certain trace element ratios as an indication of the nature of depositional environments of

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the sediments. Variations of trace element content within and between sedimentary sequences are described, and for the Ecca Series regional variations of trace element levels are mapped where possible. Correlation coefficients are used whenever possible as an aid to elucidating the behaviour of the trace elements. Results of this work are compared with those found by other workers. in this field in different parts of the world, and for reliable comparisons to be made, every effort has been made to ensure that the trace element data presented here are of the highest possible quality. In the two main analytical techniques used, emission spectrography and X-ray fluorescence spectroscopy, international rock standards have been used to control the quality of the results.

The thesis is presented in two volumes. Volume I contains the text and Volume II the sample localities, hand-specimen descriptions, sample mineralogy and sample classification. Vol. II also contains analytical results, figures, diagrams and a sample locality map. All figures and tables referred to in Vol. I which have the letter "A" affixed to the number, are to be found in Vol. II.

3. ANALYTICAL PROCEDURES

3.1 SAMPLE PREPARATION:

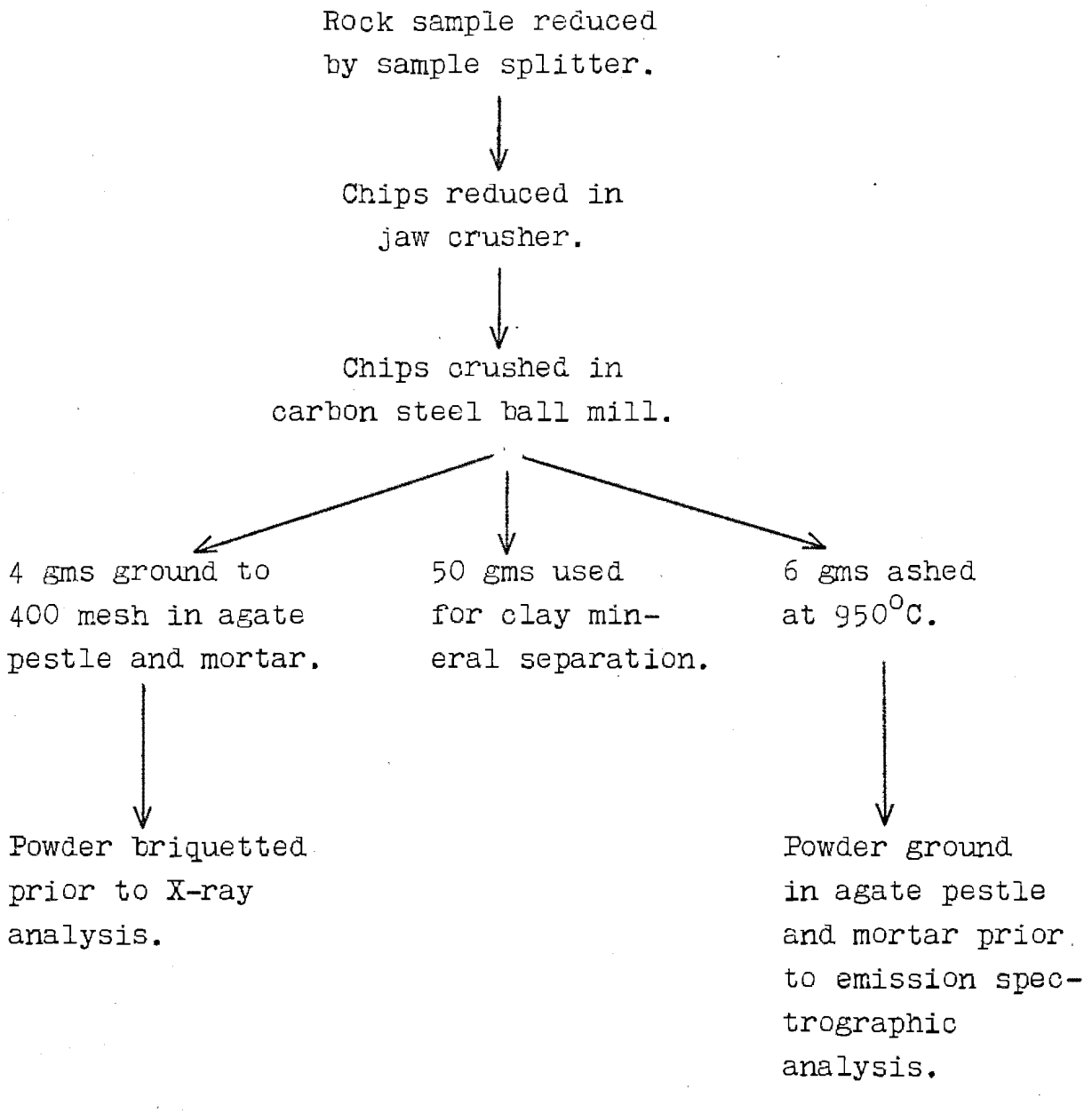
Samples were received in the form of about 500 gram rocks or sections of borehole cores. They were reduced to half inch chips in a sample splitter after fragments containing weathered surfaces had been removed by hand-picking. At this stage the chips were carefully examined for the presence of fossils and segregated mineral crystals like pyrite. Crushing in a hardened steel jaw crusher followed to reduce the chips to one cm size or less fragments. The samples were then pulverised in a carbon steel ball mill for ten minutes to produce less than 80 mesh powder. Four grams of this powder was subsequently reduced to about 400 mesh in an automatic agate pestle and mortar and then briquetted by the method of Baird (1961) for X-ray diffraction and fluorescence analysis.

The ball mill treatment was designed to disaggregate the sample rather than crushing all the mineral grains finer so that 50 gm portions of this material could later be used for clay mineral separations. 6 gm of this powder were also removed and ashed at 950°C in a muffle furnace, the loss of weight on ignition being recorded. This material was reduced to about 400 mesh in the automatic agate pestle and mortar prior to emission spectrographic analysis.

A flow diagram of the sample preparation methods is given in Figure 1.

Figure 1.

SAMPLE PREPARATION FLOW DIAGRAM



3.2 CLAY MINERAL SEPARATION

Tourtelot (1964) pointed out that most investigations on argillaceous rocks give tacit recognition to the concept that most trace elements occur primarily in the clay fraction. However, this hypothesis cannot really be accepted until separated fractions of argillaceous rocks have been analysed and these results compared with the whole rock results. For example, Sr, Rb, Zr and B can have more than one mode of occurrence in sedimentary rocks. Sr and Rb occur in calcite and potash feldspar respectively which are common accessory minerals in argillaceous rocks. Zr and B occur in the detrital heavy minerals zircon and tourmaline respectively and this may be their major mode of occurrence in sediments derived from granitic or pegmatitic terrains. Accordingly it was decided to separate the clay mineral fraction from thirty three samples selected from various formations.

As about 6 gm of material was required for analysis a separation procedure had to be adopted which would provide this yield per sample. Size separation by settling in a column of water in a 1 meter glass tube of 6 cm diameter was first attempted but had to be abandoned as sufficient amounts of separated clay could not be recovered. Only small quantities of material could be introduced at the top of the column to avoid turbidity currents which caused mixing throughout the column.

The technique finally adopted was one of gravity settling in 2 liter beakers of water. About 15 - 20 gm of rock powder were placed in a 250 ml beaker of distilled water. As suggested by Brindley (1961) dis-

aggregation of the sample particles was achieved by adding a few drops of ammonia and subjecting the beaker to ultrasound. A Dawe automatic ultrasonic cleaning tank was used and the samples were treated for five hours. Fig. 1A shows that little further dispersion took place after this length of time and Fig. 2A illustrates that virtually all quartz and feldspar have been removed from the less than two micron fraction although much clay material has been left in the two larger size fractions. Bk 11, a sample containing appreciable quartz and feldspar, was used for these determinations. Approximate mineral proportions were calculated from X-ray diffractograms, using a procedure described by Weaver (1967). An encouraging feature of this work was that there was no apparent separation between the clay minerals which indicates that, for the Bokkeveld samples at least, chlorite and illite have the same particle size distributions and settling characteristics, and, therefore, the separated clay fraction is representative of the clay minerals in the whole rock.

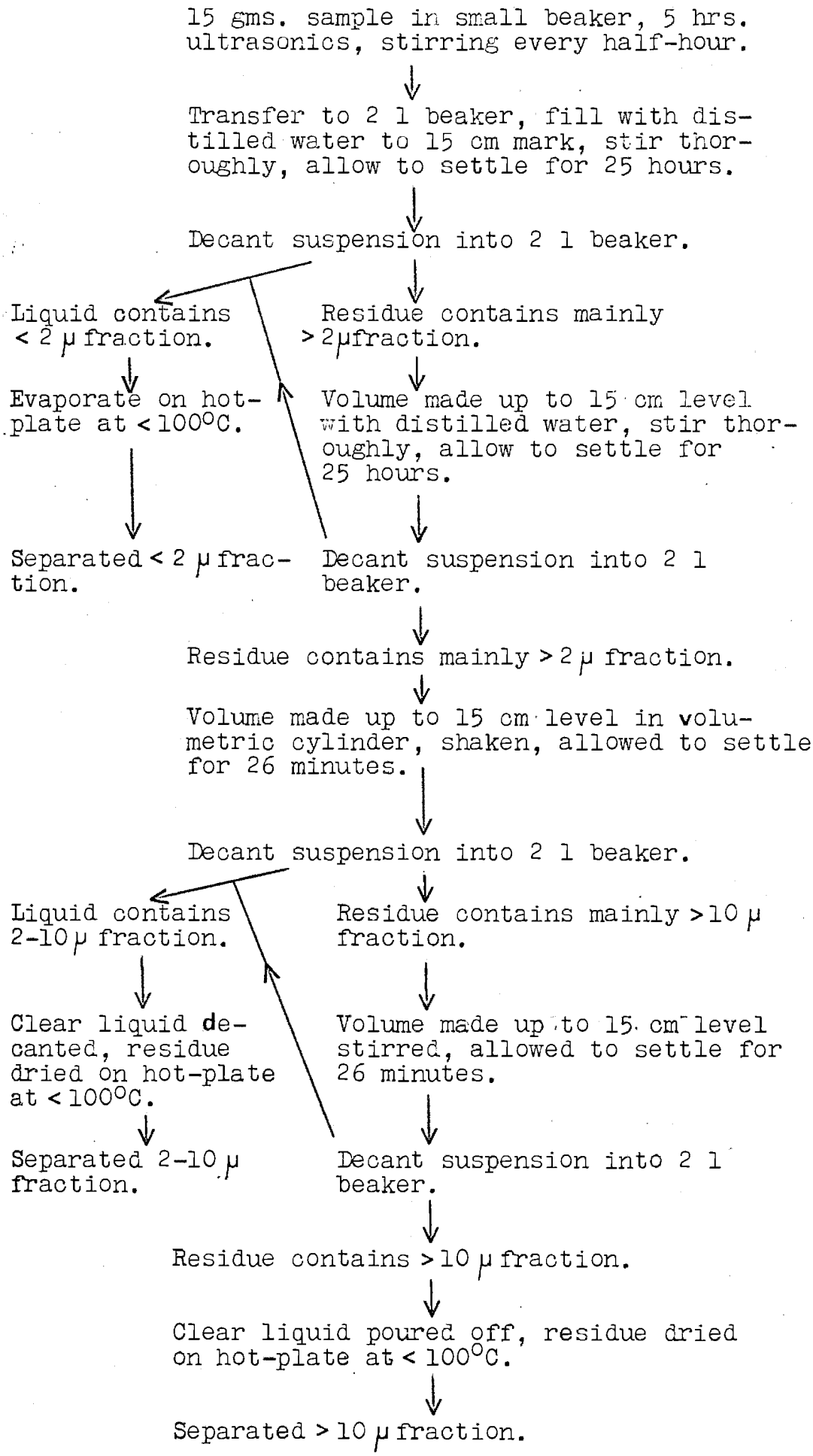
After ultrasonic disaggregation the slurry was transferred to a 2 liter beaker, distilled water was added and, after stirring, the beaker was allowed to stand for 25 hours (Jackson et al., 1950). After this time the suspension, which contained the less than two micron fraction, was removed by decantation and evaporated to dryness on a hot-plate in a fume-cupboard. Distilled water was added to the residue in the beaker and the process was repeated. The residue containing mainly the greater than two micron fraction was transferred to a volumetric cylinder which was then filled with distilled water, shaken and allowed to stand for 26 minutes.

The suspension which contained the 2 - 10 micron fraction (Jackson et al., 1950) was transferred to a beaker and the process was then repeated. In this manner three size fractions were obtained; less than 2 microns, 2 10 microns and greater than 10 microns. Fig. 2 is a flow diagram of the clay separation process.

The whole procedure was repeated until at least 6 gm of clay material from each sample was obtained. The dried clays were then ashed at 950°C in a muffle furnace prior to X-ray and emission spectrographic analysis.

Fig. 2

Clay separation flow sheet



3.3 X - RAY DIFFRACTION

An analytical procedure developed by Fesq (1967) was used for the X-ray diffraction studies of the sedimentary rocks. A Philips PW 1050-30/1054 diffractometer and generator was used, and the instrumental settings are shown in Table 1.

The 4 gm whole rock powder briquettes prepared for X-ray fluorescence (XRF) analysis were used for diffraction using a special sample holder made in the Department of Geochemistry, U.C.T. For further detailed examination of the clay minerals involving routine procedures

Table 1

Instrumental conditions for X-ray diffraction analysis

Tube	Cu K_α
Filter	Ni
Slits	Divergent 1° Collimating 0.2° Scatter 1°
Generator	48 kV, 20 mA
Counter	Proportional with discrimination
Goniometer speed	2° 2 Θ /min
Chart speed	800 mm/hour
Rate meter	16
Time constant	1
Range (2 Θ)	2° - 64°

such as heat treatment, glycolation and acid leaching, a modified Philips sample holder was used (Fesq, 1967). The routine identification of the clay minerals was carried out following the scheme used by Weaver (1967). The carbonates, feldspars, quartz, sulphides and iron oxides were identified using the American Society for Testing Materials (ASTM) card index system.

The mineralogy of all the samples used in this study is presented in Table 1A. It will be noticed that no attempt has been made to give a quantitative estimate of the concentrations of clay minerals present in each sample based on the peak height of the 001 reflections on the X-ray diffractogram. The clay minerals are only given as being present in dominant, subordinate or trace amounts. It is felt that the quantitative analysis of fine-grained sedimentary rocks is fraught with too many difficulties to be accurately carried out. Factors of unknown importance are:- reproducibility of sample preparation, presence of allophane, mass absorption differences, degree of crystallinity and particle size and preferred orientation effects. Also Gibbs (1965, 1968) has pointed out that in samples containing a mixture of clay minerals with different size distributions, size segregated mounts are produced by many of the mounting techniques currently used. Although he considers the dry powder press technique acceptable, the method used here, it is considered very possible that this method might produce enhanced peaks for the clay minerals containing the largest size distribution. However, the most serious problem lies in the method of calculation of the concentrations of clay minerals from the peak heights of their 001 reflections on the X-ray diffractograms. Amongst others, Weaver (1967, pg. 50) has pre-

sented a method for doing this which corrects for differences in diffractive ability between the clay minerals. Pierce and Siegel (1969) have pointed out that they used five different methods described in the literature using the same diffractograms for each method. They showed that not only did they get different concentrations for the clay minerals, but adjacent samples showed different trends for different methods. This means that although each method might be internally consistent, results from different laboratories cannot be compared with any degree of confidence, and for this reason no quantitative work in this respect has been attempted.

3.4 EMISSION SPECTROGRAPHY

3.4.1 INTRODUCTION

Today a wide variety of instrumental methods are used in the geochemical analysis of geological materials. These include colorimetric, polarographic, X-ray fluorescence (XRF), atomic absorption, neutron activation, isotope dilution, mass spectrometric and emission spectrographic procedures. The so-called classical chemical methods are no longer widely used in geochemical research. Each general procedure has its own analytical advantages and ideally the choice of analytical method for the determination of a particular element will depend on several factors. Included are factors such as availability of analytical technique, type of samples being analysed, element concentration levels present in the samples, precision and accuracy required and speed and cost of analysis. Although Ahrens (1961) has pointed out that it is possible to excite some 70 elements in the d-c arc of emission spectrography, it is by no means possible to

determine all these elements quantitatively at the concentration levels found in sedimentary rocks by a single standard method. For many trace elements XRF offers better accuracy and precision and is more rapid than emission spectrography unless a direct reader is being employed. For these reasons the majority of trace elements being dealt with in this study have been determined by XRF. A further factor in favour of this method was that sample mounts were already prepared, as the briquettes used in X-ray diffraction are the same as those used in XRF for the heavier elements.

Be, Yb, Sc, Co and V were determined by emission spectrography as their determination by XRF was either impossible or very difficult for reasons given in the section dealing with XRF. Y was determined by both methods.

The analytical method adopted for this study is fundamentally that suggested by Ahrens (1951, 1954) for the determination of the involatile group of elements and has since been used by several workers in this field eg. Spencer (1966), El Wakeel and Riley (1961), Hirst (1962), Weber and Middleton (1961) and Nicholls and Loring (1962). In this procedure selective distillation is reduced by adding carbon powder to the samples which are arced to completion. A single internal standard, palladium, is used. Variations of this technique have been used by Lonka (1967), who mixed NaCl and $CaCO_3$ with the carbon powder, and Cronan (1969/1970), who used a NaCl/carbon buffer. However, Carr and Turekian (1961) preferred to mix their samples with $CaCO_3$ only in a one to one ratio.

3.4.2 METHOD OF ANALYSIS

The material used for emission spectrographic analysis was the powder which had been ashed at 950°C in an automatic muffle furnace after reduction to about 120 mesh in a carbon-steel ball-mill. 0.100 gm sample or standard was mixed with 0.200 gm of a carbon-tetramminepalladous nitrate, $[(NH_3)_4Pd](NO_3)_2$, mix containing 1000 ppm Pd. Thorough mixing was achieved by grinding for 15 minutes in a mechanical agate mortar and pestle. This gave an arcing mixture of 667 ppm Pd which produced a convenient intensity of the Pd line used.

The use of a matrix of spectrographically pure graphite and a high amperage ensured a high temperature arc burn and the consequent complete volatilisation of the less volatile elements. It also prevented bubble formation in the electrode with its attendent undesirable selective distillation. $CaCO_3$ was not used in the matrix as its presence was found to cause excessive sputtering of the sample into the arc. An inert atmosphere of argon and oxygen was applied through a modified Stallwood jet (Baumgartner, 1967) to reduce cyanogen, which interferes with the Sc and Co analysis lines, and to remove the flamy fringe around the arc column which might cause self-absorption of the Yb and Be lines which are ground state lines.

The wavelengths of the analytical lines used are given in Table 2 and the analytical details and instrumental settings of the spectrograph are presented in Table 3.

Plate calibration was achieved using the two step method described by ASTM (1964) and first proposed by Churchill (1944). An iron spectrum, recorded

Table 2

Wavelengths of analytical lines used in emission spectrographic analysis (in Å).

Sc	4246.829
Co	3453.505
Y	3242.280
Yb	3289.370
V	3183.982
Be	3130.416
Pd	3258.780

through a 1 to 2 ratio step sector, was included on each plate and a selection of Fe lines was used for plate calibration purposes. Using combinations of two steps of Fe, first a preliminary curve was drawn on a Respectra calculating board and from this a calibration curve was constructed. It was not possible to use one calibration curve for the whole wavelength region as a distinct change in emulsion response (gamma) in the Ilford Ordinary N.30 plates used was found between Co 3453 and Y 3327. However, a negligible change of gamma was found between plates of the whole batch for any one wavelength region, so that only two calibration curves were needed for the whole analytical run, one for each wavelength region. Thus one calibration curve was used for Sc and Co, and the other for Y, Yb, V and Be. Inter-element analytical line intensity ratios with Pd were calculated from the board following the Respectra instruction manual. Background corrections were made for all lines read on the first step. A Hilger and Watts non-recording microphotometer was used to read the plates.

Working curves were constructed for each

Table 3

Analytical details of the emission spectrographic techniques

Electrodes	- sample	National Carbon Co. graphite, L3806 AGKSP. Cavity depth 2.5 mm., internal diameter 2.8 mm., sidewalls slightly reduced.
	- top	Morganite carbon sharpened to point.
	- loading	Elpac automatic packer.
	- model	Jarrell-Ash Co. (Jaco) 3.4 meter Ebert, plane grating 15,000 lines/inch resolution 5.1 Å /mm.
Spectrograph:	Slitwidth	15
	Slit focus	18.7 divs.
	Step-sector	3 steps, 4 to 1 ratio
	Wedge	5 divs.
	Rack	6 divs./burn
	Amperage	11 amps d.c., Fe 3 amps
	Atmosphere	Ar 6 l./min., O_2 1.5 l./min. (4:1).
	Wavelength range	2965 - 4315 Å.
	Wavelength order	First.
	Wavelength setting	6.25 divs.
	Arcing time	Until completion of burn.
	Pre-burn time	5 secs.
	Plate position	centre of camara.
Excitation		d.c. arc, anode.
Arcings		Samples arced in duplicate, standards arced ten times.
Photographic plates		Ilford Ordinary N. 30, backed.
Exposures per plate		13 samples, one Fe.
Developer		Kodak DX - 80, 7 mins.
Fixer		Amfix ultrarapid fixer, 5 mins.

element for each of the three steps on three-cycle logarithmic paper. The three working curves for each element thus covered a wide range of concentrations, but for most samples only one working curve for each element was found necessary. Figs. 3A, 4A, 5A, 6A, 7A and 8A, are the working curves for Sc, Co, Y, Yb, V and Be respectively. Error bars shown are intensity ratio standard deviations.

3.4.3 QUALITY OF DATA

The accuracy of emission spectrographic analysis is very dependent upon the absence of different matrix effects between samples and standards, and between individual samples. Matrix effects were reduced to a minimum by the use of a high amperage and by making the arcing charge two-thirds carbon so that arcing characteristics were predominantly those of carbon and were very little influenced by sample or standard rock type. In this way any bubble formation and selective distillation was also eliminated as pointed out earlier.

The use of standards of precisely known trace element concentrations is also vital in obtaining accurate analyses. To avoid systematic error it is preferable that these standards be silicate rocks and not chemical compounds to avoid differences in volatilisation and excitation of a particular element due to differences in chemical bond types. Consequently three international rock standards were used - G-1, W-1 and S-1. These were supplemented by combinations of the same rock powders mixed in different proportions. Values used are shown in Table 4, and are the recommended values taken from Fleischer (1969) for G-1 and W-1, and the median values of Sine et al., (1969) for S-1.

Table 4

Standard values used for emission spectrographic run

	Sc	Co	Y	Yb	V	Be
G - 1	3	2.4	13	0.8*	16	3
W - 1	34	50	25	2.2	240	0.8
S - 1	15	18	450	70	88	24
G-1/W-1 1/1	18.5	26	19	1.5	128	1.9
G-1/W-1 3/1	10.8	14.3	16	1.2	72	2.5
G-1/S-1 9/1	4.2	4.0	57	7.7	23	5.1
G-1/S-1 19/1	33	48	46	3.5	232	2.0

* Average of neutron activation analysis and isotope dilution data listed by Fleischer (1962, 1965, 1969).

Points for the standards containing S-1 did not lie on the working curves for the elements Co and Yb. The cause of the high S-1 Co intensities could not be determined, but the low S-1 Yb intensities indicates a true concentration of less than 70 ppm Yb in S-1. W-1 could not be used for Be owing to interference from Ti 3130.8 which is a high intensity line as W-1 contains 1.07% TiO_2. In general shales contain slightly less TiO_2 and considerably more Be than W-1 so this interference problem does not normally arise.

The natural rock standards were supplemented for the elements Be and Co by a series of artificial standards prepared by Dr A.J. Erlank of the Geochemistry Department, University of Cape Town, containing 1000 ppm, 316 ppm, 100 ppm, 31.6 ppm, 10 ppm, 3.16 ppm and 1 ppm

trace elements. The artificial base, a granite shale mix containing 70% SiO_2, 15% Al_2O_3, 5% K_2SO_4, 3% Fe_2O_3, 3% Na_2CO_3, 2% MgO and 2% $CaCo_3$, was sintered for six hours at 900°C and used to dilute a Jarrell-Ash S.Q. mix containing 1.30% of 45 elements. A series of standards were made using a dilution factor of $\sqrt{0.1}$, a procedure suggested by Ahrens and Taylor (1961).

A measure of the precision is given by the coefficient of variation, C, which is the standard deviation expressed as a percentage of the mean. When dealing with duplicate analyses C is determined as follows (Youden, 1951):

$$C = \sqrt{\frac{(\Sigma d^2)}{2N}}$$ where N is the total number of samples and d is the difference between each duplicate result expressed as a percentage of the duplicate result. For a single sample analysed N times C is given by (Youden, 1951):

$$C = \sqrt{\frac{(\Sigma d^2)}{N-1}} \cdot \frac{100}{\bar{x}}$$ where $\bar{x}$ is the average and d is the difference between each result and the average. C was determined by both methods, in the second case being derived from twenty replicate analyses of sample AEc1.

Thus 68% of all 2N individual measurements will lie within C% of the true value for that sample as given by the method. Youden (1951) also shows that $C/\sqrt{N}$ gives a measure of the precision of the averaged result, where N is the number of times each sample has been analysed. Table 5 shows the coefficients of variation obtained for the six elements analysed by this emission spectrographic technique. C_1 and C_2 are the coefficients of variation for for each individual measurement calculated from a series of

Table 5

Precision of emission spectrographic technique (%)

	Sc	Y	Yb	Co	V	Be
C_1	6.7	7.4	9.7	7.9	11.2	8.7
C_2	7.8	8.0	8.6	6.7	10.1	9.5
C_3	4.8	5.2	6.9	5.6	7.9	6.1
C_4	5.5	5.7	6.1	4.7	7.1	6.7

duplicate analyses and from twenty replicate analyses respectively. C_3 and C_4 are coefficients of variation for each reported average of the duplicate analyses calculated from a series of duplicate analyses and from twenty replicate analyses respectively, i.e.

$$C_3 \text{ is } C_1/\sqrt{2} \quad \text{and} \quad C_4 \text{ is } C_2/\sqrt{2}$$

The coefficients of variation of the reported averages are seen to range between 4.8% and 7.9% which is very satisfactory for an emission spectrographic technique of this type in which several elements are determined simultaneously. Chief contributions to the precision are probably made by

(i) difficulties in mixing such small quantities

(ii) errors associated with microphotometer readings, and

(iii) occasional sputtering in the arc causing changes in excitation of the elements being determined.

As a check on the accuracy of the method

ten international rock standards, BR, GR, GA, GH, G-2, GSP-1, AGV-1, PCC-1, DTS-1 and BCR-1, (Flanagan, 1970) were analysed simultaneously as independent unknowns. Ten replicate analyses of each standard were carried out. These results, together with those for several more recently issued standard rocks, have been submitted for publication and are currently in press (Hofmeyr, 1971). The results for BR, GR, GA and GH are shown in Table 6 together with the recommended values taken from Roubault et al. (1969). The results for G-2, GSP-1, AGV-1, PCC-1, DTS-1 and BCR-1 are shown in Table 7 together with average and median values taken from Fleischer (1969). Included are a few more recently reported analyses for Co and Be.

An examination of the comparison of results in Tables 6 and 7 shows a close agreement for the elements Sc, Co, Y, V and Be. The Yb results of this work, however, are lower than those published by other analysts for the same standard rocks, and this is undoubtedly due to the new recommended value of 2.2 ppm Yb in W-1 (Fleischer, 1969) upon which the results of this work are largely based, compared to the old recommended value of 3 ppm (Fleischer, 1965). The new value is based on results obtained by modern isotope dilution and instrumental neutron activation analysis techniques.

It is clear that the emission spectrographic results presented in this thesis do not suffer from any systematic bias and are sufficiently precise for meaningful conclusions to be drawn. Except for Yb the absolute values of the samples can be compared with the results obtained by other analysts studying sedimentary rocks.

Table 6

Comparison of trace element data in ppm for standard rocks, BR, GA, GH and GR.

		Sc	Co	Y	Yb	V	Be
BR	This work	26	58	45	2.4	250	N.D.**
	Rec. mean*	-	50	-	4	240	1
GA	This work	6.5	6	23	1.5	41	1
	Rec. mean*	7	5	-	2.5	36	4
GH	This work	2	6	78	4.2	8	7.1
	Rec. mean*	-	1.5	-	8	5	6
GR	This work	7.1	12	18	1.4	67	5.8
	Rec. mean*	7	10	19	2	65	5.5

*Roubault et al. (1969)

**N.D. = not determined

Table 7

Comparison of trace element data in ppm for standard rocks, G-2, GSP-1, AGV-1, PCC-1, DTS-1 and BCR-1

		Sc	Co	Y	Yb	V	Be
G-2	This work	3.4	6	12	0.5	37	2.6
	Ave. (1)	4.6	5.7	12.1	1	37	2.3
	Med. (1)	4	5.0	12	1	35	2.5
			4.2 (2)				3.20 (3)
GSP-1	This work	6.4	6.0	29	1.4	54	1.5
	Ave. (1)	9.1	8.2	34	2.1	55	1.0
	Med. (1)	8.4	7.0	31	2	53	1.0
							1.76 (3)
AGV-1	This work	11.3	13	25	1.6	118	2.3
	Ave. (1)	12.5	16.6	23	1.9	127	1.8
	Med. (1)	11.7	16	24.5	2	124	1.8
				12.0 (2)			1.23 (3)
PCC-1	This work	9.8	125	4	0.9	33	0.5
	Ave. (1)	8.2	116	-	-	29	-
	Med. (1)	8.5	110	-	-	30	-
			111 (2)				0.03 (3)
DTS-1	This work	4.2	150	4	0.7	9.2	0.5
	Ave. (1)	3.8	135	-	-	16.9	-
	Med. (1)	4	141	-	-	12.5	-
			162 (2)				0.07 (3)
BCR-1	This work	31	35	48	3.2	315	N.D. (4)
	Ave. (1)	36	37	42	4.3	414	2.0
	Med. (1)	33	36.7	47.4	4.4	423	2.0
			41.3 (2)				1.59 (3)

(1) Flanagan (1969) (2) Laul et al.(1970) (3) Meehan (1969) (4) N.D. = not determined

3.5 X - RAY FLUORESCENCE SPECTROMETRY

3.5.1 INTRODUCTION

As has been mentioned earlier, the bulk of geochemical data for sedimentary rocks, and incidentally for igneous and metamorphic rocks as well, has been provided by emission spectrographic methods, as these have been best suited to obtaining data of acceptable accuracy and precision for many trace elements for large numbers of samples. Although more sophisticated methods of analysis, such as isotope dilution and instrumental activation analysis, have been developed, these are not suitable for rapid analysis of large numbers of samples. In recent years, however, X-ray fluorescence spectrometry has been increasingly utilised in the analysis of sedimentary materials. The general principles of the technique are described by Jenkins and de Vries (1967). Ahrens et al. (1967) and Willis (1970) determined several trace elements by XRF in manganese nodules, and Cowgill (1966) describes an XRF technique for determining 41 elements in lake sediments. XRF is capable of producing major element data of excellent quality (von Michaelis et al., 1969), and data produced by Willis et al. (1971) on lunar rocks and soil and published by Carmichael et al. (1967) on standard rocks illustrate the success of the method for obtaining good quality data on trace elements as well.

However, the difficulties of determining Co and V in particular by XRF are underlined by the unsatisfactory data of Carmichael et al. (1968). Table 8 compares their data for the U.S.G.S. standard rocks with the average and median values given by Flanagan (1969). The Co K_{α} spectral line cannot easily be used as it is

interfered with by Fe K_β and it also lies on the long wavelength side of the Fe K absorption edge which makes matrix corrections difficult. Co K_β can be used as the analysis line but it suffers from possible interference by Ni K_α and is also a very weak line at the concentrations commonly found in sedimentary materials. V K_α is strongly interfered with by Ti K_β and V K_β is strongly interfered with by Cr K_α. By using a series of correction factors Co K_α and V K_α can be used in the determination of these elements, but as only a small proportion of the measured intensity of the peaks is due to the analysis line K_α radiation the accuracy of the method must be impaired, and the consequent results somewhat uncertain. Thus in this work Co and V have been determined by emission spectrography. Sc was determined by the same method, as in XRF Sc K_α is heavily interfered with by Ca K_β when the PET (Pentaerythritol) analysing crystal is used. If cyrstals with higher resolving power are used, this wavelength region lies outside the angular range of the goniometer. Be is too light and Yb concentrations are too low

Table 8

Co and V data for U.S.G.S. standard rocks in ppm

		G-2	GSP-1	AGV-1	PCC-1	DTS-1	BCR-1
Co	Ave. (1)	5.7	8.2	16.6	116	135	37
	Med. (1)	5.0	7.0	16	110	141	36.7
	XRF (2)	10	20	30	90	100	60
V	Ave. (1)	37	55	127	29	16.9	414
	Med. (1)	35	53	124	30	12.5	423
	XRF (2)	20	50	115	40	10	400

(1) Flanagan (1969)

(2) Carmichael et al. (1968)

in sediments for these elements to be determined by XRF and emission spectrography was consequently used. Y was determined by both methods. Elements which were analysed by XRF were Zn, Cu, Ni, Zr, Nb, Y, Pb, Th, Cr and Ga.

The X-ray spectrometers available for this project were a Philips PW 1220 semi-automatic Spectrometer with a 2kW generator and an older Philips PW 1540 instrument with a 1 kW generator. Both instruments were of the flat crystal type and had facilities for pulse height selection. Corrections were always made for sample position and for dead time effects.

3.5.2 ZINC, COPPER AND NICKEL

Zn, Cu and Ni were determined on the PW 1220 spectrometer using an Au target tube and pulse height selection. The analysis is complicated by the presence of trace quantities of Zn, Cu and Ni in the X-ray tube, which caused interference on the analysis lines by Rayleigh scattering. Correction for this interference was accomplished by ascertaining the ratio of the nett intensity of the Au L_{α} line to the nett intensity of the analysis lines using Ni-free blanks. This ratio was constant for samples of differing mass absorption. The Au L_{α} line of the shale samples was measured and this ratio used to calculate the X-ray tube contribution to the analysis line, which could then be subtracted to leave the nett intensity due to the element in the sample only.

Background intensities at the peak positions were measured by first counting several samples chosen at random at four carefully chosen background positions and then plotting the results graphically fitting a spline

curve to the points. Theoretical background intensities could then be obtained by interpolation at peak positions. Factors for obtaining the background at each peak position were calculated from backgrounds as follows:

$\text{Factor}_{\text{element}} = (Bg_{1(or4)} + Bg_2 + Bg_3) / Bg_{\text{element}}$ at peak position where the element is Zn, Cu or Ni.

Average factors for each element were then calculated and used to calculate the theoretical background intensities at the peak positions of the shales as follows:

$$Bg_{\text{element}} \text{ at peak position} = \frac{(Bg_{1(or4)} + Bg_2 + Bg_3)}{\text{Factor element}}$$

Nett peak intensities were then obtained by subtraction of the background from the total measured intensity at the peak positions. In the determination of Zn and Cu backgrounds 1, 2 and 3 were used, while for Ni backgrounds 2, 3 and 4 were used.

As Fe is the heaviest major element found in normal shales, for wavelengths shorter than the Fe K absorption edge only very small changes in mass absorption coefficients should occur. Thus a single measurement of mass absorption coefficient will suffice for the K lines of all elements of greater atomic number than Co. Reynolds (1963, 1967) has shown that the intensity of the Compton scattered Mo K_α radiation (0.711 Å) from the molybdenum target tube is inversely proportional to the mass absorption coefficient and can be used as a measure mass of absorption for elements heavier than Co. This method of matrix correction was the one adopted here for the elements Zn, Cu and Ni.

To determine the mass absorption coefficients

the time taken to accumulate 128,000 counts of the Compton scattered portion of the Mo K_α primary beam was measured for the standards G-1, W-1, K_2SO_4, CaF_2 and U.S.B.S. sample No 99, all of known mass absorption coefficient, and for all the samples. For the standards a plot of mass absorption coefficient versus time was constructed by linear regression analysis and from this graph the mass absorption coefficient of the samples at 0.9 Å was obtained. Each sample was run twice and the result averaged. The instrumental conditions for the determination of the mass absorption coefficients are set out in Table 8(i). This method works well for shales as there is not a great deal of variation in mass absorption coefficient. The low mass absorption coefficient region is limited by the requirements of large sample thicknesses, and high mass absorption coefficient region is limited by the difficulty of accurately measuring a weak peak (Compton Mo K_α) that is imperfectly resolved from a strong one (Rayleigh Mo K_α). The mass absorption coefficients of the samples studied varied in general from

Table 8(i)

Instrumental conditions for the determination of mass absorption coefficients

Instrument	PW 1540
Target tube	Mo
kV	48
mA	20
Counter	Scintillation
Collimator (μm)	160
Analysing crystal	Topaz
Pulse height selection	Not used
Line	Compton K_α
Position ($^o2\theta$)	31.64
Counts	128,000

10 to 12, with those of the Fe-rich chlorite shales extending up to 15 and those of the carbonaceous kaolinite shales extending down to 6. Reynolds (1967) points out that this technique is unsatisfactory for mass absorption coefficients greater than 20, but this eventuality did not arise here. That the briquettes of the sample of very low mass absorption coefficients were of adequate thickness was verified by counting briquettes of different thicknesses in this low range of mass absorption coefficient.

The concentrations of Cu, Ni and Zn in the samples were calculated according to the method of Reynolds (1963) as follows:

$$\text{ppm } Z_X = \frac{\text{cps } Z\ K_{\alpha},X}{\text{cps } Z\ K_{\alpha},\text{std}} \cdot \frac{\mu\ 0.9\text{Å},X}{\mu\ 0.9\text{Å},\text{std}} \cdot \text{ppm } Z_{\text{std}}$$

where Z is an element,

X is an unknown,

cps $Z\ K_{\alpha},X$ and cps $Z\ K_{\alpha},\text{std}$ refer respectively to the intensities in counts per second of the background-corrected $Z\ K_{\alpha}$ peaks in the unknown and standard,

$\mu\ 0.9\text{Å},X$ and $\mu\ 0.9\text{Å},\text{std}$ refer respectively to the mass absorption coefficients of unknown and standard measured at wavelength 0.9Å,

ppm Z_{std} refers to the concentration of the element Z in the standard.

Instrumental conditions for the determination of Zn, Cu and Ni are set out in Table 9.

Table 9

Instrumental conditions for the determination of Zn, Cu and Ni

Instrument	PW 1220
Target tube	Au
kV	60
mA	32
Counter	Flow and scintillation
Collimator	Fine (150 μm)
Analysing crystal	LiF (220)
Vacuum	Used
Sample spinner	Used
Pulse height selection	Used

	Au	Zn	Cu	Ni	Backgrounds
Line	L_α	K_α	K_α	K_α	-
Position (°2θ)	52.97	60.27	65.25	70.97	59.15, 64.05 68.00, 72.50
Times (secs)	10	120	120	120	60

W-1 was used as the standard and the values of Zn, Cu and Ni used were those recommended by Fleischer (1969) and shown in Table 10. U.S.G.S. standard rock BCR-1 was run as an unknown and these results are included in Table 10 together with the average and median values taken from Flanagan (1969), the XRF data of Carmichael et al. (1968).

Table 10

Zn, Cu and Ni data in ppm for W-1 and BCR-1

	Zn	Cu	Ni
W-1 (Fleischer, 1969)	82	110	78
BCR-1 This work	121	16	11
Ave. (Flanagan, 1969)	138	22	14
Med. (Flanagan, 1969)	120	21.2	12
XRF (Carmichael et al., 1968)	125	15	15

The Zn data compares well, but the Cu results may be a little low, although the result of this work for BCR-1 agrees with the XRF value found by Carmichael et al. (1968). The Ni result for BCR-1 is satisfactory although Carmichael et al.(1968) obtained a slightly higher answer. However, it is pertinent to point out that the Cu and Ni levels in shales are much higher than the concentrations in BCR-1 and are liable to be more accurate.

A Fortran 1V program, written by the author and run on the IBM computer, was used for the calculation of results. The program is listed in Appendix **5.**

Counting errors and detection limits, based on three times the standard deviation of the background count rate (Jenkins and de Vries, 1967), for Cu, Ni and Zn are less than 1 ppm and less than 2 ppm respectively.

3.5.3 ZIRCONIUM, NIOBIUM, YTTRIUM, THORIUM AND LEAD

The concentrations of Zr, Nb, Y, Th and Pb were determined in two runs using both X-ray spectrometers and the instrumental conditions used are tabulated in Table 11. The seven background positions used were carefully chosen to avoid tailing from spectral lines. Background intensities at the peak positions were interpolated from a count rate versus 2θ plot which was constructed by hand using a spline curve to obtain a best fit of the background points. Nett peak intensities were calculated after corrections had been made for line interferences of Rb K_β on Y K_α, Sr K_β on Zr K_α and Y K_β on Nb K_α. These corrections are made as follows

using the interference of Rb K_β on Y K_α as an example:

$$\text{cps Y } K_\alpha = \text{cps Y } K_\alpha^{*} - (\text{cps Rb } K_\alpha \times F)$$

where F is an intensity correction factor of cps Rb K_β /cps Rb K_α , this factor being determined on an Rb-rich blank and Rb K_β being measured at the Y K_α position.

cps Y K_α^{*} is the total intensity measured at the Y K_α peak position.

cps Y K_α is the corrected Y K_α^{*} intensity.

Calculation of the concentration of the elements was then carried out for Zn, Cu and Ni using the method of Reynolds (1963). Mass absorption coefficients determined using the Compton Mo K_α could be used as all the analysis spectral lines have a wavelength shorter than the Fe K absorption edge.

Although Rb and Sr were determined for interference correction purposes they do not form part of this work and are not reported here.

Table 11.

Instrumental conditions for the determination of Zr, Nb Y, Th and Pb (Rb and Sr)

Instrument	PW 1220	PW 1540
Target tube	W	W
kV	65	54
mA	30	18
Counter	Scintillation	Scintillation
Collimator	Fine (150 µm)	Fine (160 µm)
Analysing crystal	LiF (220)	LiF (220)
Pulse height selection	Used	Used

Table 11 (cont)

	Nb	Zr	Y	Sr	Rb	Th	Pb	Backgrounds
Line	K_α	K_α	K_α	K_α	K_α	L_α	L_α	-
PW 1220								
Positions ($^o2\theta$)	30.36	32.03	33.81	35.76	37.91	39.16	40.32	27.35, 29.65 33.05, 34.55 36.85, 38.70 40.95
Times (secs)	40	40	40	40	40	40	40	20
PW 1540								
Position ($^o2\theta$)	30.26	31.91	33.71	35.67	37.80	39.08	40.28	27.23, 29.53 32.93 34.43, 36.73 38.58, 40.83
Times (secs)	60	60	60	60	60	60	60	30

One standard, G-1, was used and W-1 was run several times as an independent unknown. Standard values used are taken from Fleischer (1969) and are shown in Table 12 together with data for W-1.

Table 12

Nb, Zr, Y, Th and Pb data for G-1 and W-1.

	Nb	Zr	Y	Th	Pb
G-1 Fleischer (1969)	20	210	13	52	49
W-1 This work	6	87	25	4	8
Fleischer (1969)	10	100	25	2.4	8

Based on the results for W-1, it appears that the Zr data is a little low and the Nb data is uncertain, but the Pb and Y data are very satisfactory. The good agreement between the XRF and emission spectrographic techniques for Y is shown in Table 13 which contains Y data determined by both methods for a series of six Bokkeveld shale samples.

Table 13

Comparison of Y data determined by XRF and emission spectrography (ES)

	ppm Y by ES	ppm Y by XRF
Bk 302	57	51
Bk 318	36	41
Bk 321	44	42
Bk 361	32	32
Bk 373	38	40
Bk 389	20	22

Counting errors and detection limits for Nb, Zr and Y are less than 1 ppm and less than 2 ppm respectively. Those for Th and Pb are less than 2 ppm and less than 4 ppm respectively.

3.5.4 CHROMIUM

The determination of Cr by XRF is slightly complicated by the interference of V K_β on Cr K_α and by the presence of Cr in the W target tube giving rise to a low intensity of the Cr K_α Rayleigh scattered line. At the levels of Cr and V commonly found in shales, however, V interference was found to be negligible and was ignored during calculation of Cr results. Tube interference by Cr, however, was significant, and was corrected for in a similar manner described for Zn, Cu and Ni using a blank SiO_2 briquette.

A matrix correction using the Compton Mo K_α mass absorption coefficient cannot be used for Cr as the wavelength of Cr K_α lies on the long wavelength side of the Fe K absorption edge. A mass absorption coefficient could be calculated using the major element composition of the shales, but in this case immediate difficulties would be found when dealing with the carbonaceous Ecca shales. The correct distribution of the loss on ignition factor between water, carbon and hydrocarbon is impossible. Consequently the background intensity was used as a measure of mass absorption and Cr concentrations were calculated using peak to background ratios. Instrumental conditions are presented in Table 14. Background intensities were calculated using the ratio method described earlier from factors derived from a spline-curve-fitted plot of background intensities.

Three background positions were used.

A single standard, W-1, was used using the value of 120 ppm recommended by Fleischer (1969). The counting error and detection limit of Cr by this method is less than 2 ppm and less than 4 ppm respectively.

3.5.5 GALLIUM

Ga was determined using a method developed and described by Willis (1971) which used the Ga K_α line and corrects for Cu K_β and Zn K_β interference on background positions. As a Mo target tube is used a matrix correction can be made simultaneously by the measurement of the Compton Mo K_α peak and results were calculated using the method of Reynolds (1963). Instrumental conditions are given in Table 14.

G-1 and W-1 were used as standards using the recommended values of Fleischer (1969) of 18 ppm and 16 ppm Ga respectively. Counting errors and detection limits are both less than 2 ppm.

Table 14

Instrumental conditions for the determination of Cr and Ga

	Cr	Ga
Instrument	PW 1220	PW 1220
Target tube	W	Mo
kV	60	80
mA	28	25
Counter	Flow	Flow and Scint.
Collimator	Fine (150 μm)	Fine (150 μm)
Analysing crystal	LiF (220)	LiF (220)
Pulse height select.	Used	Used
Spectral line	Cr K_α	Ga K_α
Peak position ($^o2\theta$)	107.1	38.91
Background Pos.	99.0, 11.0, 115.0	38.05, 39.60
Times (secs) Peak	120	120
Backgrounds	60	60

3.6 GAMMA-SPECTROSCOPY - URANIUM AND THORIUM

U and Th were determined on a selected suite of 31 samples by gamma-spectroscopy by Mr J.B.M. Hobbs of the Physics Department, University of Cape Town. This method used is described in detail by Cherry et al. (1970).

Samples were ground to less than 120 mesh, packed to a height of 7 cms. into plastic screw-topped bottles of standard size, left sealed for at least three weeks and then counted for between eight and twenty-four hours. All samples were counted twice, and if any individual result was more than two standard deviations from the mean, than that sample was counted a third time.

Below 20 ppm Th the gamma-spectroscopic results did not agree well with the XRF results which tended to be 10 to 15 percent higher. At the higher Th levels the agreement was satisfactory. A comparison of results is shown in Table 15. Th and U results for the selected suite of samples are presented in Table 22A.

Table 15

Comparison of Th results determined by XRF and gamma-spectroscopy (in ppm).

	Th-gamma	Th-XRF
Bk 13	15	17
Bk 14	18	22
Bk 17	17	21
Bk 22	17	20
Bk 25	17	19
Ec 5	27	27
Ec 15	45	45
Ec 16	56	64

4. NOTES ON THE ORIGIN AND DISTRIBUTION OF TRACE ELEMENTS IN SHALES

As about 60 percent of the minerals in normal shales are probably clay minerals, with the bulk of the remainder being quartz, it is clear that the bulk of elements present in trace quantities are located in the clay fraction. Possible exceptions to this generalization would be the presence of detrital minerals such as zircon which might well contain the bulk of zirconium occuring in a littoral sediment. However, it is of interest to speculate at which stage during the sedimentary cycle these trace elements become incorporated in clay mineral structures. This requires a knowledge of origin of clay minerals which immediately plunges one into a basic controversy which confronts all clay petrologists. Are clay minerals deposited in a basin of sedimentation of detrital or authigenic origin?

The problem of whether clay minerals in a sedimentary environment are derived from their source rocks or whether they are predominantly derived by precipitation from solution is one which cannot easily be solved. It is clear that both mechanisms do operate and it is also now generally accepted that clay minerals undergo various structural and chemical changes during transportation, sedimentation and burial. It is not clear, however, which processes predominate and under which conditions.

Clay mineral studies of Modern and Recent sediments are revealing in this respect as it is unlikely that diagnetic processes would have been sufficiently active to cause marked mineral alterations. In their

studies of Recent Pacific Ocean sediments, Grim et al. (1949) concluded that the accumulating sediments were terrestrially derived, but that kaolinite was suffering progressive alteration to illite. In his work on sediments collected from various oceans of the world, Dietz (1941) concluded that the clay mineral distribution on the sea-floor is regionally similar to that on land, with kaolinite predominating in tropical oceans and illite and montmorillonite in temperate and polar regions. However, he also presented strong evidence that illite is developed at the expense of montmorillonite from source material being carried to the sea.

Millot et al. (1963) were satisfied that no change in supply occurred during the Triassic formation of the French Jura as there were only very slight clay mineral changes near the coast during the entire Triassic period. Changes in the clay mineralogy towards the centre of the basin of deposition led them to conclude that the inherited illites were subjected to basin influences and were imperceptibly changed, first into random mixed layers, then into regular mixed layers of the corrensite type, and finally into well-crystallised chlorite. The chlorite phase is only reached in the middle of the basin where subsidence is strongest. Similar work by Millot (1942) and Keller (1956) on ancient marine sediments indicated the development of illite and chlorite at the expense of kaolinite and montmorillonite in the marine environment. Thus an older school of thought favoured the concept of clay minerals being so completely structurally and chemically altered in their depositional environment that they could be considered

authigenic in origin.

A more modern school of thought is represented by Weaver (1958a, 1958b, 1967) who firmly believes that clay minerals are predominantly detrital in origin, reflect primarily the character of their source area and are not strongly modified by the depositional environment. He also concludes that the process of diagenesis in altering clay minerals is not as effective as was commonly thought. Millot (1970) has decided that he overemphasized the importance of authigenic formation of clay minerals, and on the basis of modern clay mineral research now concludes that although the phenomenon does exist it is not nearly as general as he previously supposed.

There is some ambiguity in the literature regarding the term diagenesis. Pettijohn (1957) defines it as a group term describing the chemical rearrangements and replacements taking place on the sea-floor or after the sediment has been removed from contact with sea-water, the former being halmyrolysis and the latter epigenesis. Weaver (1959) is more specific and prefers to restrict the term diagenesis to alterations which modify the basic lattice and to use absorption for changes which only affect interlayer material, and this approach is adopted here. Syngenetic describes processes occurring while the minerals are still in contact with overlying water and epigenetic is used to describe alterations occurring after burial and removal from contact with overlying water. Amstutz and Bubenicek (1967) use the same definitions for diagenesis, epigenesis and syngenesis.

Weaver stated that generalities based

on an inadequate number of data, had been developed, upon which a strong case for diagenesis was advanced. He studied the X-ray analyses of clay minerals from thousands of sediments and came up with the following conclusions on the distribution of the clay minerals.

(1) Organic-rich marine black shales contain illite and mixed layer illite-montmorillonite and seldom kaolinite.

(2) Montmorillonite is quite common in ancient sediments. Illite is the dominant clay mineral in old sediments as weathering and diagenetic conditions prevalent at that time favoured its formation and preservation.

(3) Kaolinite is most common in continental and near-shore sediments, and is rarer in older sediments because continental and near-shore sediments tend to be preferentially destroyed by erosion through geological time.

(4) Sediments containing both illite and montmorillonite are common, proving that the alteration from one to the other is not a common process.

Weaver (1961) has showed, however, that post-depositional alteration of montmorillonite in the Washakie Basin of Wyoming does take place. Depth of burial causes the collapse of the expanded montmorillonite layers. This epigenetic alteration starts at 1700 m and at 4000 - 5000 m 70 percent of the montmorillonite layers have collapsed to form illite structures. That diagenetic changes in clay minerals definitely do occur was also demonstrated by Kulbicki and Millot (1963) but this was in sandstone which are porous and thus allow percolating solutions more access to interstitial clay material than would probably be the case in impervious shale sequences. They found the alteration of illite to kaolinite and, under the influence of saline solutions, the conversion of kaolinite to illite took place.

Lateral variation of clay mineral content within a basin of sedimentation can be explained by forms of marine diagenesis, but other explanations proposed are distribution of clay minerals by current action, difference in supply from various source sediments and, possibly of most importance, different flocculating characteristics of the various clay minerals. Whitehouse et al. (1960) determined the settling velocities of illite, kaolinite and montmorillonite in waters of varying salinity, and found that the settling velocity of montmorillonite was only slightly changed by increased salinity. The settling velocities of illite and kaolinite, however, were sharply increased by increases in salinity and this effect is the likely cause of the concentration of kaolinite in near shore sediments.

Age dating of sediments has been carried out in an attempt to unravel the complex depositional histories of the constituents of sediments. Hurley et al. (1960) showed that glauconite was an unsuitable mineral for dating the age of deposition using the K-Ar method due to probable post-sedimentation argon leakage and potassium gain by absorption. Hurley et al. (1963) obtained K-Ar ages of 200 - 400 m.y. for the clay fraction of North Atlantic pelagic sediments proving that the bulk of the clay fraction must be of a detrital origin and must have suffered very little alteration in the marine environment. If these ages are anomalously high they could only be explained by the unlikely loss of K by desorption. Strong evidence for Weaver's (1958a) conclusions that shales in general do not originate in toto in their depositional environment and are not strongly modified by the depositional environment was provided by Hower et al. (1963). They found that the K-Ar age for the whole rock and six size fractions

ranging from $<0.08 \rightarrow >62\ \mu$, of an Upper Ordovician Sylvan shale varied from 350 m.y. for the finest to 540 m.y. for the coarsest. They were of the opinion that the whole rock age of 450 m.y., which agreed with the estimated true age of sedimentation, was fortuitous. The coarse 10Å layer silicate was a 2 M muscovite polytype, a muscovite of detrital origin carrying inherited Ar which accounted for its high age. The young 10Å material had a 1 Md muscovite structure and probably had an epigenetic origin, accounting for its formation later than the time of sedimentation, although the possibility exists that the low age is caused by argon leakage, which overcompensates for inherited radiogenic argon, or by absorption of K during deposition in the marine environment.

This work proves that for these shales at least very little alteration of clay minerals took place during transport and deposition of the clay material, and that no diagenetic change of this clay material occurred during its 450 m.y. post-depositional history. It also indicates that the detrital clay material was added to by much younger diagenetic clay, although this is less certain. Dasch (1969) expected to find homogenisation of Sr isotopes in marine sediments if diagenetic processes were active, but the fact that the isotopic composition of clay material in sediments was similar to that of the source area and not of sea-water led him to postulate that useful provenance information could be gained from Sr isotopes. Savin and Epstein (1970a, 1970b) found that the oxygen and hydrogen isotope composition of clay minerals in ocean sediments and shales reflected the provenance of these samples, and they could

and Mg, and Be for Si.

Cation exchange and sorption processes occur in the weathering environment and during stream and river transport and undoubtedly part of the trace element content thus acquired is fixed permanently and probably only released during epigenetic changes. However, changes in equilibrium will occur between the relatively pure aqueous conditions of weathering and transport and the more concentrated saline solution of sea-water at the site of deposition. Syngenetic adsorption and cation exchange processes allow equilibrium to be approached, but the extent to which these reactions proceed is closely linked with the rate of sedimentation. Nicholls and Loring (1960) discussed the reactions at the depositional site of the alkali elements.

Non-detrital material can also be incorporated in sediments through the agency of living organisms. Apart from shell fragments and skeletal remains, originally formed from elements extracted from sea-water, accumulating in sediments, the soft parts may also be responsible for the indirect incorporation of non-detrital elements in sediments. Trace elements are taken up by organisms which later die, sink to the bottom and are incorporated in the sediments. On decomposition these organisms release their trace elements which are then available for incorporation in the sediment by precipitation or by sorption processes. As such a large number of elements have been found to be concentrated in some planktonic species, Nicholls et al (1959) suggested that eventually all metallic elements of the periodic table would be found to be spectacularly concentrated in

some planktonic species or another. The organic compounds themselves can scavenge trace elements from the overlying water by chelation processes and then become fixed in the sediment by adsorption onto clay minerals. The concentration and preservation of these bituminous organic compounds can lead to the formation of oil shales, but a discussion relating to the origin of petroleum deposits is not relevant here.

Black shales often have an exceptionally high trace metal content and Brongersma-Saunders (1969) generalised that in areas of ocean upwelling plankton were extremely abundant and thus accumulated trace metals in a limited area where they could later be incorporated in the sediment. He postulated this theory to account for the high metal content of the famous Kupferschiefer of Germany. The decomposition of the plankton under anaerobic conditions would release trace metals which would be converted to sulphide by the hydrogen sulphide produced by the reduction of sulphates and from the decomposing bacteria themselves. Variations of this postulated mechanism are the direct incorporation in the sediments of the trace metal rich remains of plankton in the form of bituminous material, and the precipitation from solution of chalcophile elements by hydrogen sulphide. Calvert and Price (1970) found spectacular concentrations of Cu, Ni, Pb, Zn in organic rich sediments presently accumulating under anaerobic conditions off Walvis Bay, South West Africa, an area of intense upwelling. They believed that the metals were intimately connected with the organic fraction of the sediment although they did not postulate a specific mechanism.

Apart from the bituminous fraction the kerogen fraction is also capable of concentrating trace elements in shale. Kerogen is here simply defined as the non-calcareous organic fraction insoluble in organic solvents as described by Saxby (1970). It consists primarily of coaly plant residues and humic materials. Szalay (1967) reported the concentration of U, Th, lanthanides, Cr, Zn, Cu, Ni, Zr and Fe amongst others by humic acids which are derived from lignin. Gad et al. (1969) found Cu, Ni, V, Ag and Mo were strongly associated with the kerogen fraction of Whitbian Triassic sediments and Nicholls and Loring (1962) discovered that Co, Ni and Mo were clearly associated with organic carbon in Carboniferous sediments. In a detailed study Degens et al. (1957) found Ni and V concentrated in the organic fraction of marine shales, and Pb, Zn, Cu and Sn in the organic fraction of fresh-water shales.

It is clear that organic matter of this type is a powerful complexing agent and can be expected to extract significant amounts of trace metals from overlying waters during deposition, but an obvious difficulty in elucidating the mechanisms of such reactions is the factor of the inherited trace metal content of such material, although Tourtelot (1964) believes that the incorporation of trace elements by plants during growth contributes very little to the trace element content of the resulting carbonaceous shale.

Precipitation of ferric and manganese hydroxides occurs under suitable physico-chemical conditions and their extensive adsorptive powers can account for the scavenging of several trace metals from sea

waters. Mason (1966) mentions V, Co, Ni, Cu, Zn and Pb amongst others as elements which can be incorporated in the oxidate fraction of sediments. Wedepohl (1964, 1967) concluded that the ore metals in the waters under which the Kupferschiefer was deposited originated from the reduction of older iron oxides of red sandstones, in which oxides Cu, Ag, Pb, Zn, V, Cr and Mo had previously been fixed. After release from the iron oxides these metals were precipitated as sulphides by the hydrogen sulphide produced by bacterial decomposition, but he is of the opinion that the metals themselves did not originate from the living organisms.

From detailed calculations Goldschmidt (1932) showed that the amount of all metals, except possibly sodium, which had been added to the sea during geological time was far in excess of the quantities at present resident in the sea. These conclusions, which have since been verified by several other workers, proved that the observed concentrations of metals in the sea do not represent the simple accumulation to date of metals supplied to the sea by rivers, but that these metals have been effectively removed from solution by operative mechanisms and have been incorporated in the sediments and eventually locked away in sedimentary rocks. Krauskopf (1956) examined the concentrations of thirteen metals in sea-water with respect to their solubilities as various compounds and came up with the remarkable results that sea-water is greatly understaurated with all thirteen elements. This means that sea-water cannot be a simple thermodynamic system controlled by the laws of mass action with all the components in solution in equilibrium with each other. The removal of elements is not governed

solely by reactions like the precipitation of carbonates in the presence of excess CO_3^{2-} or of sulphides under reducing conditions. Adsorption and chelation by organic molecules and adsorption by clay minerals must be tremendously effective processes in scavenging metals from sea-water and fixing them in the sediments. The availability of such metals to be adsorbed must be a controlling factor in the metal uptake of the sediment and this leads to the possibility of using the trace metal content of sediments as a paleosalinity indicator as data such as that of Kharkar et al. (1968) shows that the metal content of river water is considerably lower than that of sea-water. This possibility using data for some South African shales is explored in Section 8.

Thus the general conclusion is that the bulk of the trace elements contained in a sediment reached the depositional environment already firmly incorporated in clay minerals, but that a small proportion is derived from the overlying sea-water and is incorporated in the sediment by several mechanisms.

The composition of meteoritic dust and windblown dust of continental origin has always been regarded as a factor of negligible importance in the composition of marine sediments. This has also been assumed in this work because of the lack of any data concerning the rate of supply of these materials to the oceans. However, the author thinks it likely that when research in this direction is commenced it will be revealed that surprisingly large quantities of material enter the oceans without ever being involved in transportation by rivers of streams.

The incorporation of trace elements

in and the development of other types of sediments are not relevant to this discussion on shales. These sediments include phosphorites, manganese nodules, limestones, dolomites, sandstones, tillites and evaporite deposits. The first four mentioned are principally of authigenic origin and during their formation are undoubtedly responsible for much of the removal of trace elements from sea-water.

5. THE TRACE ELEMENT GEOCHEMISTRY OF SOUTH AFRICAN SHALES

5.1 INTRODUCTION

In this section the abundances and distribution of trace elements in South African fine-grained sedimentary rocks are presented and discussed. The samples have been grouped into their stratigraphic horizons and are examined, where possible, in order of decreasing geological age. So far the Precambrian formations of eastern and western southern Africa have not been satisfactorily correlated as the two regions are separated by the Doringberg fault zone (Martin, 1965) and there is thus some doubt attached to the order of ages of these formations in this work.

The geology of all the sequences which have been sampled is presented briefly, although it does not form part of this work, as it is felt that the trace element geochemistry of shales can only be fruitfully discussed when treated in relation to the general geology. All knowledge concerning age, thicknesses, lateral extent, changes of lithology etc., can be of use in unravelling the history of the trace element content shales. The mineralogical compositions as determined by X-ray diffraction of all the samples included in this work are tabulated in Table 1A but are summarised as each system or formation is discussed.

It should be pointed out that the aim of this work was to acquire knowledge of the trace element geochemistry of as many shale components of the South African stratigraphic column as possible. No attempt was made at the onset to solve specific problems, as so little of the geochemistry of these rocks was

known, but it was hoped that the results of this work would bring possible problems to light and delineate likely areas of future research.

For the maximum amount of knowledge to be gained about any single formation, a sampling and analytical program would had to have been undertaken which would have been far beyond the extent of this work in which sixteen sequences of sedimentary rocks have been studied. Consequently sampling has been somewhat random and some sequences have received more attention than others. However, to some extent a compromise has been reached and some sequences have been sufficiently well sampled for meaningful conclusions to be drawn from the analytical data. These sequences are the Fig Tree Series, the Bokkeveld Series and, in particular, the Ecca Series. Core samples from ten boreholes in the Ecca Series provide an extensive lateral and vertical sampling pattern. Thus an attempt can be made to map the regional trace element distribution pattern for the entire depositional period of the Ecca Series.

The treatment of a vast number of raw data presents some difficulty as it is obviously impossible to discuss each element separately for each group of rocks and retain a sense of logical coherence. To overcome this difficulty the total data are first presented in Tables 2A to 22A and the element concentration averages and standard deviations for each group of rocks are contained in Tables 23A and 24A. Table 24A contains the averages for the carbonaceous and non-carbonaceous shales and a grand average for all trace elements determined in this work for all samples. For comparison purposes the average trace element abundances

in pelitic rocks compiled by Wedepohl (1971) is given in Table 27A. Also shown in this table are the averages for the continental crust as given by Taylor (1964) and included for convenience are the carbonaceous, non-carbonaceous, average separated clay and grand average trace element data for the rocks analysed in this work. Tables 2A to 22A also contain Ga/Al, Ni/Co and V/Cr ratios. Table 25A contains the averages of these ratios for the various groups of South African argillaceous rocks and Table 26A lists the averages of these ratios for the various components of the Ecca Series of the Karroo System. The discussion of trace element abundances in this section is concerned chiefly with deviations from these averages. The correlation between trace element content and mineralogy is critically examined.

Kendall rank and multiple regression analysis correlation coefficients have been computed for all groups of rocks for trace elements, percentage loss on ignition and for the two major elements Al and Fe (used by kind permission of Danchin, 1970). An account of the derivation of the two correlation coefficients is out of place here, but as the results calculated independently by the two methods, were not found to differ much in general, only the multiple regression analysis correlation coefficients are included in this work and are listed in Tables 28A to 42A. To gain an idea of the variation in abundance of all trace elements analysed, a series of histograms are presented in Figures 9A to 25A depicting frequency distributions of each element in the complete sample population.

A study of the correlation coefficients

provides much information on the distribution of the trace elements within the rocks and also on their comparative behaviour in the sedimentary environment. Diagrams of interesting inter-element and element ratio correlations are presented.

The interpretation of correlation coefficients has been carried out with a great deal of care as they are subject to some limitations. For small numbers of observations, i.e. number of samples, as in the Witteberg Series, the correlation coefficients generated tend to be extreme and in these cases the correlation coefficients are treated with some reservation. Negative correlations have not been discussed as they are frequently extremely difficult to interpret and also Chayes (1960) has shown that where the sum of variables cannot exceed a certain constant, as is the case when percentage or ppm data is being handled, then positive correlations tend to be suppressed and negative correlations increased.

The perfect model in which correlation coefficients would reveal the behaviour and distribution of elements is one in which the highest correlation coefficients observed would be between those elements which occur only in the same mineral. This situation, of course, is rare in the sedimentary environment, the closest approach probably being the concentration of several metals in manganese nodules. Some elements occur in a number of mineral phases reducing the possibility of the correlation coefficients being very informative. Some pairs or groups of elements follow each other closely through several mineral phases, thus generating

high correlation coefficients. Conversely elements occurring only in the same phase need not generate high correlation coefficients if their relative concentrations differ in that phase between samples. This situation might arise in the case of closely associated elements located in the same detrital heavy mineral occurring in a single basin of deposition but derived from different source areas in which the heavy mineral concerned had different compositions. However, an attempt has been made to interpret all the definite and interesting correlations, especially if they are common to more than one group of rocks, but it is clearly impossible to interpret every good correlation. It must also be borne in mind that the high correlation coefficients are only used as a guide to the probable distribution and behaviour of the trace elements in shales.

Of necessity there is some rep tition between this section and the next in which the distribution and behaviour of each individual element in the South African shales as a whole are discussed. Every effort has been made to reduce this repetition to a minimum. Section 6 could have been treated before Section 5, but it was felt that a discussion of trace element distribution in the various shale sequences before the general discussion of each individual element was more logical.

The Ecca Series has been treated in the most detail as mentioned earlier. Variation of some trace element abundances with height in the succession have been plotted and some of the Middle Ecca boreholes and some very interesting regularities and trends have emerged. An attempt has also been made to plot the distribution of trace elements in the Ecca on a horizontal scale, but no conclusive trends have emerged from this study.

5.2 SWAZILAND SYSTEM

FIG TREE SERIES

The Swaziland System is considered to be one of the oldest systems of sedimentary rocks on this planet, if not the oldest, and is remarkable for such an ancient system in that considerable sections of it have remained relatively unmetamorphosed and it is thus a well-preserved relic of ancient geological times. Allsopp et al.(1968) established a minimum age of 3000 m.y. for the system by the Rb-Sr isochron method, indicating a significantly earlier age of deposition. U/Pb ages of 3400 m.y. (van Niekerk, 1967) for the underlying Onverwacht volcanics suggest an age of perhaps 3300 m.y. for the Fig Tree Series. It is possible that these were the earliest sediments on Earth deposited beneath a primordial sea.

The Swaziland System, well described by Visser et al. (1956), occurs as a folded synclinal belt forming the Barberton Mountian Land in the eastern Transvaal. About 110 km long and 30 km wide the system strikes NE-SW and straddles the Transvaal-Swaziland border. It comprises the following series, listed in order of decreasing goelogical age:
Onverwacht Series, Fig Tree Series, Moodies Series.

The Fig Tree Series is underlain by the former basic volcanics, dolomites, slates and jasper of the Onverwacht Series, and is overlain by the basal conglomerate and thick quartzite formations, separated by thin shale units of the Moodies Series. The Fig Tree Series itself consists of fine-grained and coarse-grained slates and greywackes with interleaved horizons of banded chert, banded

ironstone and banded jasper. The series reaches a maximum development of 2500 meters (Haughton, 1969). Carbon is widespread in the Onverwacht and Fig Tree Series and fossil algal remains have been identified in both series. Engel et al. (1968) consider the Onverwacht alga-like forms to be the oldest recognisable lifelike forms yet found on Earth.

Twenty-three samples of the Fig Tree Series have been analysed and for three of them less than two micron fractions have been separated and analysed. The samples fall into three lithological groups.

(1) The shales themselves are usually dark grey, well laminated and well-preserved. They consist predominantly of iron-rich chlorite and illite with subordinate quartz and occasional traces of plagioclase feldspar. Chlorite is normally more abundant than illite. Danchin (1970) found the SiO_2 content to vary between 51 and 59 percent, and and Al_2O_3 content between 11 and 18 percent and the Fe_2O_3 content between 8 and 17 percent.

(2) The greywackes contain considerably less clay minerals and more quartz and albitic plagioclase feldspar. Potash feldspar is also occasionally present. There is a complete gradation between the shales and greywackes, the greywackes in this study usually containing more than 58 percent SiO_2 and less than 12 percent Al_2O_3.

(3) The ferruginous shales contain more than 15 percent Fe_2O_3 and range up to 40 percent. They consist predominantly of iron-rich chlorite and the iron minerals hematite, magnetite and goethite.

The chief interest in the rocks of the Fig Tree Series lies in their great age and the possibility

that they are the earliest formed shales and were accumulated beneath a primordial ocean perhaps only just formed by massive condensation from the atmosphere or degassing of the Earth's mantle or, more likely, a combination of both mechanisms. If sediments of greater age were formed on other parts of the world, which is likely, they have since been removed either by progressive erosion or by severe metamorphism following deep burial, culminating in granitisation processes which have tended to eliminate sedimentary characteristics. However, the exciting possibility does exist that shales of Fig Tree age might represent the period in the Earth's history of most rapid crustal evolution during which a thick relatively stable crust was being developed from a thin relatively unstable one. That the Earth's crust must have been unstable at least in this area is shown by the composition of the Onverwacht Series which underlies the Fig Tree Series. The Onverwacht comprises vast outpourings of lava varying from dark andesitic or basic types to subordinate acid types (Haughton, 1969). Included are definite basic rocks of pyroclastic origin. The sequence is at least 15 km thick and nowhere has the base been proved to have exposed (Condie et al., 1970). The Fig Tree Series has been invaded by younger intrusive ultrabasic rocks of the Jamestown Igneous Complex and by various younger intrusive granites, such as the Kaap Valley granite, the Mpageni granite and the Salisbury Kop granite, which are normally associated with orogenic phases of deformation of the Swaziland System. Although much of the sediment comprising the Fig Tree Series undoubtedly originates from weathered Onverwacht lavas, pre-Swaziland granites must have existed at that time as well to provide much of the detritus. All the shales and greywackes of this study contain abundant quartz and some contain

potash feldspar showing that they were at least partially derived from granites.

From their petrological and petrographic study, Condie et al. (1970) concluded that the Fig Tree sediments were derived from a source area of diverse composition, including basic rocks, granitic-metamorphic rocks and volcanic rocks. Some detrital material was also derived from contemporary volcanic activity. They were of the opinion that the granitic-metamorphic source rocks of the Fig Tree sediments may be preserved in the Ancient Gneiss Complex described by Hunter (1968) in central Swaziland and for which Davies (1969) reports an age of 3340 m.y. However, the status and age of the Ancient Gneiss Complex must be regarded as a little uncertain as much of the grandiorite gneiss of which they now largely consist has been formed by granitisation of older rocks (Haughton, 1969). The fact remains that pre-Fig Tree granitic rocks must have existed indicating that igneous differentiation or partial melting of the Earth's mantle must have occurred as early as these times and that at least in places the Earth's crust was a minimum of 16 km thick (the maximum exposed thickness of the Onverwacht Series). The immature greywacke textures described by Condie et al., (1970) show that the original detritus was not transported great distances prior to deposition and burial, and also prove beyond reasonable doubt that the sediments of the Fig Tree Series were not derived from pre-existing sedimentary rocks thus supporting the possibility that these might be the oldest shales still existing on Earth..

Danchin (1967) interpreted the high Ni and Cr content of the Fig Tree shales in terms of an ultramafic source area for these rocks whereas Condie et al. (1970), while agreeing that an ultramafic source rock

component must be responsible for the high Mg, Fe, Ni and Cr contents of the shales, decided on the basis of the mineralogical composition of the greywackes and shales, as well as the major and trace element compositions, that ultramafic rocks comprised at the most only 10 percent of the source material.

The twenty-three greywackes and shales of this work have been analysed for fifteen trace elements and it is of interest to attempt a reconstruction of the source area in terms of the relative proportions of probable igneous rocks. The average igneous rocks considered are ultrabasic, basaltic and granitic and the trace element data used are those from Vinogradov (1962) for ultrabasics and Taylor (1964) for basaltic rocks and granites. For Y and Yb in ultrabasic rocks the averages of the data listed by Hermann (1970) have been used. The complete data of Turekian and Wedepohl (1961) could have been used without changing any conclusions although in ultrabasic rocks their value of Nb seems far too high and their value for Cr might be a little low. It should be remembered that the data of Taylor (1964) is largely based on the work of Turekian and Wedepohl (1961) except that later analyses have been taken into account. Table 16 contains the average trace element content of the Fig Tree rocks, the average shale of Wedepohl (1971) and some selected average igneous rock types of Vinogradov (1962), Turekian and Wedepohl (1961), Taylor (1964) and Herrmann (1970). It is immediately apparent that the trace element content of the average Fig Tree sediment is markedly different from the average shale of Wedepohl (1971). Only V, Cu and Zn and, to a lesser extent, Sc, Ga and Y show concentrations which are similar to the the average shale.

Table 16

Element concentrations in ppm of the Fig Tree rocks compared to principal igneous rock types, an igneous composite and shales

	Fig Tree (1)	Ultrabasic/basaltic/ granitic. 2/3/2	Ultrabasic (1)	Ultrabasic (1)	Basaltic (2)	Basaltic (4)	Basaltic (4)	Shale (5)
Be	1.4	1.7	0.X	0.2	1	0.5	5	3
Sc	20.0	18	15	5	30	38	5	13
V	115	124	40	40	250	250	20	130
Cr	883	660	1600	2000	170	200	4	90
Co	38.4	78	150	200	48	48	1	19
Ni	502	635	2000	2000	130	150	0.5	68
Cu	51.0	51	10	20	87	100	10	45
Zn	114	63	50	30	105	100	40	95
Ga	13.7	11	1.5	2	17	12	18	19
Y	28.7	23	0.X	2.9 (6)	21	25	40	41
Zr	87.5	125	45	30	140	150	180	160
Nb	5.3	15	16	1.0	19	20	20	18
Yb	1.4	2.2	0.X	0.8 (6)	2.1	2 (3)	4 (3)	3.7
Pb	10.2	7.9	1	0.1	6	5	20	20
Th	6.4	5.8	0.004	0.005	4	2.2	17	12

(1) This work
(2) Turekian and Wedepohl (1961)
(3) Vinogradov (1962)
(4) Taylor (1964)
(5) Wedepohl (1971)
(6) Herrmann (1970)

An attempted reconstruction of the composition of the source area contains several inherent uncertainties. The most important of these is the fact that very few reliable trace element analyses of early Proterozoic igneous rocks exist. Thus the assumption is being made that igneous rocks of great age did not differ much from their modern analogs. Furthermore, although the ultrabasic rock data of Vinogradov (1962), and Turekian and Wedepohl (1961) are very similar, trace element concentrations can actually vary considerably depending on the actual rock type. The composition of the average ultrabasic rock is very dependent on the relative proportions assigned to kimberlite, dunite, peridotite or pyroxenite. For example, the Sc data listed by Frondel (1970) show Sc to vary from 1 ppm in dunites to 200 ppm in pyroxenites. Consequently the ultrabasic rock data must be considered with some reserve. A further tacit assumption is that the trace element content of a shale is largely a function of the source rock composition and that such factors as intensity of weathering and environment of deposition have exercised a minimal influence on the final trace element composition of the shale. That this is a reasonable assumption is discussed in Section 4.

The differences in trace element content between the average Fig Tree sediment and the average shale for the purposes of this argument are assumed to be chiefly due to differences in source rock composition and the effect of any combination of mechanisms which might have resulted in the enrichment of some elements and the depletion of others in the depositional environment is minimal. From the textures of the Fig Tree greywackes Condie et al. (1970) deduced that the weathering of the

source rocks was mild which supports the contention that little enrichment or depletion of trace elements occurred during weathering of the source rocks.

An examination of the data presented in Table 16 reveals some striking facts. If the trace element content of the average Fig Tree rock is compared to the average ultrabasic rock of Vinogradov (1962) and the average basalt and granite of Taylor (1964) it is immediately apparent that the source area must have comprised all three rock types. Rare intermediate rock types are not considered in this discussion as it is not likely that they played a major role in the provenance of the Fig Tree shales.

The Cr, Ni, Nb, Zr and Yb data show that the final sediments must have been partially derived from ultrabasic rocks. The Zn, Cu, Sc and V data indicate that rocks of basic composition must have been present in the source area and the Th, Pb, Y, Ga and Be contents of the Fig Tree shales can only be explained by invoking the presence of granites in the source area. If the average Fig Tree sediment is assumed to approximate the average composition of the source rocks, it is a simple matter to calculate the proportion of principal igneous rock types required in the source area to produce an average Fig Tree sediment of the observed composition. Although Ahrens (1954a, 1954b, 1963a) has pointed out that the distribution of most trace metals in granites is lognormal i.e. positively skewed, average and not most frequent concentrations of trace elements in granites are used in these calculations as it is felt that the process of weathering and erosion involve the total exposed granite and not random samples of it.

Therefore average abundances are more meaningful than most frequent abundances as the "most typical" abundance is not the one required.

The model does not fit all elements equally and in its construction major emphasis has been placed on those elements whose concentrations in the average Fig Tree sediment are most different from the average shale of Wedepohl (1971) and whose concentrations in ultrabasic rocks are known with some degree of confidence. These elements are Cr, Ni, Pb, Th, Tb and Zr. The Cr and Ni data alone suggest that between 25 percent and 45 percent of the source area must consist of basic rocks.

A simple ratio of 2/3/2 of ultrabasic, basic and granitic rocks gives a surprisingly good fit for most of the elements analysed. An increase in the ultrabasic proportion renders the Ni content too high and the Pb and Th contents too low. An increase in the basaltic proportion renders Pb and Th too low. An increase in the granitic proportion renders Be, Zr, Nb and Yb too high. Elements whose predicted values differ markedly from those observed are Co, Nb and Zn and, to a lesser extent, Zr and Yb. The predicted values of Co, Nb, Zr and Yb are higher and that of Zn lower than the observed values. These differences could be conveniently explained by the ancient igneous source rocks being slightly different in composition from their modern equivalents. If ancient granites contained less Zr, Nb and Yb and ancient ultrabasic rocks contained much less Co than their modern equivalents then the observed differences could be explained. Alternatively the differences would also be much reduced if the ancient

source area contained a greater ultrabasic proportion than predicted, but the ultrabasic rocks contained much less Cr, Ni and Co than their modern analogs. Perhaps the true average Co content of ancient ultrabasic rocks is much lower than the 200 ppm of Vinogradov (1962) or the 150 ppm of Turekian and Wedepohl (1961) for modern ultrabasics. However, Co is strongly enriched in olivine and it is difficult to visualise low olivine ultrabasics or low Co olivines. It should also be pointed out that the Fig Tree sediments are quite variable in composition and that the predicted values for Co, Nb, Zn, Zr and Yb actually all fall within the observed concentration range for these elements in the Fig Tree Series sediments. Condie et al. (1970) recorded an average concentration of 134 ppm Zr in the greywackes of the Sheba Formation, a constituent of the Fig Tree Series. This is very close to the predicted value in this work of 125 ppm Zr.

The high abundance of Zn and low abundance of Co compared to predicted abundances might possibly be a function of weathering in the source area and the composition of the water in the depositional environment, both conditions arising from a primordial atmosphere of a composition different to that observed today. The primordial atmosphere was deficient in oxygen owing to the paucity or absence of plant life at that time. Deposition of the Fig Tree sediments would have taken place during the second stage of the development of the primordial atmosphere according to Holland (1962). He deduced that at this time the atmosphere was weakly reducing and consisted principally of nitrogen with minor amounts of water vapour, carbon dioxide and argon. Oxygen produced by the photochemical dissociation of water

vapour in the upper atmosphere would be consumed in oxidising the more reduced constituents of the volcanic gaseous exhalations. A significant partial pressure of oxygen only began to be built up in the atmosphere with the much later extensive development of plant life on Earth. From paleontological evidence Cloud (1965) concluded that green plant photosynthesis existed between 1700 and 2000 m.y. ago but that atmospheric oxygen only became available in relatively large quantities from about 1200 m.y. ago as most oxygen produced was consumed in the oxidation of the vast quantities of ferrous iron on Earth. Thus at the time of the weathering of the source rocks of the Fig Tree sediments virtually no oxidation of the abundant ferrous to ferric iron occurred with the conséquent precipitation of ferric hydroxides which are efficient Co scavengers. Further evidence of the lack of oxidising conditions in the weathering environment is provided by Ga which shows no correlation with Fe which is now largely in the ferric state in the Fig Tree sediments. Ginzberg (1964) pointed out that Ga^{3+} readily proxies for Fe^{3+} in minerals, and the lack of correlation between these two elements in the Fig Tree sediments indicates that Fe was initially incorporated in the sediments in the ferrous state and underwent partial oxidation to the ferric state much later in its history. It is likely, therefore, that far more Co remained in solution in the ancient oceans compared to younger sediments in which Co was efficiently scavenged by ferric hydroxides. Consequently the Co contents of the ancient Fig Tree sediments are much lower than ultrabasic igneous rocks. If this explanation of the low Co abundance in the Fig Tree sediments is correct then the concentration of Co in the primordial sea must have been

much higher than in later oceans and the very high Ni/Co ratios in the Fig Tree Series (average 17.9 as shown in Table 25A) indicates that Co is not as readily incorporated as Ni into Fe-rich chlorites.

Condie et al. (1970) recorded up to 14 percent dolomite in the Fig Tree greywackes which indicates carbonate or bicarbonate enriched overlying waters, possibly due to a carbon dioxide enriched atmosphere resulting from abundant volcanic exhalations on land and beneath the sea and the lack of plant life to extract the carbon dioxide from the atmosphere by photosynthesis. Holland (1962) was of the opinion that the carbon dioxide content of his Stage II atmosphere was much higher than the modern content. Carbon dioxide is weakly soluble in water to form the bicarbonate ion which can be reduced to form carbonate ion. Dolomite is precipitated owing to the high concentration of Mg in the overlying water, the Mg being derived from the Mg-rich ultrabasic source rocks. Zn is readily co-precipitated with Mg as their ionic radii are very similar, besides which the solubility of $ZnCO_3$, smithsonite, is very low. Co does not readily form carbonates.

Thus the differences between the observed and predicted concentrations of Zn and Ni in the Fig Tree sediments can be readily explained in terms of the probable composition of the atmosphere existing in early Proterozoic times. More detailed aspects of the geochemistry of Co and Zn are dealt with in Section 6 in which the elements are discussed individually.

To summarise, the composition of the Fig Tree shales is very different from the average shale and this is attributed to the presence of ultrabasic

rocks in the source area. The average Fig Tree sediment composition could be derived from a source area containing ultrabasics, basaltic rocks and granites in the ratio 2/3/2. This is approximately 30 percent ultrabasics, 40 percent basaltic and 30 percent granites. The proportion of 30 percent calculated for granites on the strength of the trace element composition of the Fig Tree Series is far lower than the proportion estimated by Condie et al. (1970) but they were dealing with only greywackes whereas the samples analysed in this work were principally shales.

Predicted abundances which are not observed in the Fig Tree sediments are those for Co and Zn, but these can be explained in terms of the probable composition of an early atmosphere.

The presence of all three principal igneous rock types in the source area is essential for the production of the observed composition of the Fig Tree sediments.

5.3 KHEIS SYSTEM

The Kheis System is represented in this study by a single shale, illite-rich with subordinate carbonates and hematite. The Kheis System consists of three series and is considered by Martin (1965) to be older than 2600 m.y. although this age is by no means definite. It is not known from which series this sample originates.

The trace element composition and a few inter-element ratios of the single sample analysed are listed in Table 3A. Compared to the average South African argillaceous rock it is strongly enriched in Be and Zr but very depleted in the other elements analysed in this work. These results indicate that the Kheis

sediments are derived from a granitic source area, but further observations cannot be made from the analysis of only one sample.

Although the Kheis System sediments are extremely old it is interesting to note that this trace element composition from the western section of Southern Africa is completely different to the composition of the Proterozoic Swaziland and Witwatersrand sediments of similar era from the eastern section of Southern Africa.

5.4 THE WITWATERSRAND SYSTEM

The Witwatersrand System is a tremendously thick pile of sediments with intercalated lava flows and other volcanic material. It outcrops in the Transvaal but extends beneath the Karroo System in the Orange Free State where it is mined for gold. Because of its vast mineral wealth it is unlikely that any other rock system has been geologically documented in such great detail. It is divided into the following series:-

Kimberley-Elsburg Series
Main-Bird Series
Jeppestown Series
Government Reef Series
Hospital Hill Series

The Jeppestown Series and Government Reef Series, which are represented in this collection, reach thicknesses of 1230 m and 2100 m respectively in the Central Rand (Pretorius, 1964). Brock and Pretorius (1964) calculated the maximum thicknesses developed to be 2700 m for the Government Reef

and 1300 m for the Jeppestown Series respectively. They thin out considerably in a south-easterly direction. The two series comprise solely alternating shale and quartzite horizons Brock and Pretorius (1964) considered that the sediments were slowly deposited in a gradually sinking ovoid basin 450 km long striking SW-NE with the SW end being the most rounded.

The ten samples analysed contain dominant chlorite with lesser amounts of quartz, illite, and plagioclase feldspar. Magnetite was detected in two samples. The samples came from borehole JY 8 in the Klerksdorp district. Five, JP 6-10, are from the Government Reef Series, and five, JP 1-5, from the Jeppestown Series.

Trace element concentrations and some inter-element ratios are presented in Table 4A. Average concentrations are included in Table 23A and average ratios in Table 25A. Correlation coefficients are listed in Table 29A.

In general, the trace element content of the average Witwatersrand shale shows it to be far closer in composition to the average Fig Tree shale than to the average South African argillaceous rock. Similar to the Fig Tree shales, the elements Ni, Cr are strongly enriched and Cu and Co less so. The elements Y, Yb, Be, Zr, Nb, Th and Pb are markedly depleted. As can be seen in Table 25A, the Ni/Co and V/Cr ratios are far closer to those of the Fig Tree Series than the average South African argillaceous rock. These results indicate that the source rocks for the

Witwatersrand System must have been similar in petrology to the source rocks of the Fig Tree sediments although they probably contained a smaller ultrabasic component as the Ni concentrations and, therefore, the Ni/Co ratios are significantly lower.

Again the usefulness of the correlation coefficients is somewhat reduced by the paucity of samples, but an obvious feature is the lack of significant correlation coefficients with Fe indicating that this major element did not play a major role in the incorporation of trace elements in these sediments and in this respect is once more similar to the Fig Tree sediments. Well correlated groups of elements include Y - Yb, Co - Sc - Cr - V - Ni and Al - Ga - Zn.

5.5 SINCLAIR GROUP

KUNJAS SERIES

The five Kunjas samples analysed in this work were obtained from a phyllitic shale horizon. They consist of dominant illite, probably sericite, and quartz, with sub-ordinate plagioclase feldspar and traces of carbonates. Martin (1965) considered that the Kunjas sedimentary material was deposited in irregular, partly disconnected, basins, as the Kunjas beds tend to peter out and then re-appear beneath the overlying Sinclair Formation.

The Kunjas Series outcrops in the Helmeringhausen area, South West Africa, and attains a maximum thickness of about 1600 m in the west (Haughton, 1969). It consists of a sequence of basal conglomerates and phyllites and forms the base of the Sinclair Group. Using Rb-Sr age determinations carried out by Dodson, von Brunn (1969) considered the age of the sediments of the Kunjas Series to be between 1290 - 1020 m.y., the ages of granites which pre-date and post-date them.

Trace element concentrations and some inter-element ratios are presented in Table 4A. Average concentrations are listed in Table 23A and average ratios in Table 25A. These samples are not very rich in clay minerals and this is reflected to some extent in the marked depletion in concentration shown by most of the elements analysed in this work. Notable exceptions are V and Zr. The presence of abundant Zr can be explained in terms of a granitic or pegmatitic source area but the average concentration of 167 ppm V, ranging from 151 ppm to 187 ppm, is not so easily explained as this is the highest group of V concentrations encountered in this work. As these samples are phyllites they have been subjected to low-grade metamorphism and perhaps post-depositional migration of some elements, including V, has occurred, although if this were the case elements normally associated with V might have been expected to have been enriched as well.

5.6 DAMARA SYSTEM

The Damara System, which covers a considerable extent of central South West Africa and is divided into several facies, is unfortunately only represented by one sample in this study. This is an illite-chlorite shale and is derived from the south-eastern part of the Damara Syncline.

Trace element concentrations and some inter-element ratios for the single sample are presented in Tables 5A and 23A. The analysis of only one sample does not allow meaningful conclusions to be drawn concerning the Damara sediments. The concentrations of Zn, Co, Ni, V, Cr and Zr are slightly higher than those of the average South African argillaceous rock and this could be interpreted as reflecting the presence of a small amount of sulphide or that the sample consists of a large proportion of clay minerals.

5.7 MALMESBURY FORMATION

The sediments of the Malmesbury Formation outcrop over a considerable portion of the South-Western Cape. As they are frequently isoclinally folded, dips are generally extremely high and strike faulting is considerable in extent resulting in scanty knowledge of the true thickness of the succession. Haughton (1969) considers the thickness to be vast and that the beds are of geosynclinal deposition. Sediments in the Vanrynsdorp area of southern Namaqualand have long been considered to be a part of the Malmesbury and were mapped as such by Jansen (1960) but Kröner (1968) showed that they were almost definitely part of the Nama System and that the Malmesbury Formation was not represented in the area. From Rb-Sr age determinations Allsopp and Kolbe concluded that the age of deposition of the Malmesbury sediments could not greatly exceed 595 ± 45 m.y. The sediments of the Malmesbury Formation consist of a variety of shales, greywackes, quartzites and grits with occasional conglomerates, limestones, dolomites, cherts and basic lavas and tuffs (Haughton, 1969). Frequently, however, arenaceous clay-slates (or greywackes) alternate with more argillaceous shales and it is from these horizons that samples used in this study have originated. Of the five samples analysed three are argillaceous and two arenaceous. One of the arenites, Mm 2, was collected in the Vanryhnsdorp area from the sequence now

correlated by Kröner (1968) with the Nama System. The samples are all illite and quartz-rich with subordinate amounts of plagioclase feldspar. One argillaceous sample, Mm 7, was used for a less than two micron clay fraction separation.

Trace element concentrations and some inter-element ratios are presented in Table 5A. Average concentrations are listed in Table 23A and average ratios in Table 25A. Correlation coefficients are tabulated in Table 30A.

The arenaceous character of Mm 2 and Mm 4 is reflected in their trace element contents which show a marked depletion in concentrations for all trace elements analysed here except Zr. The depletions result from large amounts of quartz and feldspar acting as a diluent, and the enrichment of Zr is undoubtedly due to the present of more detrital zircon in the arenaceous than argillaceous samples. Too few samples were analysed for the correlation coefficients to be of much use and the diluting effects of quartz and plagioclase feldspar have also tended to generate extreme correlation coefficients. However, established correlations are observed in the Malmesbury sediments as well. These correlations include Ga-Al, Co-Ni and V-Cr. The Ga/Al, Ni/Co and V/Cr ratios are perhaps lower in the arenaceous than in the argillaceous sediments although this is based on the results of only one argillaceous sample as Mm 2 is now considered to belong to the Nama as mentioned earlier. The ratios in the arenaceous sample for Ga/Al, Ni/Co and V/Cr are 1.88×10^{-4}, 2.18 and 0.97 respectively compared to averages of 2.42×10^{-4}, 2.72

and 1.21 in the three argillaceous samples. These ratios might be useful in distinguishing between the arenaceous and argillaceous members of the Malmesbury Formation, but too few samples have been analysed here to confirm this.

5.8 CANGO FORMATION

The Cango Formation occurs in the Southern Cape near Ladismith and outcrops along a strike of 120 km reaching a maximum width of 16 km (Haughton, 1969). They consist of a series of shales, conglomerates, limestones, slates, feldspathic grits and quartzites. The Cango Formation is usually correlated with the Malmesbury Formation, but its exact position in the South African stratigraphic column is uncertain. Four Cango shales were analysed and they all contain dominant illite and quartz with minor amounts of chlorite and traces of plagioclase feldspar.

Trace element concentrations and some inter-element ratios are listed in Table 5A. Average concentrations are included in Table 23A and average ratios in 25A. In general, the trace element concentrations are similar to those for the Malmesbury Formation, with which this formation is often tentatively correlated, although the concentrations of Ga, Cu and Zn tend to be a little higher. Ga/Al, Ni/Co and V/Cr ratios are very similar to those of the Malmesbury Formation and almost identical to those of the average South African argillaceous rock.

5.9 NAMA SYSTEM

The sediments of the Nama System cover extensive regions of southern South West Africa south of Rehoboth and also extend into Little Namaqualand to the Vanrhynsdorp district. Martin (1965) considers their age to be slightly older than 510 m.y. The system has been divided into four series, three of which contain shale horizons and have consequently been sampled for this work. In order of decreasing age the four series are (1) Kuibis (2) Schwarzkalk, (3) Schwarzrand and (4) Fish River.

Trace element concentrations and some inter-element ratios for the three series of the Nama System analysed are presented in Table 23A and average ratios in Table 25A. Correlation coefficients were only calculated for the samples of the Fish River Series and these are tabulated in Table 31A.

5.9.1 Kuibis Series

This series consists of massive quartzites with subordinate beds of sandstone containing intercalated whitish shales (Haughton, 1969) and attains a maximum thickness of 220 m in the Fish River Canyon. Illite is the dominant clay mineral but the samples also contain abundant quartz with lesser amounts of montmorillonite and potash feldspar. Four Kuibis rocks have been analysed together with the less than two micron fraction of two of them, KUI 2 and KUI 4.

Compared to the average South African argillaceous rock the Kuibis samples are very depleted in Cu, Zn, Co, Ni and Cr and enriched in Zr. Although ground-

-water leaching might be responsible for the partial removal of some of these trace metals, the most likely reason for these low trace element levels is that the Kuibis sediments were derived from a pure granitic-terrain source area. Compared to the whole rock analyses the separated less than two micron fractions are strongly depleted in Zr indicating that their abundances in these shales are largely dependent on the presence of detrital zircon. Virtually all the remaining elements are strongly enriched indicating that they are largely incorporated in the illite fraction. The concentration of 11 ppm Be in KUI 4 is the highest for all the samples analysed in this work. This concentration might have been attributed to the presence of detrital beryl and it was to test this possibility that the less than two micron fraction of this sample was separated. Surprisingly enough, this fraction contained 17 ppm Be, about four times as much as the average separated clay fraction. This enrichment of Be in the clay fraction is extremely difficult to account for, but is probably due either to adsorption by newly formed clay minerals in the weathering environment of a source area containing beryl-rich granites or pegmatities, or hydrolysis of Be in the depositional environment followed by incorporation in the hydrolysate fraction. It might possibly be due to adsorption by the clay minerals of a very finely divided beryl, although this is considered unlikely. The concentration of 300 ppm Cu in the clay fraction of KUI 4 is considered erroneous and due to contamination by Cu at some stage during the clay separation process or briquetting stage. An enrichment from 14 ppm Cu in the

whole rock to 300 ppm in the separated clay fraction is not considered possible.

The average Ga/Al and V/Cr ratios are similar to those of the average South African argillaceous rock but the average Ni/Co ratio of at least 3.78 is very high and might be due to the partial removal of Co by surface leaching as these are outcrop samples.

5.9.2 Schwarzkalk Series

The maximum development of this series is 300 m.(Martin, 1965) and it consists entirely of dark, bituminous limestones with a few intercalated shales. Two samples were obtained from this series but were discarded when X-ray diffraction analysis revealed them to be limestones and not shales.

5.9.3 Schwarzrand Series

This series reaches a maximum thickness of 400 m in the type area where it consists of soft, grey-green to bluish-grey shales with sandstone and black limestone intercalations. Limestone becomes more predominant towards the south. Nappe structures of this and the preceding series are conspicuous in the Naukluft Mountains. Four illite-chlorite shales, containing variable amounts of plagioclase and potash feldspar, have been analysed together with the less than two micron fraction from one sample, SCHR 3.

The average trace element concentrations of the shales from the Schwarzrand Series are very close to those from the average South African argillaceous rock and there is little of further interest concerning them. The average V/Cr ratio is unusually high but the Ga/Al and Ni/Co ratios are normal.

5.9.4 Fish River Series

This series, the topmost member of the Nama System, consists of conglomeratic quartzites, shales and red and purple argillaceous sandstones. A maximum thickness of 700 m has been preserved and Martin (1965) describes the series as a shallow-water deposit with conspicuous current-bedding, ripple marks and clay pellet horizons. The fourteen samples analysed are very variable in composition but are characterised by being illite-rich with subordinate amounts of montmorillonite, chlorite and occasionally kaolinite. Plagioclase and potash feldspar are normally abundant constituents of these rocks. Calcite is frequently present and the diffraction lines of hematite and goethite were detected in a few samples.

The average trace element concentrations only reveal that the Fish River sediments are perhaps a little depleted in Ga, V and Cr and enriched in Cu relative to the average South African argillaceous rock. The Ga/Al, Ni/Co and V/Cr ratios are very close to the average for all the sample as well. The correlation coefficients are not very informative due to the small number of samples and to variable amounts of detrital quartz and feldspar. Total SiO_2 varies from 58.6 to 81.9 percent (Danchin, 1970).

5.10 CAPE SYSTEM

5.10.1 BOKKEVELD SERIES

The Bokkeveld Series, which follows conformably on the Upper Sandstones of the Table Mountain Serie of the Cape System, occurs only in the southern Cape Province and from Cape Town extends north to near Vanrhynsdorp and

east of Grahamstown. In the type area near Ceres the succession consists of five shale bands separated from each other by four layers of sandstone. Apparently a maximum thickness of 1700 m is reached in the Ceres area (Haughton, 1969) although du Toit (1939) considers 800 m to be the full thickness. North and South of here the succession decreases in thickness.

Illite and chlorite are the major cl clay minerals in this series with illite usually being dominant. In a few samples chlorite is only present in trace amounts. Montmorillonite is normally present as well. Plagioclase feldspar occurs in minor amounts but potash feldspar is rare.

The Bokkeveld Series is Lower Devonian in age and marine invertebrate fossils of this period are abundant in its lower half. These consist chiefly of brachiopods, lamellibranchs and arthropods (particularly trilobites) but also include gasteropods, cephalopods, pteropods and fish spines. The upper shales have yielded mainly plants, especially SPIROPHYTON, but a few marine forms have been recorded. From the fossil evidence the lower half of the Bokkeveld sequence was clearly deposited beneath the sea, the environment being a shallow benthic one (du Toit, 1939). The upper half of the sequence was deposited under more fluviatile conditions although the alternation of arenaceous and argillaceous beds indicates that frequent oscillations of the sea-floor took place. The appearance of plants at the top of the sequence indicates a very shallow depositional environment towards the end of the Devonian.

Thirty seven Bokkeveld samples and the separated clay fractions of four of these were analysed. Eleven samples were taken from the first shale band, thirteen from the second, one from the third, three from the fourth and two from the fifth. The position in the succession of the remaining samples was not recorded by the collectors.

Trace element concentrations in Bokkeveld samples are recorded in Table 7A and correlation coefficients in Table 32A. The average Bokkeveld shale listed in Table 23A is surprisingly similar in composition to the average shale of Wedepohl (1971) listed in Table 27A. Only Cu, Co, Ni, Yb, Zr, Th and Pb exhibit significant differences. These differences could be due to the source rocks of the Bokkeveld Series being dominantly granitic in composition as the Zr, Th and Pb concentrations are high and the Cu, Co and Ni concentrations are low. Compared to the average South African shale the average Bokkeveld shale is slightly enriched in V and depleted in Co and Cu.

As only six samples have been collected from the three uppermost shale bands it is not possible to compare their geochemistry with the two lowermost shale bands. The twenty-four samples from these two shale bands vary in composition from chlorite shales to illite shales with a complete gradation between these two extremes. However, there is no trend of change in mineralogy with height in the succession. This is shown clearly by samples Bk 18 to Bk 34, which represent a cross-section of the Bokkeveld Series at one locality from the top of the Table Mountain Series to the base of the Witteberg Series. There is also

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no apparent systematic change of trace element content with height in the succession. Danchin (1970) found the major element content of the Bokkeveld Series samples to be remarkably constant. There is also no apparent systematic change of mineralogy or of trace element content on a horizontal scale. Samples have been collected from a strike length of 650 km, Bk 18 - 34 originating from the westernmost end of the basin of sedimentation and Bk 302 from the easternmost. Any gradual systematic change if any of mineralogy or trace element content with horizontal distance is obscured by the normal overall variation. Similarly there are no significant regular changes in samples Bk 18 - 34, Bk 361, Bk 373 and Bk 389 which represent a distance of 100 km across the western end of the basin in a north-south direction.

These results suggest that the composition of the source area remained unchanged throughout the period of supply of detritus to the Bokkeveld basin of sedimentation. No different rock type was "unroofed" by progressive erosion, and the rivers delivering material to the sea did not encroach on areas of different rock composition. Perhaps slight changes in climatic conditions were responsible for the changes of clay minerals formed during the weathering of the source rocks. The sandstone bands which separate the shale bands were probably formed by changes of the ancient sea-level. The fact that potash feldspar is virtually absent from the Bokkeveld Series suggests that either chemical weathering was sufficiently intense to completely break down all potash feldspar present, or else it was a rare constituent of the source rock which might have been dioritic or tonalitic in composition. Alternatively the sediments could

have been partly derived from a pre-existing sedimentary rock.

All the trace elements analysed, except Y, Yb, Zr and Nb, are considerably enriched in the less than two micron fraction indicating that they are associated with either the fine clay mineral fraction or other finely divided mineral phases. Zr and Nb are largely incorporated in the detrital heavy mineral fraction, Zr in zircon and Nb in ilmenite, magnetite, sphene and anatase, but both elements are also present in the separated clay fraction. The depletion of Y and Yb in the separated clay fraction is interesting and difficult to interpret. Perhaps the answer lies in the experimental work of Haskin et al. (1966) who found Y and the lanthanides to be associated with the pure quartz fraction of the St. Peter sandstone presumably as iron oxide inclusions or coatings. If Y and Yb were scavenged by iron oxide coatings or in iron oxide inclusions of the quartz grains in the Bokkeveld shales then they would have been removed from the clay fraction during the clay separation process. If the iron oxide coatings were "scrubbed off" during the ultrasonic treatment they would still be removed in the settled coarse fraction as ferric hydroxide (limonite) has a greater density than the clay minerals. Cu, Zn, Ni and V show greatest relative enrichment in the separated clay fraction, suggesting that they are most abundant in the finest clay mineral fraction and have probably been incorporated by cation exchange or adsorption processes, possibly partly during weathering processes, partly during river transport and partly during deposition in the marine environment.

The Ga/Al ratio shows no significant change in the separated clay fraction thus in this case providing no

evidence of preferential adsorption and incorporation of Ga over Al in the finest fraction. Ni/Co ratios appear to be higher in the separated clay fraction but the data may be misleading as the samples might have suffered leaching by groundwaters before collection with the preferential loss of Co over Ni. If the data are meaningful they indicate that either Ni is preferentially adsorbed over Co on the finest clay particles or Co has been preferentially incorporated in a heavy mineral fraction, possibly an authigenic hydrated iron oxide, and has been partially removed during the clay separation process. Many of the Bokkeveld Series Co analyses are extremely low and it seems likely that they have suffered Co removal by surface leaching. Co appears to be more easily leached during weathering than Ni. Butler (1953) found the Ni/Co ratio to decrease with depth in a soil profile illustrating this difference in chemical behaviour between Ni and Co. However, the distributions of these elements are discussed in more detail in Section 6.

The V/Cr ratio of 1.17 (Table 25A) in the Bokkeveld Series is significantly lower than the average of 1.51 in the four separated clay fractions from these rocks. Surface leaching is not considered to have affected the concentrations of these elements so that this difference in the V/Cr ratio is a meaningful one. The cause of this increase might be two-fold. V is probably preferentially adsorbed onto the finest clay particles, and more Cr than V is removed in the detrital heavy mineral fraction. If all the Cr was in the clay mineral fraction then the degree of enrichment should be greater than is actually observed because of the dilution effect of quartz and plagioclase being removed. Thus it seems likely that a small proportion of the Cr is located in the detrital heavy mineral fraction

of the Bokkeveld Series samples.

Good correlations, discussed in detail in Section 6, are observed between the following pairs of elements: Ga - Al, Ga - LOI, Ga - Cr, Ni - Co, V - Cr, Cr - Al, Cr - LOI, Y - Yb. Other correlations noted are Zn - Ni, Zn - Co, Zn - Fe, V - Sc, Co - Fe, Ni - Fe, Sc - Al and V - Al. These correlations suggest that Zn, Co and Ni are largely associated with an iron-rich phase, probably a hydrated iron oxide, and that V and Sc tend to be more closely associated with the clay fraction than any other fraction. In view of the earlier conclusion that Y and Yb might be chiefly located in iron oxide coatings, it is felt that the absence of any correlation between Y and Yb merits an explanation. It is quite feasible that Y and Yb follow each other closely in the hydrolysate fraction and in the clay mineral fraction. Their presence in the clay minerals is quite independent of Fe which is also present in clay minerals in amounts of a few percent, peaking in the Fe-rich chlorites.

As the Bokkeveld Series consists of true shales of undoubted marine origin it provides a convenient model for testing the use of trace elements as indicators of environment of deposition. The feasibility of using trace elements in this way is discussed in Section 8.

5.10.2 WITTEBERG SERIES

Resting conformably on the Bokkeveld Series, the Witteberg Series has the same distribution as that series, the boundary between the two series being purely arbitrarily chosen as the base of the first prominent white

weathered quartzite. Theron (1962) divided the series into three stages in the Willowmore district. The Lower Stage (200m) consists mainly of shales and intercalating sandstones, the Middle Stage (620m) essentially of sandstones, and the Upper Stage (550m) of dark shales with a few intercalated sandstones, the total thickness in this area being about 1270m. Plant and fish remains have been recovered from the upper half of the succession and du Toit (1939) has concluded that the series was deposited under moderately shallow fresh-water conditions deepening towards the south, and to range in age from Middle Devonian to Lower Carboniferous.

Seven Witteberg shale samples were analysed and from one, Wb 6, the less than two micron fraction was separated and analysed. The samples all contain dominant illite and quartz, with minor amounts of chlorite and montmorillonite and occasional plagioclase feldspar and siderite. Compared to the majority of shales examined in this study and in particular the Bokkeveld shales, these shales are remarkably feldspar free which might well indicate the source rocks to have been of a sedimentary nature and quite possibly not the source material for the Bokkeveld Series as well. As their major element compositions are so similar Danchin (1970) concluded that they were derived from the same source rocks. The degree and type of chemical weathering, perhaps brought about by climatic changes in the source area, could also be responsible, although the clay mineralogy of the shales of the Bokkeveld and Witteberg Series is identical.

Trace element concentrations and some interelement ratios are set out in Table 8A. Average

concentrations are listed in Table 23A and average ratios are included in Table 25A. Correlation coefficients are presented in Table 33A.

The average trace element composition of the Witteberg shales is remarkably similar to the average Bokkeveld shale (Table 23A) which supports the possibility that they have been derived from the same source rocks. However, Cu and Co contents are slightly higher and the V content slightly lower than the average Bokkeveld shale. These differences might be the result of changes in the environment of deposition as the Bokkeveld is of marine origin and the Witteberg of fresh-water origin. The Ni/Co and V/Cr ratios are also different and thus might be used as indicators of depositional environment. The possibility is discussed in Section 8 which deals with the use of trace elements as indicators of the environment of deposition.

The use of correlation coefficients is handicapped by the small number of samples and the fact that varying amounts of quartz, acting as a diluent, has tended to cause element concentrations to vary sympathetically thus generating artifically high correlation coefficients. However, it is clear that Ga, Cu, V, Cr and Sc correlate well with Al and are thus associated with the clay mineral fraction.

5.11 KARROO SYSTEM

5.11.1 DWYKA SERIES

The Dwyka Series in the south follows conformably on the Witteberg Series of the Cape System but to the north and north east it lies unconformably on ancient rocks indicating a massive extention of the basin of deposition in these directions. The rocks of this series have long been recognized as the final product of glacial weathering and transport. In the north the rocks show the characteristics of glacial moraines but towards the south, where they attain their maximum development of 1330m (du Toit, 1939), final deposition occurred sub-aqueously and some bedding features are apparent. Haughton (1969) has divided the series into the Tillite Stage and the Upper Stage. The Tillite Stage reaches a miximum thickness of 830m in the south and is considered to be the largest pile of sediments of its type known. Varve-like shale bands are intercalated between beds of tillite in the northern part of the main basin. Hart (cited by Haughton, 1969) deduced from fossil evidence that marine conditions existed during Dwyka times. The Tillite Stage is followed conformably by the Upper Stage which consists of fine-grained shales reaching a miximum thickness of 180 m. The upper part of these shales consists of a zone of black shale which weathers white on atmospheric exposure and is a conspicuous feature in the Karroo. This very interesting shale contains limestones and pyrite and du Toit (1939) considers it to have been deposited as black, highly sulphuretted muds in fairly deep water. In spite of Hart's evidence, the presence of fossil plants and tree trunks indicates that the Upper Stage, and probably the whole series, is of fresh-water origin.

Six samples of the Upper Stage sediments were obtained, two LDW 3 and LDW 4, being from the "White Band". Four samples were collected from its occurrence in the south, near Sutherland and Laingsburg, the other two being collected in the west near Vioolsdrift in South West Africa. All are very quartz-rich with traces of plagioclase and potash feldspar and should be termed siltstones. Illite is the dominant clay mineral with much smaller amounts of kaolinite, chlorite and montmorillonite. The clay content is small but this is not unexpected owing to the cold climatic conditions prevailing in the source area which would severely retard the formation of clay minerals by chemical weathering. In this respect the sediments are similar to Recent Antarctic glacial marine sediments which Angino (1966) has found to have been deposited relatively unaltered.

Trace element concentrations and some inter-element ratios are presented in Table 8A. Average trace element concentrations are listed in Table 23A and average ratios in Table 25A.

In general most of the trace elements in the shales from the Dwyka Series are strongly depleted relative to average South African argillaceous rock listed in Table 27A. Elements which are particularly depleted include Zn, Co, Ni, Cr, Zr and Nb. The principal reason for this depletion is that the most abundant minerals present are quartz and feldspar and the clay mineral contentis comparatively low.

Angino (1966) has analysed modern glacial Antarctic sediments which are considered to be the modern analogue of the Dwyka sediments. Although they are low in carbonate and normally in total organic content, they

are very enriched in V and Cu and other trace metals analysed and all occur in concentrations far in excess of those found in the Dwyka sediments. Angino found average concentrations of 168 ppm V and 120 ppm Cu in the Antarctic glacial sediments compared to 105 ppm V and 29 ppm Cu in the Dwyka sediments reported here. However, the Antarctic Amundsen Sea sediments average 240 ppm V and 185 ppm Cu. Although these high concentrations might be derived from the source rocks it is more likely that they have been incorporated in the sediments via the organic remains of trace metal enriched plankton.

In contrast no enrichment of any of the trace elements analysed has occurred in the black shales of the Upper Stage of the Dwyka although the organic content, as measured by LOI, is as high as 10.2 percent. As these are fresh-water shales, perhaps a low trace element content of the Dwyka sea has prohibited both metal uptake in the planktonic organisms and the precipitation of metal sulphides from the overlying water following the reduction of sulphate ions by bacterial decay, these being the two proposed mechanisms for the enrichment of trace metals in organic-rich sediments as discussed elsewhere in this work.

As only two samples of these black shales have been analysed, more work is definitely justified on the geochemistry of this interesting sequence.

5.11.2 NORTHERN ECCA FACIES

5.11.2.1 INTRODUCTION

The rocks of the Karroo System, which is divided into the Dwyka, Ecca, Beaufort and Stormberg Series, cover about half of the Republic of South Africa and are also found in large areas of Botswana, Rhodesia, Malawi, Zambia, Swaziland, Mozambique and South West Africa. They completely cover Lesotho. Only the predominantly volcanic Stormberg Series is not included in this study.

More shales have been analysed from the Ecca than from any other series by far - in fact the Ecca shales constitute almost half the samples included in this study. There are several reasons for this. Of paramount importance is the fact that the Karroo System, of which the Ecca Series is the most abundant member, is an exceptionally well preserved sedimentary sequence of great areal extent and thickness and so provides an ideal example for geochemical research of a complete sedimentary basin. Only in the south has the system been involved in the tectonics which produced the Cape Folded Belt of mountains existing today. Furthermore, all supplies of coal produced in South Africa are mined from the Coal Measures of the Ecca Series and petrol is obtained by treatment of coal from the Sigma colliery at the Sasol plant in the northern Orange Free State. The economic potential of the Ecca Series, especially with regard to the search for oil, has been evaluated by drilling by several organizations. Several borehole cores have been made available to this project and these provide invaluable unweathered material for analysis. In general, it is extremely difficult to obtain suitable

unweathered samples at outcrop, particularly of the carbonaceous shales.

The Ecca Series has virtually the same distribution as the Karroo System although it is covered for most part by the rocks of the Beaufort Series and thus only outcrops as a belt of about 100 km average width. The rocks are predominantly shales and sandstones with well-developed Coal Measures in parts and minor phosphatic nodules, ferruginous limestones and calcerous concretions (Haughton, 1969). In a paper describing the laws governing lithologic cycles Szadeczky-Kardoss (1971) describes the Ecca Series as a fifty to sixty-fold repetition of fluviatile, deltaic and lucustrine cycles. He classifies the sediments as being deposited by aggrading rivers.

In a detailed petrographic and structural study of the Ecca, Ryan (1967) considered the Karroo sediments to have been deposited upon a very uneven sufrace. The Ecca Basin developed into the Karroo Trough in the south, the Natal Trough in the east and a cratonic shelf area in the north. Only the western limb of the former Natal Trough is still in existence today the rest of it being truncated by the modern coast line. Ryan has divided the Ecca Series into the Northern Ecca Facies, Central Ecca Facies, Southern Ecca Facies and Western Ecca Facies each of which is further sub-divided into Lower, Middle and Upper Groups.

The Northern Ecca Facies consists of the cratonic shelf and the Natal Trough. The Lower Group sediments were deposited in a discontinuous shallow water environment. Local pre-Karroo highlands existed, especially

the Clocolan Dome and the area north of latitude 27^{o}, as the Middle Group sediments lie directly on pre-Karroo surfaces in these areas and the centres of these areas were, in fact, only covered by Upper Group sediments. The vast thicknesses of the Middle Group sediments were accumulated rapidly and local disconformities and development of coal measures attest to very shallow water lacustrine or swamp conditions which would allow the prolific growth of coal-forming plants. Casts of tree stumps still exist - "fossil forests" at Vereeniging, Transvaal. Middle Ecca rocks consist of thick bands of sandstone and grits with shaly layers and intercalated coal seams. Much of the Middle Ecca consists of reworked Dwyka morainic debris. Although the sediments are generally considered to have been laid down under fresh-water conditions, Hart (cited by Haughton, 1969) described boron-rich glauconite and marine phyte-plankton from the top of the Middle Ecca which led him to believe that marine conditions existed at this time. However, this evidence has been disputed. The vast bulk of the sediments came from the erosion of a rapidly lifting land mass to the east and the fact that the Upper Ecca Group is composed almost entirely of shale led Ryan to believe that the Eastern Source Area was far less pronounced than in Middle Ecca times. In general the Middle Ecca sediments are thickest reaching a maximum development of 600 m in Swaziland and 350 m in Natal. The thickness of the Lower Ecca is very variable and is generally dependent on pre-Karroo topography.

5.11.2.2 Borehole Bh 134 and A Series Boreholes, Eastern Transvaal.

These four boreholes are grouped as they are all from the eastern Transvaal. Sample localities and descriptions are given in Table 1A. Thirty two samples in all were analysed from the four boreholes.

(i) Borehole A 62:

Six samples from the Middle Group were collected over a range of 35 m. They contain abundant coaly plant remains (average loss on ignition 26%) and kaolinite is the dominant clay mineral with traces of illite montmorillonite. Siderite is occasionally present and potash feldspar is abundant emphasizing the granitic nature of the source area and the rapidity of the cycle of erosion, transport and sedimentation. Trace element concentrations are listed in Table 13A. Compared to the average South African carbonaceous shale, listed in Table 23A and Table 27A, the samples are slightly enriched in Co, Ni, V, Cr, Y, Zr and Nb, whereas no elements are significantly depleted. Cu, Ni and V concentrations appear to increase with height in the succession whereas Cr, Zr and Nb concentrations appear to decrease.

(ii) Borehole A 76:

Six samples were taken from this borehole which is stiuated on the same farm as A 62 but about 3 km north. Also taken from a 35 km section they are the equivalent of the A 62 samples and are very similar in mineralogy and plant content. However, pyrite is present in one sample. Trace element concentrations are listed in Table 12A. Compared to the average South African carbonaceous shale, samples from this borehole are enriched in Ni, Cr, Zr and Nb but no elements appear to be significantly depleted. No elements

show a systematic change of concentration with position in the succession.

(iii) Borehole A 78:

Situated a few kilometers south of the previous two boreholes, this borehole was sampled over a section of 47 km to yield thirteen samples which are very similar in mineralogy to those two boreholes. However, traces of plagioclase are occasionally present. The coaly plant remains are the most abundant for any group of rocks studied and range up to 45% loss on ignition. For samples with abundant coaly remains the percentage loss on ignition can be safely used as a semi-quantitative measure of the organic content of the rock. Trace element concentrations are listed in Table 12 A. Compared to the average South African carbonaceous shale the samples from this borehole are enriched in Ni, V, Cr, Zr and Nb. In agreement with the previous two boreholes no elements appear to be depleted. V and Cr are strongly enriched at the top of the succession and Zn, Ni and Zr exhibit the same tendency but to a lesser degree. Be is enriched at the base.

(iv) Borehole Bh 134 (Springbok Colliery):

Seven samples were taken from 90 km of core from this borehole which is situated about 30 km south-west of the A series boreholes. In mineralogy and organic content they are very similar to samples from those boreholes and are considered to be their stratigraphic equivalents. Trace element concentrations are listed in Table 15A. Only Zn and Ni appear to be enriched relative to the average South African carbonaceous shale. No regular changes of concentration with height in the succession are apparent for any of the elements analysed.

As these four boreholes are located relatively close to each other they can be discussed as a single entity. Danchin (1970) deduced from Al/Na, Al/K and Na/K ratios that an increase in illite relative to potash feldspar occurred in a north-south direction. From this he inferred that the source area of these sediments lay to the north of the site of deposition which agreed with available geological evidence. From the X-ray diffraction studies it is evident that the southernmost borehole, A 78, does contain the most abundant amounts of illite but it does not seem likely that this is a function of distance from the ancient shoreline as the boreholes are only a few kilometers apart and the ancient shoreline must have been at least 200 km away.

The A Series boreholes are remarkably similar to each other in average trace element composition but Borehole Bh 134 contains slightly less Nb, Zr, Cr and V. Correlation coefficients were calculated for the A Series borehole samples as a single group and are presented in Table 34A.

Most of the trace elements in these boreholes show a side variation of concentration. For example, in Borehole A 78 Be ranges from 2.1 to 7.3 ppm, Ga from 13 to 34 ppm, Cu from 21 to 51 ppm, Zn from 36 to 127 ppm, Co from 7.5 to 55 ppm, Ni from 31 to 113 ppm, V from 32 to 308 ppm, Cr from 103 to 418 ppm, Sc from 8.6 to 18 ppm, Zr from 181 to 430 ppm, Nb from 19 to 89 ppm, Th from 13 to 34 ppm, and Pb from 23 to 44 ppm. Some of this variation is undoubtedly due to variable amounts of organic carbon, quartz. and feldspar acting as a diluent, a small proportion of the variation might be due to analytical error but the bulk of the variation is undoubtedly real and reflects marked changes from time to

time in the trace element incorporation by the rapidly accumulating sediment.

No element shows a strong correlation with the loss on ignition, here taken to represent the organic carbon content. In view of the general high organic carbon and the high level of trace element concentrations this is somewhat surprising and is interpreted as indicating that, although there is no systematic association of any trace elements with the organic material, some trace metals are incorporated by the organic fraction and sometimes in significantly large amounts, but this incorporation is not consistent and has not generated good correlations. However, the absolute trace metal concentrations show that there is a marked association with the organic content.

Although the bulk of the major element and trace element content of a sediment is regarded as being detrital in nature as it has been derived directly from the source area incorporated in particulate matter, a minor, but highly significant, proportion of the trace element content represents material brought to the site of sedimentation in solution and later incorporated into the sediment by such mechanisms as adsorption, chemical precipitation and the formation of organic complexes by chelation. Ahrens (1966) discusses the use of ionisation potentials as a measure of the stability of metal-binding organic complexes, such as the amino-acids, in oceans and sediments. As detrital material is accumulating to form a sediment it is out of equilibrium with its environment and it will have a tendency to undergo chemical changes bringing it closer to a state of equilibrium. These reactions are considered to be predominantly cation exchange reactions, although adsorption and possibly preci-

pitation reactions, influenced by the pH and Eh conditions which are controlled partially by the nature of the sediment, should also be regarded as reactions which are tending to move the sediment-water into a state of equilibrium. As Nicholls and Loring (1962) have emphasized, the extent to which a state of equilibrium is approached is dependent on the rate of sedimentation.

Nicholls and Loring (1962) attempted to use the development of authigenic carbonates and sulphides, calculated as argillaceous norms from whole rock major element data, to deduce the pH and Eh conditions of the depositional environment. These minerals can be precipitated from the waters overlying the sediment but they undoubtedly also develop below the sediment-water interface. Brooks et al. (1968) and Bonatti et al. (1971) showed that a change from oxidising to reducing conditions took place beneath the sediment-water interface and the decomposition of organic matter in this zone generaged hydrogen sulphide. The downward migration of dissolved sulphate ions followed by its bacterial reduction during the decomposition of the organic matter is the probable mechanism of the origin of the sulphide ions below the sediment-water interface. This is the most likely principal origin of the sulphide ions in the carbonaceous Northern Ecca Facies shales, although quite possibly some sulphide originates from the organic matter itself.

The development of authigenic sulphides and carbonates provides a mechanism for the incorporation of trace elements in sediments as these minerals can contain minor amounts of any elements. Hirst (1962) determined the non-detrital trace metal contents of modern sediments

from the Gulf of Paria, but the method used of leaching in 25 percent acetic acid will not account for trace metals incorporated in sedimentary pyrite which is resistant to attack by acetic acid. In this work no attempt has been made to determine the authigenic trace metal contents of these carbonaceous shales. However, Danchin, (1970) using the methods of Nicholls (1962) has determined the normative amounts of pyrite and siderite in the carbonaceous shales of the Northern Ecca Facies boreholes. These can be used to ascertain whether a significant proportion of any trace metal is included in either of these phases.

Borehole A 78 is particularly suitable for this purpose as 13 samples were taken from approximately 4 m intervals throughout the carbonaceous succession. Furthermore, normative siderite is well-developed towards the middle of the succession whereas normative pyrite is developed in the lowermost portion of the succession. Thus the relative influence of the development of both mineral species on the trace metal content can be ascertained. Fig. 40A shows the variation of normative pyrite, normative siderite, Cu, Zn, Co, V and Cr with height in the succession. In this diagram the vertical distances are not plotted exactly to scale as it is known that major compositional differences can take place over very small vertical distances.

From Fig. 40A it is clear that none of the elements plotted have any tendency to be associated to an appreciable extent in either pyrite or siderite. Although they undoubtedly do contain trace amounts of some metals, as shown for pyrite by Mitchell (1968), pyrite and siderite appear to be of minor importance in the distribution of the

trace elements dealt with in this work in South African carbonaceous shales. The results for the samples from the boreholes A 62, A 76 and Bh 134 are not plotted as they show analagous trends. The distribution of the trace elements appears to be largely controlled by their incorporation in detrital minerals derived from the source area, and their incorporation in sediments at the site of deposition by mechanisms such as cation exchange and adsorption, but not, apparently, by the formation of authigenic pyrite or siderite. The distribution of each individual element in carbonaceous shales is discussed in more detail in Section 6.

The correlation coefficients for the A Series Borehole samples listed in Table 34A show few significant correlations apart from the strong Ga-Al association. This is interpreted as indicating that most of these trace elements have a complex distribution being located in more than one mineral phase and perhaps being incorporated in inconsistent amounts in the minerals in which they do occur.

The average ratios Ga/Al and V/Cr are very similar to the average carbonaceous shale (Table 26A), but the Ni/Co ratio is distinctly higher. The V/Cr ratio shows a greater dispersion than the Ni/Co ratio which shows a greater dispersion than the Ga/Al ratio. None of these ratios appear to be controlled by possible parameters such as LOI, normative pyrite, normative siderite, Al or Fe content.

5.11.2.3 GB Series Boreholes, Northern Transvaal

These three boreholes are situated in the south-eastern Transvaalin the Wakkerstroom district close to the Natal border. They are aligned roughly north-south, the northern-most borehole being GB 48 which is 5 km north of GB 47 which is 8 km north of GB 45. They all penetrate the Middle Group Coal Measures which approach close to the surface in this area as the Upper Group shales are not well developed here. Thirty-seven samples in all were analysed.

(i) Borehole GB 45/65:

Thirteen samples were collected from a 290 m section. The dominant clay minerals are illite and kaolinite with traces of montmorillonite. Plagioclase and potash feldspar are abundant and traces of calcite, siderite and pyrite are apparent in places. The organic carbon content ranges between 2% and 13%. One sample, GB 45/64/3, was used for the separation of a less than two micron fraction.

(ii) Borehole GB 47/64:

Eleven samples were collected from a 260 m section of this borehole. Their mineralogy is very similar to that of GB 45 except that no pyrite or siderite is present. Organic carbon content ranges between 3% and 13%. Two samples, GB 47/64/7 and GB 47/64/11, were used for the separation of less than two micron fraction.

(iii) Borehole GB 48/65;

Thirteen samples from this borehole were collected from a 200 m section. They are also very similar in mineralogy to GB 45 except for an even greater abundance of plagioclase and potash feldspar. Organic content ranges from 4% to 17% with one sample measuring 28% loss on ignition being exceptionally rich in coaly material. One sample,

GB 48/65/11, was used for the separation of a less than two micron fraction.

Trace element concentrations and some inter-element ratios for Borehole GB 47/64 are listed in Table 9A, for Borehole GB 45/64 in TAble 10A and for GB 48/65 in Table 11A. Average concentrations are listed in Tables 23A and 24A and average ratios are listed in Tables 25A and 26A.

The samples of the GB Series Boreholes are similar to the A Series Boreholes in that the trace elements show a wide range of concentrations. Cu and Zn are the two elements whose concentrations show the greatest dispersion. None of the elements analysed in this work is greatly enriched or depleted compared to the average carbonaceous Northen Ecca Facies shale. Unlike Bh 134 or the A Series Boreholes, in the GB Series Borehole samples there is a marked correlation of some trace metals with the organic content as given by LOI. Fig. 29A shows the variation with height in the succession LOI and the concentration of Cu, Zn, V and Cr in the carbonaceous shales of Borehole GB 45/64. Fig. 30A is a similar diagram for Borehole GB 47/64. It is clear that the concentrations of Cu, Zn, V and Cr vary sympathetically with LOI indicating that a large proportion of these elements are associated with the organic fraction. Tourtelot (1964) maintained that insignificant amounts of trace metals are incorporated during the growth of plants which eventually form coals. If this is the case then Cu, Zn, V and Cr must be incorporated in the organic fraction by adsorption or organic complex formation at the site of sedimentation. In Section 6.6 reasons are put forward for suggesting that V and Cr are actually located

in a Ti mineral phase which is associated with the organic fraction, probably by adsorption. An interesting feature of the GB Series is that V and Cr are not enriched in the top part of the succession as they are in the A Series Borehole. Although both groups of samples belong to the Middle Ecca they are not necessarily coeval. However, the differences in the V and Cr contents indicate differences of some kind in sedimentation towards the end of Middle Ecca times in the northern part of the Northern Ecca basin of sedimentation. It is likely that at this time there was an increase in the supply of a Ti mineral, probably ilmenite, from the source area. The increase might have been due to a change of drainage pattern or the "unroofing" of previously unexposed rocks, in both cases causing an increase of Ti-rich basic rocks in the source area. If either of these possibilities were the operative mechanism a concomitant increase in Ni would have resulted which is not the effect observed. Therefore, the probable cause of the V and Cr enrichment in the northern part of the basin is the formation of V and Cr bearing authigenic anatase, or some other hydrated Ti mineral, followed by adsorption onto the organic material. Goldberg and Arrhenius (1958) record the formation of authigenic anatase in modern Pacific sediments.

The correlation coefficients for the GB Borehole Series are listed in Table 35A and show marked differences from those for the A Series Boreholes. Cu, Zn, V and Cr tend to be inter-correlated as would be expected from their sympathetic variation with height in the succession as shown in Figs. 29A and 30A. Sc, Y and Yb are strongly associated with each other and with total Fe. Perhaps the bulk of these three trace elements was scavenged by precipitating or settling ferric hydroxides which were

reduced, when located below the sediment-water interface, thus releasing Sc, Y, Yb and any other incorporated elements rendering them available for permanent incorporation into the sediment by adsorption or by the formation of a stable authigenic mineral, perhaps a sulphide. This aspect is disoussed further in Section 6.10. The normal close coherence of Co and Ni is well demonstrated in these samples. Average Ga/Al, Ni/Co and V/Cr ratios are listed in Table 26A. All three average ratios are very similar to the average carbonaceous shale and, similar to the ratios for the A Series Borehole sample, do not appear to be dependent on any obvious parameter. There is also no obvious correlation of change in ratio with rate of deposition, as the material for the GB Series Borehole sediments is considered to have accumulated far more rapidly than the material for the A Series Borehole sediments.

5.11.2.4 Dannhauser Boreholes, Central Natal:

Ten samples were obtained from two boreholes in the Dannhauser district of Natal. Eight were from a 300 m section of Borehole G.S.O. 9 and two were from G.S.O. 10. The dominant clay minerals are kaolinite and illite, but one sample Ec Dan 7, is very unusual in that it only contains traces of kaolinite. Plagioclase and potash feldspar are abundant and pyrite and siderite are occasionally present. Organic content is variable ranging between 2% and 18%. One sample, Ec Dan 9, was used for the separation of a less than two micron fraction.

The average trace element concentrations of these carbonaceous shales from the Middle Group of the Northern Ecca Facies are very similar to the average South

African carbonaceous shale. Correlation coefficients were not computed as only ten samples from the two boreholes were available. The most surprising feature of these samples is that Ec Dan 7 and Ec Dan 8 are markedly depleted in the trace elements Cu, Co, Sc and Th. However, these are the only two samples from Borehole G.S.O. 10 so variation trends cannot be studied. Ec Dan 7 contains only a trace amount of kaolinite and Ec Dan 8 contains abundant siderite but it is difficult to ascertain the role these two factors could have played to account for the depletion of these four elements. Average Ga/Al, Ni/Co and V/Cr ratios are very similar to the average carbonaceous Northern Ecca Facies shales.

5.11.2.5 Somkele Borehole, Northern Zululand:

Twenty six samples were obtained from a 1040 m section of core from this borehole which is situated in northen Zululand near Mtubatuba. In this area the sediments form part of the Natal Trough which accounts for the exceptional thickness of the Middle Ecca Group here. However, it is also possible that the upper few samples are representatives of the Lower Beaufort Shales as the location of the Ecca-Beaufort boundary here is uncertain. It is impossible to distinguish the Upper Ecca Group shales from the Middle Ecca Group shales in this borehole. They were both deposited under relatively deep-water conditions in this area, whereas to the north the Middle Ecca shales were deposited under shallow-water, almost continental, conditions, but the Upper Ecca shales were deposited in deep water as the basin of sedimentation moved northwards during upper Ecca times.

The shales are all carbonaceous and the dominant clay minerals are illite and kaolinite, illite frequently occurring in excess of kaolinite. Montmorillonite

is normally present in trace amounts and calcite and pyrite are rare. Potash feldspar is rare but plagioclase is normally abundant, the differences in abundances between these two feldspars being a surprising feature of the samples from this borehole. Organic content varies between 4% and 15%. Four samples were selected for the separation of a less than two micron fraction.

Trace element concentrations and some inter-element ratios are listed in Tables 14A. Average concentrations are listed in Tables 23A and 24A and average ratios are listed in Tables 25A and 26A. There are no very marked differences between the average trace element concentrations of the Somkele Borehole samples and the average carbonaceous shale of the Northern Ecca Facies. However, the average concentrations of Ni, V, Cr, Zr and Nb are significantly lower.

At this stage interesting comparisons can be made between the average trace element contents of the shales from the A Series Boreholes, the GB Series Boreholes, the Dannhauser Boreholes and the Somkele Boreholes. These four groups of samples lie approximately along a NW-SE trend line although the Dannhauser Borehole lies a little to the west of this line. As mentioned earlier, the Somkele Borehole is situated within the Natal Trough whereas the other boreholes are located far closer to the ancient highlands in the north-east which must have provided most of the detritus for the sediments in the northern part of the basin of sedimentation. Ryan (1967) concluded that sediments of the Natal Trough were deposited under deep-water continental sea conditions, whereas the sediments towards the north were deposited under quiet water, fluviatile conditions.

Fig. 41A shows that there is a significant change of trace element content of the carbonaceous shales as the Natal Trough is approached. Cu, Co, Ni, V, Cr and Nb concentrations increase. It is possible that the lower organic content of the shales towards the south is responsible for part of the decrease in concentration of these trace elements as most of them have been shown to be frequently associated with the organic content. These associations are discussed further in Section 6. In this case, however, the relative depletions are considered to be due to the deep-water environment of deposition, and perhaps the great distance from the ancient shoreline and source area, although if this is the case it is difficult to envisage a mechanism causing relative depletion of the trace elements. Far greater thicknesses of sediment are developed in the trough than in the near-shore fluviatile environment. It seems logical, therefore, that the bulk of the deep-water sediments must have been derived from the fluviatile near-shore sediments which were in turn derived from the north-eastern highlands source area. As the main mass of sediment is in the trough only partial "stripping" of the trace element content of the sediment during its passage through the fluviatile environment to the deep-water environment could account for the lower trace element content of the deep-water shales in the south. This does not seem likely, and a more plausible explanation for the higher trace element contents of the fluviatile near-shore carbonaceous shales is that the quiet, stagnant, shallow pool conditions prevailing provided suitable conditions for the incorporation of larger amounts of trace elements than occurred in the deep-water environment.

A further possibility which should

be mentioned is the presence of hitherto unsuspected southern highlands acting as a source area. Detritus of lower trace element content than that from the north could act as a diluent in the Natal Trough and thus be responsible for some of the trace elements having slightly low concentrations in the shales from the Somkele Borehole.

One sample, SEc 25, contains 440 ppm Cu and 221 ppm Pb - the highest contents of these two elements in any of the shales analysed. The Zn level of 138 ppm is also unusually high. As the sample contains 26.2 percent Fe (Danchin, 1970) and a high pyrite content was detected by X-ray diffraction, it seems clear that the high abundances of Cu and Pb, and to a lesser extent Zn, are due to their incorporation in the sulphide phase. It is interesting to note that no other trace metals, except perhaps Ga, is associated with this pyrite. The Ga concentration of 33 ppm produces a Ga/Al ratio of 4.17×10^{-4}, whereas the remaining ratios show a very narrow dispersion ranging from 2.08 to 2.79×10^{-4} and average 2.39×10^{-4}. This is the only sample in which Ga appears to be partly associated with the sulphide phase. Surprisingly enough Danchin (1970) determined no normative pyrite in this sample and his 6 percent normative siderite cannot account for the 26.2 percent Fe which is virtually all in the ferrous state. His sulphur determination of 0.74 percent appears grossly in error.

As expected the correlation coefficients for the Somkele Borehole samples reveal a strong association between Cu, Pb and Fe, and to a lesser extent between Ga, Zn and Fe. These correlations have not appeared in the data from the other carbonaceous shales and are perhaps

generated principally by SEc 25. Other associated pairs of elements are Y - Yb, Sc - Y, Sc - Yb, Ni - Co, V - Al, Cr - Al and Nb - Al. Most of these correlations are present in other carbonaceous and non-carbonaceous shales and are discussed in some detail in Section 6. The surprisingly low Ga - Al correlation supports the contention that Ga is partly associated with the sulphide phase in one of the samples, and perhaps in the others where pyrite is present.

5.11.2.6 Boreholes from the Vierfontein and Bothaville Districts, Western Transvaal.

Six carbonaceous shales were collected from the Vierfontein Collieries in the western Transvaal. Kaolinite is the dominant clay mineral with subordinate amounts of illite and montmorillonite also present. Plagioclase and potash feldspar are occasionally present in trace quantities, but no carbonates or sulphides were detected. One sample, Ec 14, was selected for the separation of a less than two micron fraction.

Six samples were obtained from Upper Group shales from Borehole VB 85/65, and four were obtained from the Middle Group shales from Borehole VB 79/65. Both boreholes are located in the Bothaville district of the northern Orange Free State and represent the most westerly extent of the Northern Ecca Facies as it still exists today. The Upper Ecca shales contain kaolinite and montmorillonite and the Middle Ecca kaolinite as the dominant clay minerals. Illite is subordinate in both groups. Both feldspars are abundant throughout and calcite, siderite and pyrite are occasionally present. The presence of abundant montmorillonite in the Upper Ecca shales is extremely interesting and indicates the likelihood of the deposition of massive

amounts of weathered volcanics. The massive outpourings of Stormberg lavas which terminated the Karroo period probably had their origins in the north as early as Upper Ecca times, the weathered detritus finding its way to the western portion of the northern Karroo Basin.

The trace element concentrations and some inter-element ratios in samples from the Bothaville Boreholes are listed in Table 9A and those for the samples from the Vierfontein Colliery are listed in Table 15A. Average concentrations are listed in Table 24A and average ratios in Table 26A.

The part played by montmorillonite in controlling the distribution of the trace elements is difficult to evaluate as it is only present in the samples from one borehole, which has a relatively high organic content, and is absent from the samples from the other borehole which has a relatively low organic content. The montmorillonite-rich, organic-rich samples have distinctly higher concentrations of most trace elements than the montmorillonite-free, organic-poor samples. It is extremely difficult to assess which parameter has played the controlling part.

5.11.2.7 Lower Ecca Shales:

Ten outcrop samples were collected from the Lower Ecca Shales in the Vryheid and Greytown districts of Natal. Illite is the dominant clay mineral and kaolinite and montmorillonite are subordinate. Plagioclase and potash feldspar are occasionally present in trace amounts. One sample, Ec 18, was selected for the separation of a less than two micron fraction.

Trace element concentrations and some inter-element ratios are listed in Table 15A. In general, the data for these samples is similar to those for the Somkele Borehole samples and no significantly different features are observed. The observations made and general conclusions reached regarding those samples apply equally well here.

5.11.3 CENTRAL ECCA FACIES

The sediments of the Central Ecca Facies occupy the central portions of the Karroo Basin, where a minimum thickness of 330 m is reached, and the northern limb of the Karroo Trough where a maximum thickness of 1330 m is reached. Ryan (1967) describes the facies as consisting almost entirely of shales and flagstones, no coal measures being present at all. The sediments originate from three different source areas, but due to their homogeneous lithology Ryan has not been able to subdivide the facies into groups.

Twenty six samples of the Central Ecca Facies, collected from widely spaced localities, were analysed. Seven are from a borehole in the Gibeon district of South West Africa, five are from two boreholes in the Victoria West district, and the remainder are outcrop samples. Illite is the dominant clay mineral with kaolinite, chlorite, and montmorillonite occurring in subordinate quantities. Exceptions are CV 71 and pyritic WEc 5p which are rich in kaolinite. Plagioclase feldspar is present in most samples.

Trace element concentrations and some

inter-element ratios are listed in Table 16A. Average concentrations are included in Table 23A and average ratios in Table 25A and 26A. These samples are depleted in Co, Ni, Cr, Zr and Nb compared to the Northern Ecca Facies.

Correlation coefficients for these samples, tabulated in Table 38A, show groups of associated elements. A correlation between Al - Ga - V - Nb indicates an association with clay minerals, and a correlation between Fe - Zn - Co - Ni indicates an association with ferric hydroxides. The lack of correlations appearing for the remaining elements is taken to indicate that they are incorporated in more than one mineral phase.

5.11.4 SOUTHERN ECCA FACIES

This Facies is confined to the Karroo Trough and reaches a maximum thickness of 3500 m. Ryan considers its boundary with the Central Ecca to be the estimated limit of the Southern Ecca sandstones which wedge out in a northerly direction. On lithologic grounds he has separated the Facies into Upper, Middle and Lower Groups, the last two being deposited under deep fresh-water conditions and the Upper Group being a shallow water fluviatile deposit as indicated by the presence of plant fragments and invertebrate tracks. The rocks in general consist of green and blue shale successions and thick groups of sandstones with thin intercalated shale bands. Six samples have been analysed, one an outcrop sample and the remaining five being obtained from boreholes in the Fraserburg and Laingsburg districts. They are illite-chlorite shales with traces of kaolinite and abundant plagioclase feldspar.

Trace element concentrations and some inter-element ratios for these samples are listed in Table 17A. Average concentrations are included in Table 23A and average ratios in Table 25A and 26A. Correlation coefficients are listed in Table 39A.

Trace element concentrations for these shales are very similar to those for the Central Ecca Facies and the Western Facies. They are depleted in the same elements relative to the Northern Ecca Facies as the Central Ecca Facies. The Central, Southern and Western Ecca Facies are very similar with regard to the trace elements analysed in this work. Danchin (1970) found these three facies indistinguishable with respect to their major element contents and the result of this work emphasize their close similarity.

As so few Southern Ecca Facies samples were analysed the correlation coefficients must be considered as tentative. However, they indicate that most of the trace elements are associated with Fe. These include Cu, Zn, Co, Ni, V, Cr, Sc, Yb and Pb. The established associations between Co - Ni and Al - Ga are very apparent in these samples as well.

5.11.5 WESTERN ECCA FACIES

This Facies occupies the south-western portion of the Karroo Basin and extends eastwards to about Laingsburg and also thins out fairly rapidly in a northerly direction. Ryan has also divided the Western Ecca Facies on lithological grounds into Lower, Middle and Upper Groups. The Lower Group comprises mainly a thick layer of blue-black shales, the Middle Group massive sandstones

and blue-grey shales and the Upper Group shales, siltstones and sandstones. Ryan deduced that the sediments constituting the lower one third of the succession were deposited under relatively deep water conditions while the remaining two thirds were deposited under fluvial-deltaic conditions.

Trace element concentrations and some inter-element ratios are listed in Table 18A. Average concentrations are included in Table 23A and average ratios in Tables 25A and 26A. Correlation coefficients are listed in Table 40A, The similarity of the trace element composition of the samples from this facies to those from the Central and Southern Facies has been mentioned earlier. The dispersion of the average Ga/Al and Ni/Co ratios in the four Karroo facies is small and ranges from 2.25×10^{-4} to 2.47×10^{-4} for Ga/Al, and from 1.92 to 2.38 for Ni/Co. There is a significant difference in the average V/Cr ratio of the four facies. The ratio increases from 0.85 in the Northern Facies to 1.39 and 1.56 in the Western Facies and Central Facies respectively to 2.05 in the Southern Facies. Ryan (1967) concluded that the Southern Ecca Facies sediments were largely derived from highlands located to the south so perhaps the V/Cr ratio reflects a difference in source area composition.

The significance of the correlation coefficients of the Western Ecca Facies is reduced by the paucity of samples. As with Southern and Central Ecca Facies two groups of associated elements appear in the Western Ecca Facies. Al - Ga - Co - Cu - Ni - V - Sc - Nb - Th correlations imply associations with the clay mineral fraction and Fe - Zn - Y - Yb correlations indicate

associations with the Fe hydroxide phase. These correlations are discussed in some detail in Section 6.

5.11.6 BEAUFORT SERIES

Within the main Karroo Basin the Beaufort sediments follow the Ecca Series conformably, making a huge oval extending some 1300 km in length and 500 km in breadth, (Haughton, 1969). The Beaufort sediments outcrop extensively in Southern Africa and are exposed over most of the Great Karroo, Orange Free State, Eastern Province and Western Natal. They are covered only by the Stormberg sediments and lavas in the western Orange Free State, north-eastern Cape and Lesotho. Lithologically the series has been divided into three stages - Lower, Middle and Upper - which have a combined maximum thickness of 4500 m in the southern part of the main basin.

The entire sequence is made up of altering feldspathic sandstones and blue, purple, green and red mudstones and shales. In many areas it is impossible to distinguish the Upper Ecca shales from those of the lower-most Beaufort sediments (Ryan, 1967). Ryan (1967) concluded that shallow-water continental conditions prevailed during the deposition of most of the sediments of the Beaufort Series, an inevitable conclusion because of the abundance of vertebrate fossil remains throughout the series as a whole. The lower beds contain reptiles and these give way to mammal-like reptiles and amphibians higher up in the sequence.

The eleven samples analysed were collected from widely separated localities. The sampling range extended from Coffee Bay in the Transkei in the east, to

Bloemfontein in the north, and Carnarvon in the west. The samples all consisted dominantly of illite and quartz and contained subordinate quantities of kaolinite, montmorillonite and plagioclase feldspar with occasional traces of potash feldspar.

Trace element concentrations and some inter-element ratios are presented in Table 18A. Average concentrations are listed in Table 23A and average ratios are included in Table 25A. Correlation coefficients are tabulated in Table 41A.

Danchin (1970) found a very narrow dispersion in the concentrations of the major elements, and the trace element concentrations of this work, except for Co, display the same characteristic. As these were surface samples ground-water leaching could account for the Co depletion in some of the samples. In general, the trace element concentrations are lower than the average South African argillaceous rock and this is considered to be due to the presence of abundant quartz and plagioclase feldspar acting as a diluent.

The correlation coefficients do not provide any positive information. As Fe and Al have a good correlation most trace metals correlate well with these two major elements providing a difficult case to interpret. Perhaps misleading correlations were generated by the variable amounts of quartz and feldspar.

5.12. SHALES DREDGED FROM THE AGULHAS BANK

Seven submarine shales dredged from the Agulhas Bank were supplied by Mr R. Gentle of the

Department of Marine Geology, University of Cape Town. It was speculated that these off-shore shales might belong to either the Bokkeveld Series or the Malmesbury Formation and it was hoped that the trace element contents might indicate the identity of the shales. Quartz, illite and chlorite were the dominant minerals, and subordinate amounts of plagioclase feldspar and potash feldspar were also present.

Trace element concentrations and some inter-element ratios are presented in Table 19A. Average

Table 17

A comparison of the trace element composition of the Dredged Agulhas Bank shales with Bokkeveld and Malmesbury shales

	Dredged shales	Standard Deviation	Bokkeveld shales	Malmesbury shales
Be	2.9	0.4	2.9	3.2
Ga	18.7	4.5	19.8	18.6
Cu	16.7	3.5	18.7	16.6
Zn	73.9	17.4	75.8	90.4
Co	8.4	2.6	10.5	12.9
Ni	33.1	8.3	36.9	32.6
V	105	33	127	91.6
Cr	112	11.8	106	78.8
Sc	12.6	3.7	15.5	13.3
Y	43.3	7.3	53.0	36.8
Yb	2.2	0.2	2.4	2.2
Zr	210	53	235	201
Nb	15.7	3.5	17.0	11.2
Th	14.9	6.0	16.8	18.0
Pb	20.1	8.7	30.2	22.0
$Ga/Al \times 10^4$	2.13		2.22	2.27
Ni/Co	4.20		3.88	2.44
V/Cr	0.96		1.17	1.14

concentrations are listed in Table 23A and average ratios are included in Table 25A. For convenience average trace element concentrations for the dredged shales, Bokkeveld shales and Malmesbury shales are presented in Table 17. Correlation coefficients for the dredged shales are listed in Table 42A.

On the basis of major element compositions and major element inter-element ratios, Danchin (1970) showed a high degree of probability that the dredged Agulhas Bank shales belonged to the Bokkeveld Series. No such clear-cut conclusion is obvious when the trace element data here is considered as can be seen from Table 17. This is principally due to the Bokkeveld Series and the Malmesbury Formation being remarkably similar in trace element composition. In agreement with the work of Danchin (1970), however, the data is slightly in favour of the dredged shales being of Bokkeveld identity. The averages of two elements (Y and Pb) lie outside one standard deviation from the mean of the dredged Agulhas Bank shales, whereas for the Malmesbury shales three elements (Co, Cr and Nb) lie outside this limit. Furthermore, the Ni/Co ratio is almost half that of the dredged shales, whereas the Bokkeveld shales has an average Ni/Co ratio almost identical to that of the dredged shales.

6. SOME OBSERVATIONS ON THE DISTRIBUTION OF TRACE ELEMENTS IN SOUTH AFRICAN SHALES

6.1 INTRODUCTION

In this section the distribution and behaviour of each individual element analysed in this work is interpreted in terms of the observations made in the previous section. As mentioned before some repetition is inevitable but it was felt essential to discuss each element individually. Much use has been made of correlation coefficients and the remarks on their use in the introduction to the previous section apply equally here.

6.2 BERYLLIUM

Hörmann (1969) states that in igneous rocks Be ranges from less than 1 ppm to 30 ppm but that the vast majority do not exceed 6 ppm. Ultrabasic rocks do not exceed 0.2 ppm Be (Beus, 1956) and intermediate and granitic igneous rocks contain about 2 ppm Be and from 2 ppm to 6 ppm Be respectively. Beus (1956) found Russian basalts and gabbros to contain 0.3 ppm Be. The bulk of the Be is contained in plagioclase feldspar, although the much less abundant minerals muscovite, biotite and hornblende might contain much larger concentrations. Beus (1961) found an average of 4.5 ppm Be in biotite granites and 10 ppm in muscovite and two-mica granites. Only in pegmatites do Be minerals such as beryl form and the Be content of pegmatites is thus very dependent on the beryl content. Be levels then range up to 2000 ppm.

In non-pegmatitic source rocks Be is rapidly released on weathering but because of its ionic potential of 5.7 (Mason, 1966) it is rapidly hydrolysed

and becomes incorporated in the hydrolysate fraction and is also adsorbed onto clay mineral particles. As shown by Merrill et al. (1960) it is transported to the depositional environment mainly in suspension and not in solution. Thus, somewhat like Th, its abundance and distribution in sediments is controlled more by pre-transport mechanisms in the weathering environment than by the environment of deposition.

Be results for all samples are presented in Tables 2A to 21A and the averaged results are shown in Tables 23A and 24A. Hörmann (1969) points out that although igneous rocks and modern sediments have been frequently analysed for Be, modern data for sedimentary rocks are rare. Merrill et al. (1960) found an average of 2.5 ppm Be in pelagic sediments whereas Hirst (1962) found Be concentrations of up to 8.7 ppm in near-shore clay sediments. However, Hirst (1962) considered his Be data to be unreliable as his precision was poor and his accuracy when analysing G-1 and W-1 very poor indeed. Hirst (1962) obtained his Be data by emission spectrography whereas Merrill et al. (1960) used a colourimetric technique. In general the Be results for shales listed by Hörmann (1969) vary between 2 ppm and 4 ppm and this very narrow range of concentrations is strongly verified by this work. Spencer (1966) found the Be content of the shales of a Silurian graptolite band to vary between 1 ppm and 3 ppm and he concluded that all the Be in the shales was detrital in origin. The average Be value for all samples is 3.2 ppm, for non-carbonaceous samples 2.7 ppm and for carbonaceous rocks 3.8 ppm. The non-carbonaceous value is influenced by the average Be concentrations for the Fig Tree and Witwatersrand samples which are 1.4 ppm and 1.2 ppm respectively in values probably inherited from the ultra-

basic nature of the source area. Apart from these two groups of rocks there is very little variation between average Be values for groups and even within groups there is surprisingly little variation. For example, the standard deviation for Be in 38 samples from the Bokkeveld Series (average 2.9 ppm) is only 0.6 ppm. A large part of this variation probably comprises analytical error and variations in water content and amounts of Be-free detrital quartz and feldspar which act as diluents.

The carbonaceous samples of the Northern Ecca Facies appear to be very slightly enriched in Be compared to the non-carbonaceous samples. This can be attributed either to a slight enrichment in the organic fraction or to slightly higher Be contents in the source rocks. The latter seems more likely although Be has been reported by other workers (Zuboric et al., 1964) for example) to concentrate in coal. Be correlation coefficients of this work reveal no relationship with the organic fraction and if a relationship does exist it is masked by the Be present in other phases. That this is possible for these rocks is shown by the plot in Fig. 26A of Be against L.O.I. for the thirteen carbonaceous Borehole GB 47/64 samples. A definite but not strong coherence is revealed here but not in the other boreholes.

An enrichment by a factor of about two is shown by Be in the separated less than two micron clay fractions. This indicates that very little Be is not included in the clay mineral fraction. Although beryl has a similar density to clay minerals it would probably be removed during separation of the less than two micron fraction as due to its extreme hardness, it is unlikely to be reduced to this size by comminution during trans-

port. If beryl were to occur in this size fraction higher Be concentrations would be expected, and if beryl were present at all in any of the shales it is unlikely that such a constant Be value would persist through all the samples. The enrichment trend of Be in the fine fraction also holds for the carbonaceous shales, but as the samples used for clay separation purposes only contained a few percent organic carbon, this enrichment trend does not prove that some Be is not associated with the organic fraction which the Be - LOI relationship in the GB 47/64 Borehole samples suggests. Detrital beryl apparently plays no part in the distribution of Be in the rocks. A single sample, KUI 4, contains 11 ppm Be in the whole rock and 18 ppm Be in the less than two micron clay fraction. This is an exceptional amount of Be to be incorporated in the clay fraction and provides further evidence of the absence of detrital beryl or other Be-containing detrital minerals.

The correlation coefficients of Be against the other elements analysed reveals no relationship which persists through all the groups of rocks analysed. Even within the Northern Ecca Facies, the Somkele Borehole, GB Series boreholes and A Series boreholes show very different patterns of correlation coefficients. This fact and the fact that Be shows such a remarkable uniformity of concentration is interpreted as indicating that the incorporation of Be in clay minerals is controlled by its slow rate of supply and is independent of mechanisms involving the rate of uptake of other elements. It appears that Be does not compete with other elements to occupy sites as such competition would inevitably result in a greater variation than is actually observed of Be concentrations in such a varied group of shales.

Ginzberg (1964) postulated that Be can proxy for Si in silicate minerals as they have very similar ionic sizes although the charge difference of two and the low crustal abundance of Be would only make slight substitution possible. However, bonding characteristics are very similar. Consequently the relationship between Be and SiO_2 was critically examined in the whole rocks and in the separated clay fractions to determine if any Be substitution for Si in tetrahedral sites had taken place in a regular manner. Sandell (1952) found very low concentrations of Be in the silicate minerals of igneous rocks. A negative correlation between Be and SiO_2 was observed for South African shales and this can only be interpreted to mean that no detectable substitution of Be for Si has taken place and that all Be is associated with the clay mineral fraction, probably in sorbed positions. The negative correlation is generated by varying amounts of quartz acting as a diluent. A plot of Be against SiO_2 in the Bokkeveld shales is shown in Fig. 27A to illustrate the negative correlation observed between Be and Si. SiO_2 data used is from Danchin (1970) and differs from Si concentrations by a constant factor so that the same trends are observed whether Si or SiO_2 data are used.

The frequency distribution of Be concentrations in all the rocks analysed in this work are shown in Fig. 9A. It is notable that apart from the peak due to the Fig Tree samples the frequency distribution is symmetrical and approaches normality as approximately two-thirds of the samples lie within one standard deviation of the mean. Ahrens (1954a) found that most trace elements in igneous rocks followed a lognormal distribution. Although Be was not included it is likely

that it follows a similar pattern because of its enrichment in late stage granites. The change of the frequency distribution pattern in shales implies a tendency towards thorough mixing and homogenisation in the sedimentary *environment.*

6.3 GALLIUM

The geochemistry of gallium in the igneous and sedimentary environment has long been recognized to be closely controlled by its ability to replace aluminium in all aluminium containing minerals. The anion affinity index between the two elements is 1.08 (Ahrens, 1953). The similarity of the Ga/Al ratios of granitic igneous rocks (2.35×10^{-4}) and pelagic sediments (2.4×10^{-4}) led El Wakeel and Riley (1961) and Burton et al. (1959) to conclude that the association between these two elements is so close that there is virtually no differentiation between them during weathering, transport and depositional processes. Al data in this work is used by kind permission of Danchin (1970).

Ga concentrations and Ga/Al ratios for all samples are presented in Tables 2A to 21A. Average Ga concentrations are shown in Tables 23A and 24A, and average Ga/Al ratios are set out in Tables 25A and 26A. Average Ga values range from 13.7 ppm in the Fig Tree Series to 25.5 in the Cango Formation. The average value of 20.4 ppm is very close to the average shale value of 19 ppm given by Wedepohl (1971). The Ga/Al ratios show a far narrower spread of values than the Ga concentrations and this emphasizes the extremely close coherence which exists between these two elements. Average Ga/Al ratios vary from 2.10×10^{-4} in the Fig Tree Series to 2.69×10^{-4} in the Beaufort Series.

In general, however, the ratios cluster around 2.31×10^{-4} which is the average for all South African argillaceous rocks. This narrow range of values for over 300 analyses indicates the high quality of these data which is essential if significant, but very small, differences are to be detected in the ratio. Shaw (1957) gives a range of 1.51 - 3.54×10^{-4} for 18 pelitic rocks and Nicholls and Loring (1962) quoted a range of 1.00 - 3.40×10^{-4} in the Ga/Al ratio for their Bersham carboniferous sediments. El Wakeel and Riley (1961) found an average of 2.4×10^{-4} for the Ga/Al ratio for the pelagic sediments they analysed. Hirst (1962) found an average of 2.60×10^{-4} in greenish muds, bluish clays and delta clay from the Gulf of Paria. Although these ratios are very similar, they are not identical and the differences might either be real and correlated with the geochemistry or they might be due to a slight systematic bias introduced by the method of analysis. As slight differences in the ratio are assumed to be significant only variations in data of this work will be interpreted.

The spread in Ga values of this work is due primarily to the variable amounts of quartz which acts as a diluent. A further possible contribution to the variation might be provided by the different species of clay minerals incorporating Ga in different amounts relative to Al. On this point there is some diversity of opinion. McLaughlin (1959) determined only a little Ga to be proxying for Al in Kaolinite and the work of Nicholls and Loring (1962) corroborated this and indicated that the bulk of the Ga was associated with illite. Tourtelot (1964) found that relatively large amounts of kaolinite in carbonaceous non-marine shales had no effect on the Ga content of the samples, but he did not examine the Ga/Al ratio. Hirst (1962), however, was satisfied

that a considerable proportion of Ga replaces Al in kaolinite.

Fig 28A is a plot of Ga versus Al for chlorite, illite and kaolinite rich South African shales and it clearly demonstrates the strong coherence between these two elements and also the fact that slight differences in the proxying capacity of Ga in the clay minerals do exist in the argillaceous sedimentary rocks of South Africa. The ratios for the chlorite-rich Fig Tree rocks tend to straddle the 2.1 line and the illite rich rocks from different groups tend to straddle the 2.3 line but they vary between 2.1 and 2.5. The kaolinite-rich shales show the largest variation and also tend to cluster along the 2.5 line. The average Northern Ecca Facies shale contains 9.8% Al (Danchin, 1970) and 22.8 ppm Ga. If all the Ga is assumed to be proxying for Al then the proportion of replacement is 2.3 ppm Ga per percent Al. Now a change of 0.2×10^{-4} in the Ga/Al ratio changes the proportion of replacement by 0.2 ppm Ga per percent Al or by 2 ppm Ga in a shale containing 10 percent Al. These results show that, in agreement with Hirst (1962) but contrary to the findings of McLaughlin (1959) and Nicholls and Loring (1962), Ga is virtually equally at home in any of the three clay types dealt with but does show a slight but distinct preference for kaolinite and illite over chlorite but no distinct difference between kaolinite and illite.

A few of the kaolinite-rich carbonaceous Northern Ecca Facies shales show abnormally high Ga contents and Ga/Al ratios. This excess Ga is interpreted as being associated with the organic fraction, although calculation of excess Ga using a ratio of 2.32 (i.e. Ga

presumably not bound in the clay mineral structure) revealed no systematic relationship with the amount of organic matter. However, Nicholls and Loring (1962) found a correlation between acid soluble Ga and organic carbon.

A very interesting feature is revealed by the Ga/Al ratios of the separated less than two micron fractions and this is best illustrated by comparing the average change in ratios for specific groups of rocks. For the Bokkeveld samples the whole rock/clay fraction ratio is 1.02 for the Ga/Al ratios whereas for the Northern Ecca Facies a figure of 1.23 is obtained. The former is not significant showing that Ga is not preferentially associated with any size fraction within these illite-chlorite rocks, but the latter figure is very significant and difficult to interpret. If Ga was easily incorporated into the kaolinite or organic fraction by some adsorption, ion exchange or complex formation mechanism, then the Ga/Al ratio for these kaolinite-rich samples would be expected to be very different from the illite-chlorite shale ratios which is not the case. This implies that although another mechanism is operative to cause a slight change in ratio this mechanism is not a dominant process. Furthermore the preferential incorporation of Ga in the fine fraction would produce a decrease in the whole rock/clay fraction ratio not an increase which is the observed result. The most likely explanation is for Al to have been preferentially taken up by the very fine kaolinite fraction by adsorption or ion exchange, possibly after first having been fixed by the organic matter which would explain why illite and chlorite have not participated in such a mechanism. As this fraction forms a small proportion of the total rock it has not

materially affected the Ga/Al ratio of the whole rock. It is difficult to visualise how Ga could be preferentially lost in the clay fraction to explain the decrease in the Ga/Al ratio. Hirst (1962) considered only up to 4.5 percent of the total Ga content of the Gulf of Paria sediments to be occupying exchange positions.

The foregoing discussion shows that it is likely that Ga does take part in adsorption and exchange processes in the depositional environment although Spencer (1966) considered all Ga to be detrital in origin. The Ga/Al concentrations drops from 0.30 ppm in fresh water to 0.001 ppm in sea-water (Wedepohl, 1971) a removal factor of 99.7 percent. Residence times in the ocean are 1400 years for Ga and 100 for Al (Goldberg, 1965). This data implies a separation of Ga and Al in the ocean analagous to U and Th which is probably partly real as the solubility product of hydrolysed Al hydroxide is exceeded whereas that for Ga is not thus accounting for the increase in Ga/Al ratio of sea-water compared to source rocks. However, some Ga must be scavenged by Al by co-precipitation during the formation of hydrolysis products. The higher Ga content of sea-water is also partly attributable to preferential solution during weathering, causing a drop in the Ga/Al ratio of residual deposits such as bauxites (Butler, 1953). It must be emphasized that although gallium might be extracted from overlying water by clay particles or by organic material and is definitely scavenged by precipitating Al hydroxide, it is considered that the bulk of Ga is removed from a source area still bound up in a clay structure and is transported and deposited in a depositional environment without participating in any chemical reactions or physical mechanisms.

The correlation coefficients of Ga with other elements demonstrate the close coherence of Ga and Al but no other persistent correlations emerge. However, a high degree of correlation is often shown with Cu, Ni, Zn, V, Cr, Sc and Nb, elements which are also normally associated with the clay mineral fraction.

The frequency distribution of Ga in all South African shales is shown in Fig. 10A. The distribution is asymmetrical and, unlike those for most major and trace elements, is negatively skewed. Of the major elements only Si and K commonly show negatively skewed distributions (Ahrens, 1963b). Al is slightly positively skewed in Japanese granites (Ahrens, 1963) and the distribution of Ga might have been expected to imitate that of Al because of the close coherence between these two elements. Perhaps the negative skewness of the Ga frequency distribution demonstrates the tight control Al exerts over Ga in that the frequency of very high Ga concentrations is very limited.

6.4 COPPER, ZINC AND LEAD

In the igneous environment these three elements are normally associated with sulphides as they have strong chalcophilic tendencies, although they have been shown to proxy to a very limited extent for some major elements in normal silicate minerals. For instance, some Pb is known to proxy for K in feldspars (Ginzberg, 1964). Under conditions of normal igneous differentiation none of these three elements form their own silicate minerals. Sulphides are readily oxidised and the metal contents leached when brought into contact with the oxygenated surface waters of the earth's crust.. Cu, Zn and

Pb are readily soluble and removed in solution, to eventually be added to the contents of the sea, except when brought into contact with carbonate ions when they are readily precipitated as carbonates. Goldberg (1965) gives the solubility products of Cu, Zn and Pb as 2.5×10^{-10}, 2.0×10^{-10} and 1.5×10^{-13} respectively and the theoretical solubility of these carbonates as 5.7 ppm, 4.6 ppm and 0.01 ppm respectively. The sulphides of Cu, Zn and Pb are also very insoluble and consequently they are precipitated from very reducing solutions in the presence of generated hydrogen sulphide.

Cu, Zn and Pb are incorporated in sediments in many ways but, unlike some of the elements previously discussed, they are not considered to occur in detrital heavy minerals to any great extent nor can their abundances in sediments be attributed to their occupation of structural positions in the clay minerals. As pointed out by Krauskopf (1956) and emphasized by Goldberg (1965) a comparison of the calculated concentrations of these metals at saturation point with the observed concentrations in sea-water shows that these elements are severely depleted in sea-water beyond any possibility of error in the solubility product, indicating that a mechanism or, more likely, mechanisms are operative which are very effectively removing these elements from sea-water and incorporating them in the underlying sediment.

Cu, Zn and Pb are effectively scavenged from sea-water by manganese hydroxides which grow as nodules on the sea-floor. They need not remain like that, however, for with burial during slow accumulation of sediment a zone of reduction moves upwards as demonstrated by Bonatti et al. (1971) in the east Pacific. Upon re-

duction the metals are solubilised and Mn and a few other metals tend to migrate upwards in interstitial solutions. Cu, Pb and Zn, however, are relatively immobile and are precipitated with Fe in sulphides or are available for adsorption on clay minerals and organic matter or can be precipitated as organo-metallic complexes, the organic compounds being derived from decomposing organic remains. Mitchell (1968) noted the incorporation of Cu, Pb and Zn in sedimentary pyrite. Goldberg and Arrhenius (1958) found the stability of an organo-metallic complex to be related to the basicity of the metal and found the order of stability to be Pd > Cu > Ni > Pb > Co > Zn > Cd. Numerous metal-binding organic constituents have been identified in soils, sediments and natural waters and other orders of stability have been postulated for various chemical species. Ahrens (1966) has shown that for many metals and organic compounds a measure of the relative stability of the metal-organic complex is given by the ionisation potential of the metal. The ionisation potential is a function of cationic size, cationic charge and bond type. The stabilities of complexes with the transition metals may also be influenced by ligand field effects. Many planktonic species concentrate metals including Cu, Pb and Zn, to a remarkable degree (Nicholls et al., 1959) and when abundant, as in areas of ocean upwelling, their dead remains provide a further mechanism for the removal of these metals from the sea-water and their concentration in the sediment where they are available for redistribution.

A modern analogue is the enrichment of Cu, Pb, Zn and Ni in the organic-rich sediments off Walvis Bay, South West Africa (Calvert and Price, 1970). Under oxidising conditions the adsorption of Cu, Pb and Zn in appreciable amounts follows the formation of ferric

hydroxide which frequently occurs as coatings on mineral grains. The reduction of these oxide coatings, for example by carbonaceous material in a basin of deposition, can solubilise considerable quantities of Pb, Cu and Zn which are then available for incorporation in the sediment in some other manner. Wedepohl (1967) concluded that the sources of Cu, Pb and Zn in the Kupferschiefer were older red sandstones and greywackes whose metal contents were mobilised by reduction and later incorporated by organic sediments.

Pb, Cu and Zn contents of the samples analysed in this work are presented in Tables 2A to 21A and averages for various groups of rocks are laid out in

Table 18

Copper, zinc and lead contents of various groups of rocks

		Cu	Zn	Pb
Basalt average	(1)	100	100	5
Granite average	(1)	10	40	20
Crustal average - continental	(1)	55	70	12.5
Average shale	(2)	45	95	20
Whitbian shales	(3)	41	94	21
British carboniferous shales	(4)	32.8	-	6.1
Bokkeveld shales	(5)	18.7	75.8	30.2
Northern Ecca Facies	(5)	28.2	88.8	33.5
Average South African argillite	(5)	27.7	83.9	28.5

(1) Taylor (1964)
(2) Wedepohl (1971)
(3) Gad et al. (1969)
(4) Nicholls and Loring (1962)
(5) This work

Tables 23A and 24A. Correlation coefficients of these elements against each other, against other elements analysed and against the loss on ignition (LOI) are listed in Tables 28A to 42A. Average Cu contents range from 7.5 ppm in the Kuibis Series to 51 ppm in the Fig Tree Series. Zn shows a much wider spread varying from 5.6 ppm in the Kunjas Series to 114 ppm in the Fig Tree Series. Pb displays a narrower distribution varying from 10.2 ppm in the Fig Tree Series to 33.8 ppm in the Western Ecca Facies. The average South African argillite contains 27.7 ppm Cu, 83.9 ppm Zn and 28.5 ppm Pb respectively. Table 18 shows that in general the Cu contents are distinctly lower and the Pb contents are distinctly higher in South African shales than in the average continental crust and in shales from other parts of the world. The Zn contents, however, are similar.

The correlation coefficients reveal that these three elements display slightly different distribution characteristics within any particular group of rocks and that these characteristics might change from one group of rocks to another. In the non-carbonaceous samples, like the Bokkeveld and Western Ecca Facies shales, Cu displays a very low degree of coherence with the other elements analysed which is interpreted as due to its presence in more than one mineral or phase, or if the bulk of Cu present does occur in one phase, then its concentration is irregular and bears no constant relationship to any other element studied. In general Cu shows a weak correlation with Al, Ga, Co and Ni, suggesting it to be more closely associated to the clay minerals than to any other phase. In the shales of the Witteberg Series and Western Ecca Facies its close correlation with Al indicates its presence to be chiefly within the structure of the

clay minerals, mainly illite, but in the shales of most other sequences it probably occurs as a non-detrital element having taken part in adsorption or cation exchange reactions. The general coherence of Cu with other elements would also be reduced if part of the Cu content were introduced by some organic mechanism and then made available for adsorption or sulphide formation.

The shales of the Somkele borehole of the Northern Ecca Facies are the only group of rocks in this study in which Cu is contained chiefly in a sulphide phase, probably pyrite. Although the sulphide content never exceeds one percent (Danchin, 1970), Cu shows a powerful association with Fe and Pb and a weaker one with Zn indicating the virtual total removal of Cu, Pb and,less complete, Zn from sorption positions on the clay minerals and organic matter and their co-precipitation with Fe during hydrogen sulphide generation by the decomposition of organic matter. That such a strong correlation can exist indicates that the dominant clay mineral in these rocks, kaolinite, contains negligible Cu and Pb, which findings are in agreement with the conclusions reached by Nicholls and Loring (1962).

Cu, Pb and Zn do not show sulphide control in any of the other carbonaceous groups, but Cu and Zn do show a correlation with the organic fraction in the GB Series boreholes, GB 45/64 and GB 47/64 as demonstrated in Figs. 29A and 30A, which are plots of loss on ignition and element concentration against position in the sequence. It is likely that in these samples the distribution of Cu and Zn was controlled by adsorption by organic matter whereas in the A Series borehole samples and in the rest of the carbonaceous shales the distribution of Cu, Pb and Zn was controlled by more than one phase

which tends to nullify the use of correlation coefficients as an interpretative tool.

In the Fig Tree Series shales the good inter-correlations of the group Cu, Zn, Cr, V, Ni and Co indicate the coherence of these elements in at least two phases. The chlorite-rich clay mineral fraction must contain these elements in structural sites in similar proportions from sample to sample and it appears likely that they have been adsorbed to similar degrees by the iron oxides, mainly goethite, present. Neither the chlorite nor the goethite could have played a controlling role as no correlation exists between these elements and Al or Fe. The Witwatersrand shales show analagous results demonstrating the similarity between these two ancient groups of rocks. The high Cu, normal Zn and low Pb contents of these ancient rocks compared to the average South African argillite is interpreted as representing the provenance composition and, as pointed out before, further demonstrates the basic nature of the source rocks. Table 18 shows the average depletion of Cu but enrichment of Zn in granites compared to basalts.

Zinc is an element which appears to have aroused little interest in geochemists and very few data have been published. Tourtelot (1964) found Zn to be more abundant in marine than in fresh-water shales and more abundant in off-shore than near-shore samples. Brooks et al. (1968) found Zn to decrease with depth in the interstitial water of marine sediments and attributed the enrichment at the surface of the sediment to biological concentration and release. Tourtelot (1964) also found a correlation between Zn content and the amounts of organic material present. In the GB Series borehole samples Zn

concentrations do appear to be related to the organic content as is shown in Figs. 29A and 30A, but in general this is definitely not the case and the distribution of Zn does not appear to be normally controlled by adsorption to decayed plant material or by the formation of organic complexes involving such material. The frequent correlation of Zn with Fe in South African argillaceous rocks suggests a close coherence with this element, perhaps scavenged onto oxides, included in sulphides and proxying for Fe in clay mineral lattices. The strong enrichment of Zn in the separated clay fractions indicates that the bulk of Zn is detrital and is locked away in clay mineral structures.

Nicholls and Loring (1962) considered Pb to be strictly detrital although sorption occasionally occurred. El Wakeel and Riley, however, considered Pb to be located chiefly in ferromanganese minerals with the remainder incorporated in the colloidal fraction by ion exchange or adsorption mechanisms, i.e. to be of authigenic origin. There is thus considerable diversity of opinion on the distribution of Pb in sediments.

The results of this work show Pb concentrations to cover a relatively narrow range with no significant difference between marine and non-marine rocks. None of the groups of rocks analysed contain more than 0.10 percent MnO (Danchin, 1970) removing the possibility of Pb being largely associated with a Mn phase. Apart from its association with sulphide in the Somkele borehole samples Pb reveals no constant relationship with other elements indicating the likelihood of it being contained in more than one phase. The separated clay fraction data is perhaps a little more informative. A decrease in Pb in the separated clays

from the carbonaceous shales indicates that although some Pb is associated with the clay mineral fraction most of it has been removed in the detrital heavy mineral fraction. This situation does not exist in the Bokkeveld shales, however. Here some show strong Pb enrichment in the less than two micron clay fraction whereas others show that the bulk of the Pb present is in the heavy mineral fraction. Clearly the distribution of Pb is a complex one which makes it all the more surprising that its average abundances are so uniform. Perhaps the uniformity is due to its being initially introduced into a sediment chiefly by a single mechanism, adsorption onto ferromanganese minerals, and with the solution of these minerals at depth in the sediment (and upward migration of Fe and Mn) Pb is made available for re-incorporation into the sediment by a variety of mechanisms, the dominant ones being controlled by the overall composition of the sediment at that stage. Chow and Patterson (1962) determined two thirds of the Pb of Pleistocene pelagic sediments to be of authigenic origin, the remainder being transported to the depositional area in detrital clays and heavy minerals. It is also possible that its partial incorporation in diagenetic pyrite could explain its removal during the less than two micron clay fraction separation process.

The frequency distributions of Cu, Zn and Pb in all the samples analysed in this work are plotted as histograms in Figs. 11A, 12A and 25A respectively. All three elements display asymmetrical frequency distributions. Like Ga, Zn and Pb distributions appear to be slightly negatively skewed and this emphasizes that statistical "laws" explaining the distribution of elements of silicate materials must differ for igneous and sedi-

mentary rocks. The distribution of Cu is a complex asymmetrical one and cannot be described as being positively or negatively skewed. High concentrations are less frequent than low concentrations implying negative skewness but there is a far greater range of high than of low concentrations implying positive skewness.

6.5 COBALT AND NICKEL

As these two elements display many similar characteristics and tend to exhibit a close degree of coherence they are discussed together for convenience. Although both elements can form their own minerals, their geochemistry in igneous rocks is governed by their similarity to the major elements iron and magnesium. Their proxying for these elements is so effective that virtually all cobalt and nickel is removed during the early stages of magmatic differentiation while the sulphides and dark minerals are being formed and consequently their concentrations in granites are extremely low.

The ferromagnesian minerals are rapidly broken down by surface chemical weathering and Ni and Co tend to be released and in solution behave as soluble cations. Under normal weathering conditions Ni is not oxidised to the trivalent form but under powerful oxidising conditions and in alkaline solution Co is oxidised to the trivalent form and because of its ionic potential is rapidly hydrolysed and precipitated into the hydrolysate fraction. Thus stainierite and cobaltian wad can remain in residual deposits of intensive weathering but low erosion, and in this way Ni and Co can separate in the weathering environment. However, divalent Ni is precipitated from solution as garnierite, hydrated Ni silicate of low solubility.

It forms initially as a gel. Co appears to be leached preferentially over Ni during the weathering cycle and Butler (1953) found the Co/Ni ratio to decrease in a weathering profile from rock to residual clay. Ni and Co are incorporated in clay minerals produced by weathering, as is shown by the separated clays of the Fig Tree Series, and they are also efficiently scavenged during the hydrolysis of ferric iron.

El Wakeel and Riley (1961) and Goldberg and Arrhenius (1958) point out that Ni and Co are strongly concentrated in marine sediments relative to igneous rocks and in pelagic sediments relative to near-shore sediments. Wedepohl (1971a) suggests that these high concentrations are derived from submarine volcanic degassing products and points out that they are known to concentrate in sediments slowly accumulating in regions of active volcanism. On the other hand Turekian (1968) found the continental supply of Co in rivers and streams to adequately account for the quantity of Co incorporated in marine sediments. However, it is clear that Co and Ni enter a depositional environment in solution and structurally bound in clay minerals, and that considerable amounts of these elements are later incorporated in the sediment by sorption processes. Hirst (1962) found an average of 31.5 percent of the total Co content to be non-detrital but only an average of 15.6 percent of the total Ni content to be non-detrital and this emphasizes the fractionation of these elements during weathering, transport and deposition. Undoubtedly some of the Ni content of sediments must be derived from the infall of Ni/Fe meteorites. The proportion of Ni incorporated in sediments must be strongly dependent on the rate of sedimentation. The slower the rate the greater will be the importance of meteoritic infall but

as yet there is no quantitative data relating to this subject.

Co and Ni concentrations and Ni/Co ratios for the samples analysed are given in Tables 2A to 21A, averages for groups of rocks are in Tables 23A and 24A, and averages for Ni/Co ratios are in Tables 25A and 26A. Correlation coefficients of Co and Ni for each other and against other elements are listed in Tables 28A to 42A. Average Co concentrations range from 2.4 ppm in the Kuibis Series to 18.3 ppm in the Schwarzrand Series but averaging 15.9 ppm in all the South African argillaceous rocks analysed. The Fig Tree and Witwatersrand samples average 38.4 ppm and 30.5 ppm Co respectively, these high concentrations arising from the availability of Co in the weathered, Co-rich basic source rocks and its ability to proxy for Mg and Fe in chlorite, the chief weathering product of the ferromagnesian minerals. The same argument applies to Ni which is tremendously enriched in the Fig Tree (502 ppm Ni) and Witwatersrand (257 ppm Ni) shales. Normal Ni averages range from 6.0 ppm in the Kunjas Series to 39.7 ppm in the Northern Ecca Facies with an average of 34.4 ppm Ni in all the rocks analysed excluding the Fig Tree and Witwatersrand sediments. Table 19 contains Ni and Co concentrations and Ni/Co ratios for several groups of rocks and includes a crustal average and an average shale. The data of Tourtelot (1964) is shown but not Weber and Middleton (1961), Hirst (1962), Goldberg and Arrhenius (1958) and El Wakeel and Riley (1961). The point illustrated by this table is that apart from Tourtelot's non-marine shales, the South African argillaceous rocks are distinctly lower in Ni and slightly lower in Co than average crustal material and the average shale of Wedepohl (1971).

Table 19

Ni and Co concentrations in ppm and Ni/Co ratios of different argillaceous rock groups

		Ni	Co	Ni/Co
Crustal average	(1)	75	25	3.00
Basalt average	(1)	150	48	3.10
Granite average	(1)	1	0.5	2.00
Non-marine, non-carbonaceous shales	(2)	32	12	2.67
Non-marine carbonaceous shales	(2)	19	10	1.90
Marine near-shore shales	(2)	32	11	2.91
Marine off-shore shales	(2)	53	15	3.53
Devonian pelites	(3)	64	18	3.56
Carboniferous shales	(4)	64	33	1.96
Marine Bokkeveld shales	(5)	36.9	10.5	3.88
Non-marine Northern Ecca Facies shales	(5)	39.7	16.1	2.27
Average South African argillite	(5)	34.4	15.9	2.55
Average shale	(6)	68	19	3.58
Average shale	(7)	-	19	-

(1) Taylor (1964)
(2) Tourtelot (1964)
(3) Shaw (1954)
(4) Nicholls and Loring (1962)
(5) This work
(6) Wedepohl (1971)
(7) Carr and Turekian (1961)

In the South African shales the average Ni/Co ratio varies from 1.92 in the Western Ecca Facies shales to 3.88 in the Bokkeveld Series shales. The average ratio for all the South African argillaceous rocks analysed is 2.55. A glance at Table 19 shows that although the Ni and Co contents are different there is a distinct grouping of the Ni/Co ratios of about 3.50 for

the various marine rocks and about 2.20 for non-marine rocks. The possible use of the Ni/Co ratio as an indicator of depositional environment is discussed later.

In general the correlation between Co and Ni is extremely high as is readily seen in Tables 28A to 42A. In carbonaceous samples the coefficient ranges from 0.57 in the Witteberg Series to 0.98 in the Fish River Series. It is considered likely that some Co has been lost from some Bokkeveld, Western Ecca, Beaufort and Witteberg surface samples and but for this the Co - Ni correlations in these sequences would have been even higher. Chave and Mackenzie (1961) found Co and Ni to be correlated to some extent in Pacific pelagic clays but Cronan (1969/1970) only recorded a coefficient of 0.318 in Indian and Pacific Ocean pelagic clays. Part of the reason for the reduced correlation of these two elements in pelagic clays compared to lithified shales might be explained by the work of Bonatti et al. (1971) who point out that much post-depositional redistribution of these elements takes place in these pelagic sediments owing to the presence of a reducing layer below the surface oxidising layer. Brooks et al. (1968) also found a decrease in redox potential with depth in their cores and their trace element analyses of interstitial water for core T II show a marked increase with depth of the Ni/Co ratio from 3.75 to 23.0. The dependence of the Ni/Co ratio on Eh in interstitial water is well illustrated in Fig. 31A, the data being adapted from Core T II of Brooks et al. (1968). The pH was relatively constant and ranged between 7.4 and 8.0. The dependence of the Ni/Co ratio on Eh is extremely difficult to interpret. The Eh at the surface of the sediment is too low for oxidation of divalent Co to have taken place even at the alkaline pH

of sea-water. Thus Co is not being released into interstitial solution by reduction at depth, and in any case this would have decreased the Ni/Co ratio at depth not increased it which is the observed result. The probable explanation is that Co and Ni are released by reduction of ferric hydroxides and although both elements gradually migrate towards the surface of the sediment Ni is preferentially adsorbed onto clay mineral and unreduced ferric hydroxide surfaces causing the Ni/Co ratio to decrease as the sediment surface is approached. Thus there is an active mechanism tending to partition Co and Ni in pelagic sediments and this explains their poor correlation in these sediments. The upward migration of Co and Ni into the surface sediment also explains the marked enrichment of Co and Ni in pelagic sediments as pointed out by Bonatti et al.(1971). The high correlation obtained in shales results from the process of redistribution of these elements being complete by the time advanced dehydration and lithification of the sediments have taken place.

In the carbonaceous samples of the Northern Ecca Series both Ni and Co show no correlation with loss on ignition indicating that introduction into the sediment via coaly plant material has not been a controlling factor in the distribution of these two elements in these rocks.. However, the concentrations of Ni and Co in carbonaceous rocks is not particularly low so the presence of a small amount of these elements in the organic fraction cannot be discounted. This is an agreement with the work of Le Riche (1959) but Nicholls and Loring (1962) found an overall sympathetic relationship between the Co and Ni contents and the organic fraction

suggesting an incorporation process related to the presence of organic matter.

There is no evidence to suggest that an appreciable amount of the Ni and Co content of the carbonaceous samples is associated with sulphides.

Ni and Co concentrations and Ni/Co ratios are higher in the Bokkeveld separated clay fractions than in the whole rock samples indicating that both elements are preferentially incorporated in the finest clay fraction of these marine samples and that Ni is slightly preferred to Co. No such trends are obvious in the separated clay fractions of the carbonaceous Northern Ecca Facies samples, factors consistent with some Ni and Co being in the organic fraction.

Frequency distribution diagrams are displayed for Co in Fig. 13A and for Ni in Figs. 14A and 15A. Co shows a strong positively skewed distribution whereas Ni, excluding the Fig Tree and Witwatersrand sediments, shows a symmetrical distribution which approaches normality. The difference in distribution between these two elements is interesting as they are normally closely associated in the sedimentary environment and similar frequency distributions might have been expected. Fig. 15A demonstrates the difference in Ni content between the Fig Tree sediments and the rest of the South African argillaceous sediments.

6.6 VANADIUM AND CHROMIUM

In the igneous environment V and Cr both tend to proxy for ferric iron due to similar ionic size and bonding properties. Cr is also precipitated as chromite but V does not normally form its own silicate or oxide minerals. As these two elements also show a close degree of coherence in the sedimentary environment they are discussed together here for convenience. Ultrabasic and basic rocks, therefore, contain much Cr and V in the dark minerals whereas granites contain much less V and virtually no Cr.

In the weathering environment Cr is concentrated in chromite and ferromagnesian minerals in the heavy mineral detrital fraction and Frölich (1960) and Shiraki (1966) point out that it is also concentrated in the clay mineral fraction, particularly in illite. Nicholls and Loring (1962) found virtually no acid soluble Cr, but Tourtelot (1964) considered a third to more than half the total Cr content to be acquired by the clay minerals during transport and deposition in off-shore environments. Hirst (1962) and Goldberg and Arrhenius (1958) found the contribution of non-detrital Cr and V to be very low. Curtis (1969) could find no alternative to explain the occurrence of Cr and V but that they arrived at the site of deposition firmly bound in detrital clay lattices and that the initial concentrations were insignificantly augmented by sorption from solution. He suggested that as Cr^{3+} and V^{3+} they proxied for Al^{3+} and Sr^{2+} present in interlayer K^{+} sites. Most workers have found V to be fairly evenly distributed in the various size fractions of sediments indicating that it occurs in

detrital heavy minerals and in the various clay minerals where most of it is sited in lattice positions having been incorporated during weathering of the original source rocks.

V and Cr concentrations and V/Cr ratios of the shales analysed in this work are presented in Tables 2A to 21A and average contents of these two elements in various groups of rocks are given in Tables 23A and 24A. Average V/Cr ratios are included in Tables 25A and 26A and the correlation coefficients of these two elements against each other and the other elements analysed are listed in Tables 28A to 42A.

Table 20

V and Cr contents and V/Cr ratios of various groups of rocks.

		V	Cr	V/Cr
Granite average	(1)	20	4	5.00
Basalt average	(1)	250	200	1.25
Crustal average (continental)	(1)	135	100	1.35
Shale average	(2)	130	90	1.45
Japanese shales	(3)		46	
Fig Tree Shales	(4)	115	883	0.13
Bokkeveld shales	(4)	127	106	1.17
Northern Ecca Facies shales	(4)	98.7	118	0.85
Carbonaceous S.A. argillite	(4)	98.7	118	0.85
Non-carbonaceous S.A. argillite	(4)	106	82.7*	1.28*
Average South African argillite	(4)	103	99.2*	1.01*

*Excluding Fig Tree and Witwatersrand Cr results

(1) Taylor (1964)
(2) Wedepohl (1971)
(3) Shiraki (1966)
(4) This work

Average V contents in the samples analysed range from 71.2 ppm in the Fish River Series to 127 ppm in the Bokkeveld Series while the average South African shale contains 103 ppm V. Average Cr contents in the samples analysed vary from 53.3 ppm in the Southern Ecca Facies to 118 ppm in the Northern Ecca Facies while the average for the shales analysed, excluding the Fig Tree and Witwatersrand shales, is 99.2 ppm. Averages for the last two shales mentioned are 883 ppm and 847 ppm respectively and these remarkably high results support the supposition of Shiraki (1966) that the Cr contents of shales are controlled by the composition of the source.rocks.

A glance at Table 20 shows that the average V content of South African shales are significantly lower whereas the Cr contents are approximately the same as the average continental crust and the average shale of Wedepohl (1971).

The relatively high concentrations of V in the marine Bokkeveld shales suggests a significant incorporation of V by the sediment from the overlying sea-water, a conclusion in accord with the results of Nicholls and Loring (1962) who found up to 10 percent of the V content of their carboniferous sediments to be acid-soluble. In the separated less than two micron fractions of four Bokkeveld shales, V is enriched over the whole rock by a factor of 1.87 whereas Cr is only enriched by an average factor of 1.48. A considerable amount of this enrichment is undoubtedly due to the removal of detrital quartz and feldspar and if this is allowed for it is clear that V has been concentrated relative to Cr in the finest clay fraction indicating that V has participated in sorption or exchange processes but Cr has not. It is possible that a significant proportion of the Cr is included in detrital heavy minerals.

Excluding the Witwatersrand and Fig Tree shales, the average V/Cr ratios range from 0.85 in the Northern Ecca Facies to 2.05 in the Southern Ecca Facies. The average ratio for all the shales analysed is 1.01. The Bokkeveld average V/Cr ratio of 1.17 indicates a relative increase of V or decrease of Cr in these rocks compared to the carbonaceous Northern Ecca Facies shales, as mentioned earlier.

V and Cr show different distribution patterns in the GB and A Series boreholes. In the GB series borehole samples the correlation coefficients show them to be associated with Al and loss on ignition, implying that they are incorporated in both the clay fraction and the organic fraction in rather fixed amounts. This is illustrated in Figs. 29A and 30A which show the variation with depth in two GB boreholes of V and Cr concentrations. These correlations do not hold for the A series boreholes, but it must be noted that the upper half of the boreholes contain considerably more V and Cr than the lower half. This could be interpreted as being inherited from the source rocks, the last sediments to be deposited being derived partly from basic source rocks only exposed as the long cycle of weathering and erosion, which supplied the vast amounts of Karroo sediments, had removed great thicknesses of overlying rocks. However, it is more probable that in these samples V and Cr are associated with the organic fraction in some way. In Borehole A 78, for example, in which the loss on ignition can be as high as 39.9 percent, V concentrations range as high as 308 ppm and Cr 418 ppm. Owing to the erratic nature of the association however, it is not apparent from the correlation coefficients. V and Cr are unlikely

to be concentrated in sulphides as the levels of Cu, Zn and Pb are not unusually high. They are not associated with iron hydroxides as they show negative correlations with iron besides which Danchin (1970) found the sulphide content of these samples to be very low. There is the real possibility that they are concentrated in detrital ilmenite, and a plot of V and Cr against the TiO_2 data of Danchin (1970) does show a distinct correlation as can be seen in Fig. 32A. This is also the case for the Bokkeveld shales as is shown for Cr in Fig. 33A. However, the separated clay fractions of the Bokkeveld shales show an increase in TiO_2 over the whole samples which could be interpreted as showing that detrital ilmenite is not present but that V, Cr and Ti are closely associated probably in the chlorite structures. The separated clay fractions of the GB borehole samples also show that ilmenite is unlikely to have been present in the whole rock, leading to the conclusion that not only Cr and V but also Ti is associated with the organic fraction.

The correlation of V and Cr with the organic fraction of the GB series boreholes is shown in Fig. 34A. Cronan (1969/1970) has reported the strong correlation between V, Cr and Ti in Pacific and Indian Ocean pelagic sediments but merely concludes that the correlation is due to the presence of all three elements in the detrital phases of the sediment. Nicholls and Loring (1962) found about 6 ppm V per one percent organic carbon to be adsorbed on the organic fraction, but they could find no evidence of Cr adsorption. The unexpectedly high concentrations of Ti in separated clay fractions puzzled Porrenga (1967) who stated that "Although the way in which titanium occurs in the clay fraction is unknown, it follows from our own and from literature data that Ti

must be considered as a detrital element, closely associated with the clay fraction". Goldberg (1954) suggested that Ti is present as anatase (TiO_2) or TiO_2 hydrate deposited with the clay mineral flakes. If a hydrated form of ilmenite was closely associated with the clay fraction in this way it could well contain the bulk of Cr and V camouflaged in its structure, which, being acid insoluble, could lead to the mistaken conclusion that these elements were largely structurally bound in the clay minerals.

The carbonaceous samples analysed in this work are kaolinite-rich and virtually monomineralic with respect to their clay mineralogy. It seems unlikely that much Ti, Cr or V could be structurally bound in kaolinite. In the light of the previous discussion it seems much more likely that flakes of Cr and V-bearing ilmenite, of either detrital or authigenic origin, have been preferentially adsorbed by the organic material thus explaining the correlation between Cr, V and Ti, the relatively high Cr and V contents in the carbonaceous shales and the correlation between Cr and V and the organic fraction as represented by loss on ignition.

The work of Marchand (1970) could be taken to corroborate these conclusions. Working on the same samples he found Cr to be only slightly enriched in his separated organic fraction in apparent contrast with the results found in this work. The reason, however, is clear. The adsorbed Ti, V and Cr bearing phase was largely removed by his organic fraction separation process which included violent ultrasonic "scrubbing" for prolonged periods. To the best of the author's knowledge this interpretation of the distribution of part of the Cr and

V contents of carbonaceous shales has not been expounded before.

Frequency distribution diagrams for V in all the South African sediments analysed in this work are shown in Fig.. 16A and for Cr in Figs. 17A and 18A. The marked difference in Cr content between the Fig Tree sediments and the rest of the South African argillaceous rocks is clearly displayed in Fig. 18A. The frequency distributions of V and Cr, as shown in Figs. 16A and 17A respectively are asymmetrical and show a marked tendency to be positively skewed. The two elements show a very similar dispersion pattern and this is in keeping with their coherence displayed in the sedimentary environment where they are both principally located in ilmenite. Perhaps the positively skewed distributions are inherited from the source rocks, as Ahrens (1963a) notes the log-normal distribution of V in basaltic and granitic rocks and Ahrens (1954a) notes the extreme dispersion and log-normal distribution of Cr in basaltic and granitic rocks.

6.7 THORIUM AND URANIUM

It has long been known that, in general, sedimentary rocks have a much greater range in Th and U concentrations and in Th/U ratios than primary igneous rocks. This is due to the fact that under plutonic conditions, which tend to be more reducing, Th and U are both in the tetravalent state and behave almost identically because of the great chemical similarities within the Actinide Series of which they are members. However, under the oxidising conditions prevailing when in contact with the oxygen of the earth's atmosphere (or in rare late stage magmatic differentiation) Th and U tend to separate.

U^{4+} is readily oxidised to U^{6+} which forms the soluble uranyl ion and is readily leached and removed in solution during weathering processes whereas Th has no comparable state and can be concentrated in placer and residual deposits such as bauxite. Thus although the average continental Th/U ratio is 3.6 (Taylor, 1964) the ratio for sea-water is 0.0002 (Koczy, 1956) a factor difference of 70,000, reflecting the efficient separation of these two elements upon exposure to oxidising conditions at the earth's surface.

Adams and Weaver (1958) concluded that Th and U are incorporated in sedimentary rocks in the following way:

(i) in detrital heavy minerals (zircon, monazite, apatite and xenotime)
(ii) in common detrital minerals
(iii) in minerals precipitated from sea-water
(iv) adsorbed in iron and aluminium hydroxides
(v) adsorbed on clay minerals and organic matter
(vi) adsorbed on carbonate surfaces

They pointed out the dependance of the Th/U ratio on the mineralogy of the source rocks, thoroughness of oxidation and weathering and position from the shore, and showed how the ratio could be used to distinguish between marine and continental red and yellow shales. Marine clays have a high U content and consequent low Th/U ratio, whereas continental clays exhibit the reverse features.

All the samples included in this work were analysed for Th by X-ray fluorescence and a selection of forty-four of different ages and derived from different depositional environments were analysed by gamma-ray spectroscopy for U and Th. The results shed much light on the history of these shales and also provide information

on the distribution of Th and U in shales. The analytical results and the Th/U ratios are given in Table 21.

Table 21

Some Th and U data (in ppm) and Th/U ratios for various groups of rocks

		Th	U	Th/U
Sea-water	(1)	4×10^{-8}	2×10^{-4}	0.0002
Crustal average	(2)	9.6	2.7	3.6
Basalt average	(2)	2.2	0.6	3.7
Granite average	(2)	17	4.8	3.5
Precambrian greywackes	(3)	9.1	1.6	5.7
Mancos shales	(4)	10.2	3.7	3.1
Green and grey shales	(5)	13.0	2.7	4.4
Bentonites	(5)	24.0	5.0	5.8
Average shale	(5)	12.0	3.7	3.8
Russian Precambrian granites	(6)	33	5.7	5.8
Colorado Precambrian granites	(7)	25.5	5.0	5.1
Canadian Shield	(8)	10.3	2.5	4.1
Australian Shield	(9)	20	3.0	6.7
Namaqualand granite-gneiss	(10)	74.8	19.3	4.5
Average South African argillite	(11)	17.8	-	-

(1) Koczy (1956)
(2) Taylor (1964)
(3) Rogers, Condie and Mahon (1969/1970)
(4) Pliler and Adams (1962)
(5) Adams and Weaver (1958)
(6) Filippov and Komlev (1959)
(7) Phair and Gottfried (1964)
(8) Shaw
(9) Lambert and Heier (1968)
(10) Hobbs (1971)
(11) This work

penetrating the Namaqualand granite-gneiss. The weathered samples from the top 10 m of the core have not been considered. For these samples Hobbs found the average Th and U concentrations to be 74.8 ppm and 19.3 ppm respectively, and the average Th/U ratio to be 4.5 (Table 21). Th concentrations ranged from 20.4 ppm to 121.4 ppm and U concentrations ranged from 1.9 ppm to 12.0 ppm. This establishes the area to be a high Th and U province and also the possibility of granites of this age being amongst the source rocks of the Cape and Karroo System sediments. In view of the difference in ages between the granites and the sedimentary rocks analysed here it is possible that the Karroo sediments may have been derived from pre-Karroo sediments, now removed by erosion, themselves derived from the granites, but this seems unlikely as Ryan (1967) and Danchin (1970) both conclude from their independent studies that the Karroo sediments are in fact derived from granites. Considering the vast amount of sediment involved it seems likely that granites of the age of the Namaqualand granite-gneiss acted as source rocks.

Th, U and Th/U data for selected groups of South African shales are shown in Table 22.

Table 22

Th, U and Th/U data for selected groups of shales

	Th	U	Th/U
Fig Tree	6.0	0.7	8.8
Fish River	15	2.9	5.0
Bokkeveld	19	2.7	7.0
Northern Ecca Facies*	24	6.0	4.4
Central Ecca Facies+	17	3.2	5.6
Western Ecca Facies	15	3.4	4.5

*Excluding BEc 4270, Ec 14 and Ec 16

+Excluding AEc 1

The Bokkeveld samples analysed all originate from the lower half of the succession which du Toit (1954) concluded was deposited under shallow-water marine conditions. The paucity of feldspar indicates thorough chemical weathering of the source rocks and a probable slow rate of accumulation in the basin of deposition. From the prolonged contact of the sediments with the overlying sea-water a maximum extraction by adsorption of U from the sea-water by clay minerals in the sediment could be expected to have taken place. However, a low U content and high Th/U ratio of these shales indicates that this was not the case. The likely explanation is that although chemical weathering of the source rocks was thorough and erosion and transport of the weathered material to the basin of deposition was slow, the source area was much larger than the depositional area resulting in a fast accumulation rate although the rate of supply was slow. This possibility demonstrates the possible theoretical use of the Th/U ratio as an indicator of changes in the rate of sediment accumulation and linked with this is its use as an indicator of changes in distance from the depositional area to the ancient shoreline as suggested by Weaver and Adams (1958). With increasing distance the proportion of detrital to authigenic clay minerals decreased producing a decrease in Th, an increase in U due to the slower accumulation rate, and a resultant marked decrease in the Th/U ratios. As the Bokkeveld samples were collected from surface outcrops the possibility exists that some U was removed by ground-water leaching but the constant level of about 2.7 ppm U in these rocks renders this unlikely.

The average enrichment factor of Th in the clay fraction of the Bokkeveld samples is 1.8. This

demonstrates that the bulk of the Th is incorporated in the clay fraction and is not associated with any resistate heavy minerals such as zircon. It also shows that Th is enriched in the fine-grained clay fraction indicating that it is not structurally bound but has probably been incorporated in the clay by a process of adsorption or cation exchange during weathering of the source rock and is now extremely firmly lodged in the clay mineral structure. The smallest clay particles have the most broken bonds and thus provide more adsorption sites per unit mass than the large particles. Scott (1968) also found Th to be enriched in the smallest size fractions of river sediments. Spears (1966) came to the somewhat surprising conclusion that in a South Staffordshire tonstein all the U is contained in zircon and all the Th is contained in kaolinite. Although zircon does contain much of the U and some of the Th it seems likely that at least some of the U was incorporated in the sediment during the period of sulphide formation when reducing conditions must have prevailed.

The single Dwyka sample analysed has a Th/U ratio of 6.0 which is not too dissimilar from the average of 4.6 by Sugimura and Angino (1966) in Antarctic glacial marine sediments. The much higher levels of Th and U in the Dwyka sample once again reflect the high Th and U nature of the source rocks.

The content of the Northern Ecca Facies is also unusually high, averaging 24 ppm, and indicating a granitic source area as mentioned earlier. Three samples from the Vierfontein Colliery average 48 ppm Th and as they are organic rich (average loss on ignition is 28%) it appears likely that the Th enrichment is due to some biogenic agent, perhaps forming "thucolite" as is found in the

Carbon Leader of the Witwatersrand System. In general, however, there is no correlation between Th and the organic fraction and in this respect this work supports the findings of Adams and Weaver (1958).

The average U content of 6.0 ppm is higher than any groups in Table 21 or 22 and merits an explanation. There is no direct relationship between total U and organic content indicating that U is not directly extracted from the overlying water by the plant material in the sediment or possibly the U present in other phases is sufficiently large to mask a possible U-organic content relationship. The enrichment of U in these carbonaceous shales is probably due to reducing conditions being generated at the water-sediment interface by the decomposition of plant material. This caused the slow reduction of the soluble uranyl ion to the relatively insoluble tetravalent uranium ion which was then rapidly hydrolysed out of solution and incorporated in the sediment by adsorption either on the clay minerals or the organic material. The extent of this mechanism would depend on the rate of sediment accumulation and the Eh and pH of the environment i.e. the strength of the reducing conditions. Sediment accumulation was shown by Danchin (1970) to be rapid and the scarcity of sulphides suggests that conditions in general were only reducing enough to cause the uptake of a few ppm U in the sediment.

The Th/U ratio of 4.4 has no especial significance as both the Th and U levels are so unusual but it is interesting that it is similar to the ratios for the Central and Western Ecca Facies, and all three average Th/U ratios are distinctly lower than that of the Bokkeveld sample. Thus the fresh-water shales have lower ratios

than the marine shales which is the reverse trend to that postulated by Adams and Weaver (1958). This indicates that the use of the Th/U ratio should be restricted to variations in a single depositional area as there are too many factors, apart from environment of deposition and distance from the shore-line, which affect the Th/U ratio for it to be reliably used to compare widely separated sedimentary rocks.

AEc 1 contains 25 ppm U and has a Th/U ratio of 0.8. This high U level is probably due to incorporation in the organic fraction (LOI of 23%) by an adsorption or cation exchange process following reduction. Less than one percent of iron in the ferric state (Danchin, 1970) indicates that at some state in its history the depositional environment was a very effective reducing one indeed. The samples from this borehole merit further study for radioactive elements.

The Fig Tree samples contain 6.0 ppm Th, 0.7 ppm U and have a Th/U ratio of 8.8. This exceptionally high ratio could be attributed to the rapid accumulation of sediments under highly oxidising conditions. However, as has been mentioned when discussing the Fig Tree sediments, it is fairly certain that not only were atmospheric conditions unlikely to be strongly oxidising during Fig Tree times but it is highly likely that they were actually reducing. The high Th/U ratios are partly explained by the fact that the average ratio must have increased from an original value of about 6.5, as U decays radio-actively more rapidly than Th. This original ratio is in keeping with the range of high ratios found in sedimentary rocks of South Africa, and the low Th and U concentrations, are inherited from the probable basic nature of the source

rocks. This aspect is dealt with more fully in the section on the Fig Tree Series. Although the average basalt contains 2.2 ppm Th (Table 21), which is considerably less than the average for the Fig Tree shales, the original basic source rocks probably contained considerably more Th and U than the average basalt compatible with the high Th and U content of this continental craton. Present day weathering might be partly responsible for the low U values, but this is considered unlikely.

Chlorite, kaolinite and illite rich rocks have been included in this study of U and Th but no clear picture has emerged of either of the two elements being preferentially associated with any particular clay mineral. A detailed study within a single basin would be more likely to reveal any such relationship.

The correlation coefficients of Th with other elements listed in Table 28A to 42A, show predictably that Th does not follow very coherently any of the elements dealt with here. In some groups of rocks, especially the Southern and Western Ecca Facies, it does show some correlation with Al and consequently Ga. This can be attributed to its distribution being controlled largely by the mechanisms of formation of clay minerals in a source area in which Al is always a major constituent. Very little Th appears to be incorporated in a sediment from the overlying water, and Bonatti et al.(1971) also showed that Th exhibits no syngenetic mobility whatsoever.

The frequency distribution of Th in all South African sediments analysed in this work is given in Fig. 24A. The frequency distribution of U was not plotted as it was felt that too few U analyses were available.

Fig. 24A shows that the frequency distribution of Th is fairly symmetrical but shows a slight tendency to be positively skewed. This effect is produced by the few high Th content carbonaceous shales of the Northern Ecca Facies.

6.8 ZIRCONIUM

Zirconium is a commonly analysed element owing to its high abundance in most geological materials and its relative ease of analysis. It does not commonly occur in major igneous rock forming silicates but forms its own mineral zircon (mainly in granites) and is included in small amounts in such accessory minerals as rutile, sphene, magnetite and ilmenite, replacing Ti in Ti minerals as its ionic size is not much larger. As shown in Table 23 it tends to enrich slightly in granites but in general is evenly distributed throughout most igneous rocks.

The bulk of Zr entering a depositional environment is normally considered to be located in the detrital heavy minerals listed above, but a significant proportion is released during chemical weathering and transported to the sea as ions in solution whereupon it is rapidly hydrolysed, like Th, at the pH of sea-water and precipitated as a colloidal hydrous oxide which can be scavenged by manganese oxides or sorbed by clay minerals. Nicholls and Loring (1962) considered some Zr to proxy for Al in clay minerals formed during source rock weathering. Evidence for kaolinite and montmorillonite incorporating Zr at the expense of Al was presented by Degenhardt (1957).

Concentrations of Zr for the samples analysed are presented in Tables 2A to 21A, and averages for various groups of South African shales are shown in

Tables 23A and 24A. Correlation coefficients of Zr against the other elements considered in this work are set out in Tables 28A to 42A. A few published Zr data for average rocks are presented in Table 23.

From Tables 23, 23A and 24A, it is clear that most South African shales are enriched in Zr compared to shales from other parts of the world and the continental crustal average. In a manner analagous to U and Th, this arouses the interesting possibility of Southern African being a high Zr province and immediately leads one to suspect that the mineral zircon, a favourite host for U and Th, is responsible for the observed phenomena. If the bulk of U and Th in the basement granites were contained in abundant zircon, then the high abundances of all three elements in the sedimentary rocks derived from these

Table 23

Zr abundances in ppm in some groups of rocks

		Zr
Basalt average	(1)	150
Granite average	(1)	180
Crustal average (continental)	(1)	165
Russian Archean granite average	(2)	
Shale average	(2)	160
Shales average	(3)	200
Ultramafic rocks and dunites	(3)	30
American fresh-water shale	(4)	200
American marine shale	(4)	183
Bokkeveld shale average	(5)	235
Fig Tree shale average	(5)	87.5
Northern Ecca Facies shale average	(5)	255
Average South African argillaceous rock	(5)	215

(1) Taylor (1964)
(2) Wedepohl (1971)
(3) Vinogradov (1962)
(4) Tourtelot (1964)
(5) This work

granites could be easily explained in terms of detrital zircon. However, the correlation coefficients of Zr and Th show that these two elements do not exhibit a close coherence and other mineral phases must play a part in their distribution both in the source rocks and in the accumulated younger shales.

The Zr data for the less than two micron fractions show that the bulk of Zr present in the whole rock is normally located in the detrital heavy mineral fraction in South African argillaceous rocks. Depletion ratios for various groups of rocks are shown in Fig 35A but the proportion of Zr located in the clay minerals cannot be accurately calculated as total clay mineral contents are not accurately known. However, it is thought that as much as 80 percent of Zr can be contained in the heavy mineral fraction as depletion factors as low as one fifth occur. If four fifths Zr are contained in the few percent detrital heavy minerals then this fraction must normally contain more than 1000 ppm Zr and could range up to a few percent Zr. The bulk of Zr in this fraction is thought to be located in zircon. No relationship exists between Zr and Ti so a significant proportion of Zr cannot be located in ilmenite.

The Fig Tree and Witwatersrand shales have considerably lower Zr concentrations than the average South African shales and their separated clays do not exhibit a marked Zr depletion as the younger shales do as is seen in Fig. 36A. This suggests a lack of zircon in the source rocks, further evidence of the basic nature of the provenance of the Fig Tree Series. As shown in Table 23, ultrabasic rocks and dunites contain an average of only 30 ppm Zr (Vinogradov, 1962). Sufficient Zr could be con-

tained in the other detrital heavy minerals to account for the observed Zr contents of these shales. It will be noted from Table 23 that Zr is not very depleted in basic rocks although zircon is not customarily present.

Zircon has a density nearly twice that of the clay minerals so only vanishingly small particles of zircon would be associated with the less than two micron fraction after separation of the clay fraction by gravity settling in water. Zircon particles could possibly be adsorbed by the clay minerals but it is thought that the vigorous "scrubbing" by ultrasonics would destroy any such attachments. As up to 200 ppm Zr is recorded in the separated clays one can only conclude that this Zr is either structurally located in the clay minerals, perhaps proxying for Al as suggested by Degenhardt (1957), or that Zr has taken part in adsorption or cation exchange reactions or, more likely, is incorporated in part by all three possible mechanisms.

As is expected from its tendency to be restricted to the single mineral, zircon, Zr exhibits no coherence with any other elements which do not occur in zircon. Only Th has a slight tendency to correlate with Zr in some of the Northern Ecca Facies boreholes samples.

The frequency distribution of Zr in the South African argillaceous sediments analysed in this work is displayed in Fig. 22A. Similar in its asymmetrical pattern to those of V and Cr it shows a marked positive skewness. Perhaps, as for V and Cr, this is an inherited characteristic from the source rocks as Ahrens (1963a) notes the strong positive skewness and lognormal distribution of Zr in basaltic and granitic rocks.

6.9 NIOBIUM

In the igneous environment Nb tends to proxy for Ti as both Nb^{5+} and Ti^{4+} have ionic radii of 0.68Å. Consequently Nb is very evenly distributed throughout igneous rocks being located in Ti phases such as rutile, sphene, and ilmenite and is only enriched in late stage granite pegmatites where it forms its own minerals, normally Fe and Mn tantaloniobates. Znamenskii et al. (1962) note that when sphene is present more than 80 percent of the Nb content is concentrated in this mineral alone and that tantaloniobates develop only in the absence of sphene. The ionic radius of Nb^{5+} is not too different from that of Zr^{4+} (0.79Å) for some Nb to be included in zircon when this mineral is formed from silicate melts. The charge difference of only one also makes this substitution possible. Thus the distribution of Nb in the igneous environment tends to be restricted to the heavy minerals. In the weathering environment Nb becomes concentrated in the detrital heavy minerals but undoubtedly a portion is released into solution. There appears to be little published data on the behaviour of Nb in the aqueous environment but its ionic potential of 7.5 (Mason, 1966) would suggest low solubility and in the marine environment rapid hydrolysis and precipitation or scavenging by ferromanganese hydroxides or adsorption onto clay minerals. The low concentration of 1×10^{-5} ppm Nb in sea-water and its short residence time of 300 years (Goldberg, 1963) confirms its efficient removal from sea-water. Perhaps the removal of dissolved Nb from sea-water is closely linked with that of Ti which has an even shorter residence time.

Nb concentrations for the samples analysed are presented in Tables 2A to 21A, and the averages

for various groups of rocks are laid out in Tables 23A and 24A. Table 24 shows the Nb contents of the average South African shale compared to the crustal average and average basalts and granites. Tables 28A to 42A contain the correlation coefficients of Nb against other elements analysed. It is clear from Table 24 that there is little difference in Nb content between common igneous rocks and average shales. The Nb content of 15.7 ppm of the average South African shale is very close to the 18 ppm of the average shale of Wedepohl (1971).

The average Nb contents of groups of South African rocks varies from 10.4 ppm in the Kunjas Series to 19.9 ppm in the Northern Ecca Facies. The Fig Tree shales and Witwatersrand shales contain 5.3 ppm and

Table 24

Average Nb abundances in ppm in some groups of rocks

		Nb
Basalt average	(1)	20
Granite average	(1)	20
Crustal average continental	(1)	20
Russian Archean granite average	(2)	2.4
Shale average	(3)	18
Shale average	(4)	20
Ultramafic rocks and dunites	(4)	1
Fig Tree shale	(5)	5.3
Bokkeveld shale	(5)	17.0
Northern Ecca Faceis shale	(5)	19.9
Average South African argillaceous shale	(5)	15.7

(1) Taylor (1964)
(2) Znamenskii (1964)
(3) Wedepohl (1971)
(4) Vinogradov (1962)
(5) This work

5.5 ppm Nb respectively, and this relative depletion can be attributed to the absence of zircon from the provenance of these rocks as mentioned earlier in the section on Zr.

As can be noted from Table 24 the average Fig Tree concentration of 5.3 ppm Nb is considerably lower than granite, basalt, shale or crustal Nb averages. This indicates that a considerable proportion of the source rocks might have been ultrabasic in composition as Vinogradov (1962) records an average value of only 1 ppm Nb for ultramafic rocks and dunites. However, Znamenskii (1964) recorded an average value of 2.4 ppm Nb for Russian Archean granites and pointed out that Nb was much enriched in much younger granites. Thus the low Fig Tree Nb values are consistent with the great age of these sediments but cannot be considered to be indicative of the composition of the source rocks.

The Nb - Zr correlation coefficients frequently show a marked degree of correlation between these elements showing that Nb is included in zircon in not insignificant proportions. However, Fig. 37A shows that there is also a strong correlation between Nb and TiO_2 (TiO_2 data from Danchin, 1970). Data for the Bokkeveld Series is plotted in Fig. 37A, but Fig. 38A, which shows average Nb and average TiO_2 plotted for various groups of rocks, shows that this relationship holds for all the South African sedimentary sequences analysed here. The close association between TiO_2, Zr and Nb emphasizes the fact that 11 three elements are located dominantly in the heavy mineral fraction and their absolute concentrations are probably controlled by the proportion of heavy minerals present. This is illustrated in the Northern Ecca Facies by the A Series borehole samples which not only have the

highest average Nb contents of 30.6 ppm but also the highest average TiO_2 content of 1.04 percent.

In a manner analagous to Zr, the Nb concentrations in the less than two micron separated clay fractions demonstrate overwhelmingly that the bulk of the Nb content of the whole rock is located in the heavy mineral fraction. The amount of depletion, however, is not as great as that for Zr. The average separated clay fraction contains 13.6 ppm Nb compared to 15.7 ppm in the average South African argillite - a depletion factor of 0.87. Comparable figures for Zr are 121 ppm and 215 ppm - a depletion factor of 0.56.

Thus the separated clay fraction data for Nb indicate that a higher proportion of Nb than of Zr in a shale is of authigenic origin and probably associated with the clay minerals, but that the bulk of both elements is located in the detrital heavy mineral fraction. The authigenic Nb is probably incorporated by adsorption or cation exchange reactions, but this is mere speculation and it might well be partially incorporated in authigenic anatase which Goldberg (1954) has shown to form in modern Pacific sediments. There is no evidence to suggest that Nb is incorporated in the sediments due to any biological activity. As the minerals in the detrital heavy mineral fraction have not been identified it is not precisely known in which heavy mineral or minerals Nb has actually been concentrated.

The frequency distribution of Nb in the South African shales analysed in this work is shown in Fig. 23A and it is seen to be slightly asymmetrical about the mode but, like Cu, is not definitely positively or negatively skewed. This result is somewhat surprising as, being mainly

located in detrital Ti minerals, it might have been expected to display a similar distribution pattern to Zr, V and Cr, other elements which are largely associated with the detrital heavy mineral fraction.

6.10 SCANDIUM, YTTRIUM AND YTTERBIUM

Goldberg and Arrhenius (1958) pointed out that Sc, Y and Yb show similar behaviour in the major sedimentary cycle and for that reason they are grouped together here for convenience. They considered these three elements to be concentrated in mainly two groups of minerals in the sedimentary environment, Sc in the ferromanganese hydroxides and Y and Yb in biogenic apatite. In the igneous environment Sc tends to replace Fe and Mg in ferromagnesian minerals thus tending to be more abundant in basic than acid rocks as can be noted from Table 25. However, Sc cannot be considered to be closely correlated with Fe and Mg in ferromagnesian minerals (Hermann, 1970, Norman and Haskin, 1968). In pegmatites Sc occasionally forms its own mineral thortveitite. Y and Yb replace Ca to a limited extent in silicate minerals but become concentrated in granites and pegmatites where they are major constituents of lanthanide-rich minerals such as monazite. However, they readily proxy for Ca in apatite.

As determined by Haskin et al. (1966) none of these three elements tends to be located in detrital heavy minerals, and they are consequently released at the site of weathering where a part is solubilised but probably the bulk of the elements is hydrolysed and adsorbed by clay particles and the ferric hydroxide coatings of quartz grains. Rankama and Sahama (1950) considered $Sc(OH)_3$ to be much more soluble than $Al(OH)_3$ as Sc is not enriched in residual bauxites but in oxidate sediments like sedimentary

iron ores. More recent work (Vlasov, 1968) suggests that Sc does concentrate in bauxite but is a function of the composition of the original rock and not the newly formed aluminium minerals. Similarly the hydroxides of Y and Yb are far more soluble than Al and are readily leached in the weathering environment. They are also scavenged by iron hydroxides and, because of cationic size considerations, Y is readily accepted into calcite and Yb less so. Sc is very depleted in carbonate minerals.

In the marine environment Haskin et al. (1966) found 60 to 100 percent of the total lanthanide content to be located in the iron oxide fraction associated with the quartz grains and less than 5 percent to be located in the detrital heavy mineral fraction. They also found up to 75 percent of the lanthanide content of limestones to be located in the calcite and further experiments revealed that freshly precipitated calcite effectively removed some lanthanides from solution presumably by adsorption. Norman and Haskin (1968) stressed the fact that a good linear abundance relationship normally existed between Sc^{3+} and Fe^{3+} in sedimentary rocks. Sc is also known to be slightly concentrated in phosphorites and phosphate rocks (Frondel, 1970).

The chief interest in the lanthanides in sediments is the determination of lanthanide (or rare earth) patterns and the interpretation of the changes of patterns in sediments of different ages and the comparison of these patterns with meteoritic and crustal patterns. It was originally intended in this work to determine La by XRF and to study the La/Yb ratio in South African shales, La being light and Yb a heavy lanthanide element. However, the method was not nearly reliable enough to produce La

data of sufficient quality to match the excellent data of Haskin et al. (1968) and consequently La was not determined.

Sc, Y and Yb concentrations for the samples analysed are shown in Tables 2A to 21A and averages for shale sequences are shown in Tables 23A and 24A. Averages for particular groups of rocks are set out in Table 25 and correlation coefficients of Sc, Y and Yb against each other and against other elements analysed are listed in Tables 28A to 42A.

Table 25

The abundance of Sc, Y and Yb in ppm in various groups of rocks

		Sc	Y	Yb
Average basalt		38(1)	25(1)	2(3)
Average granite		5(1)	40(1)	4(3)
Crustal average (continental)	(1)	22	33	3.0
Shale average	(2)	13	41	3.7
Shale average	(3)	10	30	3
North American shales	(4)		27	3.1
European shale composite		15(7)	31.8(5)	3.29(5)
Russian Platform shales	(6)		30	2.6
Bokkeveld shale average	(8)	15.5	53.0	2.4
Northern Ecca Facies average	(8)	13.4	47.4	2.2
Fig Tree average	(8)	20.0	28.7	1.4
Average South African shale	(8)	14.3	43.6	2.2

(1) Taylor (1964)
(2) Wedepohl (1971)
(3) Vinogradov (1962)
(4) Haskin et al. (1967)
(5) Haskin and Haskin (1966)
(6) Ronov et al. (1967)
(7) Wedepohl (1960)
(8) This work

The average concentrations of Sc in South African shales varies from 12.2 ppm in the Western Ecca Facies to 20.0 ppm in the Fig Tree shales. Y varies from 28.7 ppm in the Fig Tree Series to 54.8 ppm in the Cango Formation sediments. Yb displays an extremely narrow range from 1.9 ppm in the Beaufort Series to 2.6 ppm in the Cango Formation although the Fig Tree shales only contain an average of 1.4 ppm Yb. The average South African shale contains 14.3 ppm Sc, 43.6 ppm Y and 2.2 ppm Yb.

From Table 25 it can be seen that the Fig Tree shales are enriched in Sc but depleted in Y and Yb compared to the average South African shale and also to shales from other parts of the world. This trend is similar to that shown by the distribution of these elements in average granites and basalts and once more emphasizes thd probably basic nature of the source rocks for these shales.

Interesting aspects of the distribution of Sc in South African shales are revealed by the correlation coefficients. In the Bokkeveld Series shales Sc shows good correlation with Al, Ga, Ni, V, Cr and LOI which is interpreted as showing the definite affinity which Sc has for the clay minerals illite and chlorite. In these non-carbonaceous samples LOI is interpreted as being structural water and hydroxyl ions and is also probably proportional to the total clay mineral content. The other elements are also regarded as being incorporated in the clay minerals by adsorption, V and Cr as mentioned earlier perhaps as tiny flakes of hydrated ilmenite or maybe authigenic anatase. Sc only shows poor correlation with Fe, Y and Yb. These correlations persist in several other non-carbonaceous shale sequences, such as the Witteberg Series, Malmesbury Formation, Fish River Series and Beaufort Series. The

correlation of Sc with V and Cr in particular is striking and suggests a similar behaviour to these two elements. However, Sc is not associated with the heavy mineral detrital fraction as mentioned earlier and one must conclude that Sc, V and Cr share very similar adsorption characteristics to illite and chlorite. Although Sc^{3+} has a very similar size to Zr^{4+} these two elements show no tendency at all to be associated in South African shales emphasizing the relative depletion of Sc in the detrital heavy mineral fraction as the bulk of Zr has been concluded to be located in this fraction. The data for the separated clays show Sc to be enriched in this fraction, further support for the conclusion that Sc is mainly closely associated with the clay minerals. The low correlation with Y and Yb can probably be attributed to the partial incorporation of Y and Yb in calcite which is occasionally present in these samples as shown by X-ray diffraction. Many more samples probably contain calcite in amounts too low to be detected by XRD.

The carbonaceous shales of the Northern Ecca Facies, however, reveal further aspects of the distribution behaviour of Sc. In these shales Sc shows absolutely no correlation with the organic content showing that the incorporation of Sc in the sediment has been independent of the organic matter. Sc now shows a strong correlation with Fe and, except for the A Series borehole samples, a strong correlation with Y and Yb. The correlation of Sc with Al, Ga, Ni, V and Cr is weak to non-existent. The correlations of Y and Yb with each other and with Fe are also extremely good in these carbonaceous samples, except for the A Series borehole samples. Sc, Y and Yb were probably scavenged by settling ferric hydroxides

which on burial in the sediment were reduced to the ferrous state and later converted to sulphides. Perhaps part or nearly all the Sc, Y and Yb content were incorporated in these authigenic sulphides, as Mitchell (1968) detected Y, La and Ce in authigenic pyrites and in greater abundances than in hydrothermal or metamorphic pyrites. The presence of La and Ce implies the presence of Yb although one cannot also infer the presence of Sc which Mitchell unfortunately did not determine. However, Mitchell presumed Y, La and Ce to be present in gangue calcite which remained even after extensive purification, and, if this is the case, then one must conclude that Sc, Y and Yb are solubilised by the reduction of ferric iron and made available for adsorption on the clay minerals and/or organic matter. The much higher correlation of these three elements with Al than with LOI indicates that they have a far greater affinity for kaolinite than for coaly plant material. The relationship between total Fe and Sc in the GB borehole samples is shown in Fig 39A. There is no relationship between Sc and Fe^{3+} which agrees with the proposed model of much ferric Fe being reduced. The good correlation between Sc and total Fe was probably aided by the extremely rapid rate of accumulation of these sediments (Ryan, 1967; Danchin, 1970) thus allowing little time for adsorption of Sc from the overlying water so that virtually the total amount of Fe and Sc in the sediment was introduced via ferric hydroxide. Although the elements have been redistributed within the sediment there has been no net gain or loss of either Fe or Sc. Consequently the original correlation is still observed. Fig 39A also shows that the rate of Sc concentration increase decreases after 6 percent Fe.

The correlation coefficients of the Fig Tree shales reveal that these three elements are in no way associated with Fe in these goethite and Fe-chlorite rich shales. Following the discussion on the Fig Tree shales this is to be expected. Because of the reducing atmospheric conditions prevailing at the time Fe was not incorporated in the sediment via the hydrolysate fraction and thus Sc, Y and Yb were not scavenged by ferric hydroxides as occurred in much later sediments. Goethite was formed by the oxidation of ferrous iron at a much later stage in the history of the Fig Tree Series. The enrichment of these elements in the separated clay fractions of the Fig Tree is strong evidence for the incorporation of these elements in the clay mineral fraction. In the separated clay fractions of the Bokkeveld shales, however, Y and Yb have been depleted relative to their concentrations in the whole rock. This indicates that the bulk of the Y and Yb present in these shales is included in the iron oxide coatings of the quartz grains which have been removed during the clay separation process.

Y and Yb both exhibit an extremely narrow range of concentrations, and, apart from the Northern Ecca Facies carbonaceous shales, the correlation coefficients do not yield much useful information. The conclusion drawn from this is that in general their incorporation into a sediment is controlled by several factors the least important of which is the organic content, and the most important of which is probably the composition of the source rocks. Under conditions of rapid sediment accumulation followed by the onset of reducing conditions within the sediment as occurred during the accumulation of the carbonaceous Northern Ecca Facies shales, Y and Yb

exhibit the same distributional pattern as Sc and the observations made concerning the goechemistry of Sc under these conditions apply equally well to Y and Yb.

Table 24 and the Y and Yb data for sedimentary rocks listed by Herrmann (1970) show that there are large differences in the concentrations of these elements in shales from different parts of the world. Sc in shales does not show such a variation from one continent to another. Y is enriched in South African shales compared to European, Russian and North American shales and the average shale of Vinogradov (1962), but is very similar to the average shale of Wedepohl (1971). The reverse is shown by Yb, however, which is depleted in South African shales relative to all other shales although it is similar to the Russian platform shales. It seems unlikely that the relationship between Y and Yb should be markedly different in South African shales compared to shales from other continents and the accuracy of these data then become suspect. It is noted (Herrmann, 1970) that the neutron activation results for Y and Yb in the European shale composite are far lower than the XRF and emission spectrographic results which leads one to conclude that XRF and emission spectrographic methods are not giving accurate results as yet. Yb is extremely difficult to analyse accurately by emission spectrography because of the difficulty of obtaining standards of accurately known concentrations. The latest recommended Yb values for G-1 and W-1 (Fleischer, 1969) are substantially lower than previous recommended values and analyses based on these standards are entirely dependent on which recommended values are utilised. As the latest values were used for this work, the results obtained are presented with con-

fidence. In addition extremely satisfactory data resulted for the more recent international rock standards analysed (Hofmeyr, 1971).

As South African shales do appear to be high in Y and low in Yb further detailed work is merited and all the lanthanides should be determined in order to construct the lanthanide patterns and to compare them with patterns from shales of other parts of the world. For instance, Haskin and Haskin (1966) note no difference between the normalised patterns of European, Russian and North American shales, and it would be interesting to determine whether South African shales followed the trend or not.

Frequency distribution diagrams for Sc, Y and Yb in all the South African argillaceous rocks analysed in this work are presented in Figs. 19A, 20A, and 21A respectively. Sc and Yb display fairly symmetrical frequency distributions which are not definitely positively or negatively skewed but Y shows a distinctly different frequency distribution to either of these elements. The distribution of Y is asymmetrical about the mode and is strongly positively skewed. The difference between the frequency distributions of Y and Yb is somewhat surprising in view of the fairly close coherence these two elements display in the sedimentary environment.

7 SOME OBSERVATIONS ON THE VARIATION OF TRACE ELEMENT CONTENT WITH GEOLOGICAL AGE

The variation with age of the major element content of fine-grained sedimentary rocks has been used by several workers to provide information on the age and evolution of the oceans and continents of the Earth. As far back as 1932 Goldschmidt reasoned that as sedimentary rocks were extremely depleted in Na compared to igneous rocks from which they were presumably derived, this missing Na must be resident in the ocean and therefore, the age of the ocean would be given by:

Total amount of Na in the ocean/Na supplied per year

Barth (1961) did not agree that the sea acted as a vast sink for all Na which could not leave the ocean except through evaporite deposits. He preferred to believe that for all elements in the ocean a dynamic equilibrium existed between supply and removal and that Goldschmidt's calculated age of the ocean was actually the residence time of Na, i.e. the average time spent by an atom of Na in the sea. Weaver (1967a) noted a decrease in the K content and a corresponding increase in the Na content between shales of the Carboniferous and Permian eras. He believed that the more acid conditions prevailing in the weathering environment favoured the development of kaolinite, and sediments derived from these source areas would be kaolinite rich and deficient in K. Thus Weaver explained a variation with time of the K content of shales in terms of changes of climatic weathering conditions. Perhaps marked differences in the concentrations of trace elements in ancient shales of different ages provide information on

differences of source rock composition, paleoclimate and perhaps provide indicators of the environment of deposition.

It is thus of interest to study the variation with time of the concentrations of trace elements in South African argillaceous rocks. The major part in time of the Earth's history is covered by these sediments which range in age from the Precambrian Fig Tree Series shales about 3000 m.y. in age to the Triassic Beaufort Series shales about 200 m.y. in age. There is a marked change in mineralogy from the older to the younger shales of the South African stratigraphic column. This is shown in Table 26 which gives the approximate clay mineral compositions of the shale sequences analysed in this work.

Table 26

Approximate clay mineral compositions of South African shales

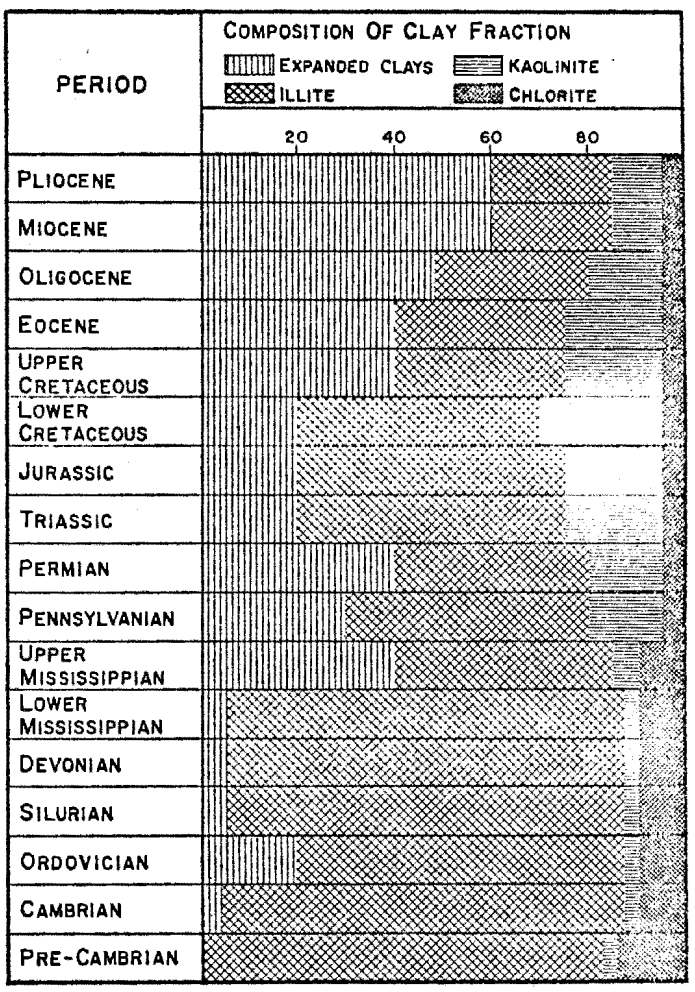
	Chlorite	Illite	Montmorillonite	Kaolinite
Beaufort		Dom	Tr	Tr
Northern Ecca		Tr	Sub	Dom
Southern Ecca	Tr	Dom		Sub
Central Ecca	Tr	Dom	Tr	Tr
Western Ecca	Tr	Dom		
Witteberg	Tr	Dom	Tr	
Bokkeveld	Sub	Dom		
Fish River		Dom	Tr	
Schwarzrand		Dom	Tr	
Kuibis		Dom	Tr	
Cango	Sub	Dom		
Malmesbury		Dom	Tr	Tr
Kunjas		Dom		
Witwatersrand	Dom	Sub		
Fig Tree	Dom	Sub		

Dom = Dominant Sub = subordinate Tr = trace

There is a progressive decrease in the amounts of chlorite in the younger shales with a concomitant increase in the kaolinite and montmorillonite contents. Illite is the dominant clay mineral virtually throughout the stratigraphic column discussed here except for the Fig Tree, Witwatersrand and Northern Ecca Facies shales. This change of observed clay mineralogy is identical to that described by Weaver (1967) for North American shales and reproduced in Fig. 3.

Figure 3

Relative distribution of the four major clay-mineral groups through the geologic periods (Weaver, 1967)



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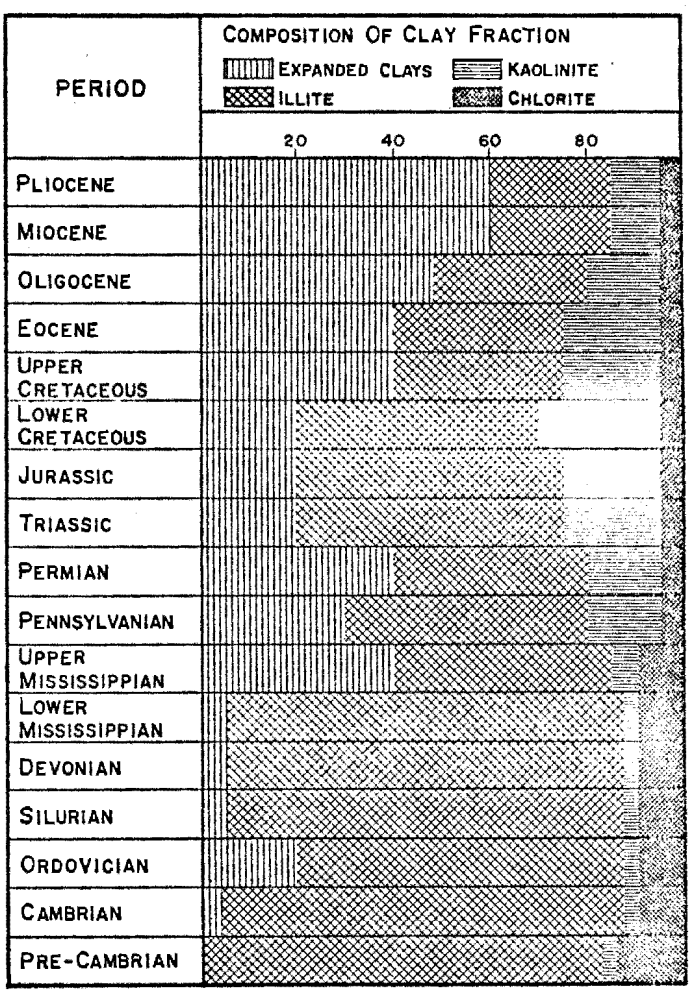

The reasons for this change of clay mineralogy with time are not definitely known and this is a subject of much controversy. They are generally ascribed to changes in the composition of the primitive atmospheres which controlled the formation of clay minerals in the source areas. The association of kaolinite with carbonaceous shales has been frequently noted and is considered to be due to the prevalence of acid weathering conditions. Weaver (1967a) attributed the generation of acid conditions to the accelerated production of humus, CO_2 and S by the prolific growth of land plants at these times. The species of clay mineral formed must be a function both of climate and source area petrology. Fe and Mg rich minerals in ultrabasic rocks probably tend to form chlorite and K and Al rich feldspars of granites tend to form kaolinite on weathering. If the broad assumption is made that acid weathering conditions produce kaolinite and if the source rock happens to be ultrabasic or basic, then Fe, Mg, Cr and Ni must be accomodated in some mineral phase other than kaolinite and is not included in the same sediment as kaolinite which seems unlikely.

The probable reason is that at the time of deposition the species of clay mineral deposited are largely dependent on the composition of the source rock. Chlorite is more abundant in ancient shales as mafic rocks probably outcropped more extensively in Precambrian times than they do today. Illite is the most readily developed clay mineral but kaolinite is developed under suitable conditions of chemical weathering.

The marked enrichment of Ni and Cr in the Fig Tree and Witwatersrand shales is clear in Fig. 42A. This has been discussed earlier and is attributed to the

presence of an ultramafic component in the source area for these rocks.

Cu, Co and Ni are strongly depleted in the Kunjas and Kuibis shales and this implies a source area control as they are both South West African Precambrian sequences. However, the younger Fish River Series shales do not show marked differences from shales from the eastern part of South Africa. Apart from these marked depletions, the average Co levels show slight variations but there is a definite tendency for Co concentrations to decrease in the younger shales. Apart from in the Fig Tree and Witwatersrand shales, the Ni pattern tends to duplicate that of Co, as would be expected, except that the variation is even less. The distribution pattern of Cu is remarkably similar to those of Co and Ni, but the scatter is greater and there is no trend with time of changing Cu concentrations although there is a regular decrease from the Witteberg through the Ecca to the Beaufort shales. However, the older Bokkeveld and Fish River shales have much lower average Cu concentrations than those of the whole of the Karroo System. V and Cr are two elements which display similar distributions after Malmesbury times. V levels are very constant throughout the South African geological column and this element shows no evidence of any enrichment in the ancient chlorite-rich Fig Tree and Witwatersrand shales. V and Cr do appear to separate to some extent in the non-carbonaceous Ecca shales, V usually being more abundant than Cr. The concentrations of Cr decrease in the younger shales reaching a minimum in the Southern Ecca Facies. The concentrations of Zr in shales increased from Fig Tree to Kuibis times and then showed a

small but definite tendency to decrease in younger shales. Be and Yb are elements which are not normally discussed together, but in the sequence of rocks studied here their average abundance distributions parallel each other remarkably closely although Be displays a wider variation than Yb. Both elements are depleted in the Fig Tree and Witwatersrand shales but subsequently the average concentrations vary very little and there is no further tendency for the averages to increase or decrease in the younger shales.

Fig. 42A shows marked enrichments for some trace elements in the chlorite-rich Fig Tree and Witwatersrand shales, but the Cango and Bokkeveld shales, which contain subordinate amounts of chlorite, do not exhibit these same features. The kaolinite-rich Northern Ecca Facies element distributions pattern shows slight peaks for the elements Be, Co, Ni, Cr and Zr. However, as has been discussed earlier, most of these enrichments are attributed to the organic and not the kaolinite content of these shales. No non-carbonaceous kaolinite-rich samples were available for analysis. Thus Fig. 42A does not reveal an affinity for any particular clay mineral by any particular element except for the Cr and Ni association with chlorite in the ancient chlorite-rich shales. No elements show marked trends of concentration variations with age, but Co and Ni show a slight decrease in concentration in the younger shales and Zr shows an increase followed by a decrease.

8. THE USE OF TRACE ELEMENTS AS INDICATORS OF ENVIRONMENT OF DEPOSITION

The reconstruction of the depositional conditions of ancient environments has long been of great interest to geologists, chiefly to distinguish marine sediments from fresh water sediments to aid them in their search for petroleum deposits. Characteristic fossils will always remain the most reliable indicator of depositional environment but unfortunately they are not always present, and not all fossils are useful as the habitats of most ancient fauna are not reliably known. Indicator clay minerals have been used for this purpose but it is now considered that their use is unreliable although there is a broad correlation between depositional environment and clay type. Fresh-water shales tend to have kaolinite as the dominant clay and marine shales tend to have illite and montmorillonite as the dominant clays. However, as mentioned earlier, Weaver (1958) showed that no particular clay mineral is restricted to any particular depositional environment. Thus to use a ratio of clay minerals like illite-kaolinite, as Degens et al (1957) did for the Pennsylvanian shales, is indicative but not conclusive evidence of depositional environment. Where it occurs, glauconite is also indicative of a marine origin but, not only is it rather uncommon in shales, but Porrenga (1968) has shown that its formation is not restricted to marine conditions.

Consequently geochemical criteria have been used by many workers in an attempt to distinguish depositional environments. Eh - pH conditions are often

a controlling factor in the formation of diagenetic minerals and much work has been done in recent years in determining the boundary conditions which control the formation of diagenetic minerals (Garrels and Christ, 1965, Helgeson et al., 1969). Thus a study of the diagenetic sulphide, carbonate and iron minerals can provide significant information to enable limiting pH - Eh conditions to be placed on a depositional environment. However, such information need not necessarily distinguish between marine and fresh-water depositional environments. Curtis (1967) concluded that the physiochemical conditions of the diagenetic environment of the British Westphalian coal measures, in which both siderite and pyrite were formed, were within the range pH 7 to 8 and Eh - 0.2 to - 0.3V. These values were maintained throughout the depositional sequence studied which spanned marine, brackish and fresh-water environments. Although he found a trend of pyritic basal sediments to sideritic non-marine strata, he concluded that pyrite formed when sulphide species were available and siderite formed under high CO_2 partial pressures but only in the absence of sulphide species. Thus derived pH - Eh data need not necessarily provide paleosalinity information. Unknown factors in ancient depositional environments which affect the equilibrium position are rate of sedimentation, availability of sulphides and partial pressure of CO_2.

Degens et al. (1957) pointed out that an effective geochemical paleosalinity environmental indicator required the following characteristics:

1) Markedly affected by salinity changes,

2) Sufficiently abundant to be precisely measured,

3) Relatively widespread,

4) Formed or concentrated in the shale itself,

5) Relatively unaffected by epigenetic changes.

Of these factors by far the most important is the first, but it is extremely difficult to find a critical indicator which is reliably strongly affected by changes of salinity.

Nicholls and Loring (1960) concluded that syngenetic adsorption is much more important than syngenetic diagenesis and this effect can be used in studying sedimentary processes. Thus chemical compositions can be more useful than mineralogical compositions. They noted that Na^+, Mg^{2+} and K^+ are strongly adsorbed by clay minerals in sea-water, the order of adsorption being dependent on salinity. At the salinity indicated they believed that K^+ was preferentially adsorbed and they wanted to use Na/K ratios as an indicator of rate of sedimentation as had been observed by Hirst (1958). They found that at constant pH and constant salinity the Na^+/K^+ ratio of the accumulating clay minerals was a useful indicator of relative rates of deposition. Nicholls and Loring (1963) suggested that the alkalis could be used as paleosalinity indicators, but Danchin (1970) concluded that Rb and Cs were desorbed from detrital clays on entering the oceanic environment and that consequently the Rb and Cs contents of marine clays were relict from their provenance weathering environments. Thus it was most unlikely that they could be used as paleosalinity indicators.

The use of boron as a paleosalinity

indicator for ancient sediments has aroused some controversy in recent years. Experimental work such as that by Harder (1961) and Fleet (1965) has proved that considerable amounts of boron are sorbed by illite under marine conditions and eventually migrate into the lattice from where the boron can only be removed by the most severe treatment. However, recycled illite being deposited in a fresh-water environment will contain considerable boron if it has previously passed through a marine cycle. Spears (1965) even came to the conclusion that the boron content of the illite was fixed during the weathering of the source rocks. Shaw and Bugry's (1966) conclusion from their work on North American shales that boron can be used with caution seems a reasonable one although it is felt by the present author that the control is largely mineralogical rather than salinity, as it has been reasonably well established that illite is dominant in the marine environment and kaolinite in the fresh-water although neither is restricted to any one environment. Harder (1961) found kaolinite to be a poor sorbant for boron compared to illite. Shaw and Bugry (1966) suggested that boron concentrations of less than 50 ppm were strongly indicative of fresh-water sedimentation and greater than 110 ppm likely to be of marine origin. In his work on South African shales Nel (1968) found that the marine Bokkeveld series contained significantly more boron than the fresh-water Ecca Series, although several anomalous results were reported.

Following Harder's (1961) work, however, this might be purely a mineralogical control and not an environmental one. Hingston (1964) also found

that at neutral pH the maximum amount of adsorbable boron calculated from the Langmuir Isotherm was much greater for illite, at 154 ppm, than for montmorillonite and kaolinite, at 17 ppm and 11 ppm respectively. Because of its high adsorption characteristics boron might have been a good indicator element, but, as Cody (1971) has strongly emphasized, its tendency to migrate to structural positions means that recycled clays can have high boron concentrations irrespective of the depositional environment.

Several workers have suggested particular trace elements which could be used as environmental indicators. These trace elements have been selected empirically on the basis of their concentrations in particular shale sequences studied by these workers. Degens, Williams, and Keith (1957, 1958) and Keith and Degens (1959) found B, Li and Rb to be enriched in marine shales and Ga in fresh-water shales. On the basis of their work and using B, Ga and Li together with V concentrations in Precambrian Finnish phyllites, Lonka (1967) concluded that the Precambrian oceans had a lower salinity than modern oceans. Tourtelot (1964) found B, Cr, V and Zn to be enriched in marine shales and Ga in non-marine shales. Levedev (1967) determined all these elements amongst others in Russian Jurassic and Lower Cretaceous clays and found only B, Sr and Ti to be consistently enriched in marine clays. Potter, Shimp and Witters (1963) concluded that B, Cr, Cu, Ga, Ni and V were significantly more abundant in marine than in fresh-water argillaceous sediments. They found that a discriminant function based only on B and V data effectively separated samples from the two types of depositional environment into two fields.

A similar study can be made of several sedimentary sequences of the South African geological column. For this purpose the results of the shales from the Bokkeveld, Witteberg, Central Ecca and Somkele Borehole (Northern Ecca) have been chosen. Of great importance is the fact that all contain illite as a dominant clay mineral so it is hoped that the possible complicating dactor of variable clay mineralogy has been largely removed. However, the Ecca samples contain subordinate amounts of kaolinite and the Bokkeveld and Witteberg samples contain subordinate amounts of chlorite so a slight difference in mineralogy is present. Also the Ecca samples contain variable amounts of carbonaceous material. The Bokkeveld samples are of marine origin and the other three groups of fresh-water origin. Their compositional similarity is shown in Table 27 which gives their average major element contents calculated on a volatile-free basis. Also included are the average concentrations of some trace elements and inter-element ratios. The closeness of the two major components, SiO_2 and Al_2O_3, is particularly striking.

The most obvious feature of the trace element data is the constancy of Ga concentrations and Ga/Al ratios. As mentioned before several workers have found Ga to be concentrated in fresh-water shales, and the probable explanation is that kaolinite-rich shales have been analysed and the high Ga content is due to the high Al content of kaolinite. Thus the Ga enrichment has been controlled by mineralogy and not by the depositional

Table 27

Average major element abundances in weight percent on a volatile-free basis (Danchin, 1970) and trace element abundances in ppm and some inter-element ratios of marine and fresh-water shales

	MARINE	FRESH WATER		
	Bokkeveld	Witteberg	Central Ecca Facies	Northern Ecca Facies-Somkele B.H.
SiO_2	67.4	66.9	66.0	68.6
TiO_2	1.0	0.9	0.7	0.7
Al_2O_3	17.7	18.8	18.0	17.8
Fe_2O_3	6.6	7.8	6.6	5.4
MgO	1.8	1.5	1.9	1.5
CaO	0.3	0.3	0.7	0.6
K_2O	3.5	3.5	3.8	3.4
Cu	18.7	28.6	30.7	24.8
Ga	19.8	21.4	21.2	20.5
Zn	75.8	74.2	78.5	82.6
Co	10.5	13.0	11.5	13.1
Ni	36.9	36.6	27.2	26.2
V	127	94.7	106	78.5
Cr	106	93.6	72.3	59.0
Th	16.8	17.0	18.0	18.6
Pb	30.2	28.0	29.8	30.7
Ni/Co	3.88	2.92	2.38	1.98
V/Cr	1.17	0.98	1.56	1.34
$Ga/Al.10^4$	2.22	2.26	2.47	2.39
$V/Al.10^4$	14.1	9.91	13.1	9.12
$Cr/Al.10^4$	11.7	10.0	7.8	6.83
$Cu/Al.10^4$	2.06	2.88	3.93	2.86

environment. In the discussion on Ga it was pointed out that there does appear to be a slight dependence of Ga/Al ratio on the clay mineral species. Fig. 28A shows that the low Al chlorite-rich Fig Tree shales tend to have lower ratios than the high Al kaolinite rich Northern Ecca Facies shales. Illite-rich shales tend to have intermediate values. This is verified by the data of Table 25A which show that the Fig Tree, Bokkeveld and Northern Ecca shales, which contain dominant chlorite, illite and kaolinite respectively, have average Ga/Al ratios ($x10^{-4}$) of 2.10, 2.22 and 2.32 respectively. This is further substantiated in Table 27 in which it is seen that the Bokkeveld and Witteberg have essentially the same Ga/Al ratio, whereas the Central Ecca and Somkele Borehole shales, which have a kaolinite component, have significantly higher ratios.

In addition to Ga, it is clear from Table 27 that Zn, Co, Ni, Th and Pb do not appear to be enriched in marine shales. However, V and Cr are more concentrated in the marine Bokkeveld shales and Cu is definitely more concentrated in all the fresh-water shales. The Ni/Co ratios are highest in the marine shales and lowest in the fresh-water shales as was mentioned earlier in the section dealing with the distribution of Ni and Co. However, as neither Ni nor Co appear to be enriched in the marine shales and as the average Ni/Co ratios show a large dispersion the use of this ratio appears to be of doubtful reliability.

Therefore, the results of this work indicate that V and Cr are enriched in marine shales and Cu in fresh-water shales. It has to be presumed that these excesses are the result of mechanisms or reactions

which have been initiated by the depositional environment and are not due to differences in source rock compositions. If these differences are a function of source rock composition then the use of these elements is merely differentiating between the shale sequences and not the environment of deposition. To establish the reliability of the use of these elements as environmental indicators much research should be done on their sorption characteristics with various clay minerals. As pointed out by Cody (1971) ideally they should form only a moderately strong sorption bond so that possible adsorption or desorption reactions can occur according to the depositional environment. If too strong a bond is formed, as with B, recycled clays can give misleading information because of inherited characteristics. If too weak a bond is formed post-depositional processes might effect a redistribution of the elements and also give misleading information. It is interesting to note that Cody (1971) also concluded that V and Cr showed potential as good indicator elements and Tourtelot (1964) found V and Cr to be enriched in marine shales. Furthermore, Potter, Shimp and Witters (1963) also found V and Cr, amongst others, to be enriched in marine shales. However, they found Cu to be concentrated in marine shales which is the opposite result to that of this work.

Cu/Al, V/Al and Cr/Al ratios were calculated for these four groups of rocks to minimise the dispersion of values caused by the diluting effect of quartz and heavy minerals. The amounts of feldspar are considered to be too small compared to the clay mineral contents to significantly affect the Al content and therefore these ratios. These ratios are presented in Table 43A and it

is clear that they show a far smaller dispersion than the absolute concentrations. The average ratios, listed in Table 27, reveal that the V/Al and Cr/Al ratios are clearly higher in the marine shales and the Cu/Al ratio is clearly higher in the fresh-water shales. All the ratios and the average ratios have been normalised and then plotted on a triangular diagram which is presented as Fig. 43A.

Two well-separated groups are formed by the marine Bokkeveld shales on the one hand and by the fresh-water Somkele Borehole and Central Ecca shales on the other. Four Witteberg samples lie well into the Fresh-water region but the rémaining three lie well in the Marine. This could be interpreted as indicating the presence of marine incursions during Witteberg times or else the samples were collected from shales wrongly identified as Witteberg. Bokkeveld shales do outcrop close to where these samples were collected.

As, of the elements determined in this work, V and Cr appear to be the two elements most consistently enriched in marine sediments, V/Al and Cr/Al ratios have been plotted against each other in Fig. 44A. Although there is some overlap, the points separate into a distinct marine and fresh-water field. Perhaps a plot of these two ratios might be suitable for comparing shales from different parts of the world. A triangular plot of these two ratios and the B/Al ratio would not be effective in separating shales from the two depositional environments as an element which is depleted in the marine environment is necessary for a triangular plot to be used. For B/Al ratios to be utilised, bearing in mind the uncertainties mentioned before with regard to inherited B content of shales, two axis plots of B/Al against V/Al, B/Al against

Cr/Al and B/Al against V/Al + Cr/Al might be useful in separating shales of different depositional environments. Unfortunately only some of the samples of this work have been analysed for B (Nel, 1968) so these plots have not been constructed. Nel (1968) found average B concentrations for the Bokkeveld, Witteberg and Somkele Borehole shales of 60 ppm, 42 ppm and 23 ppm respectively, showing that in South African shales as well B tends to be concentrated in shales of marine origin.

The results of this work indicate that V, Cr and Cu, are potentially useful as indicators of environment of deposition. There is still the possibility, however, that they are distinguishing between the Bokkeveld, Witteberg and Ecca Series and not between marine and fresh-water shales. Separated less than two micron clay fractions should be used as the higher trace element concentrations improve the precision of the analysis and also it is this fraction which is most intimately concerned in adsorption reactions and thus most likely to be more sensitive to changes in the depositional environment. Too few separated clay fractions were analysed in this work for them to be of much use in this respect.

The dangers of attaching too much importance to differences in trace element concentrations in whole rock samples is demonstrated by the data of Tourtelot (1964) which are plotted in Fig. 43A. Although he found V and Cr to be enriched in marine shales, he found no trend in the Cu concentrations and consequently his marine and fresh-water V, Cr and Cu data plot in the fresh-water region of Fig. 43A.

It is evident that much experimental work must be done on the sorption characteristics of V, Cr and Cu with different size fractions of various clay minerals before they can be reliably used as environmental indicators.

It is felt that there is no single ideal environmental indicator element. The complex composition of shales and the complexity of syngenetic and diagenetic reactions are responsible for a wide variation of trace element concentrations irrespective of the depositional environment. B, Cr, V, and perhaps Cu, data used in conjunction with other types of evidence, especially paleontological, probably provide the best means for obtaining reliable information concerning depositional environments.

9 SUGGESTIONS FOR FUTURE RESEARCH ON SOUTH AFRICAN SHALES

The Dwyka Series of the Karroo System has been very poorly sampled and studied in this work but merits much closer attention as a succession of shales at the top of the sequence are considered to have been deposited as black organic, highly sulphuretted muds in fairly deep water. In view of modern knowledge that such sediments are known to often concentrate some trace metals to a spectacular degree, such as the Kupferschiefer in Germany and the modern organic-rich muds off Walvis Bay, South West Africa, it would be most interesting to ascertain whether similar enrichments can be detected, or whether in fact no trace metals are enriched, which is what the results of this work indicate. As the whole series is considered to be of fresh-water origin, perhaps the lower trace element content of the overlying water has controlled the limited incorporation of trace elements into the underlying sediment.

The distribution of Cr in the carbonaceous shales and its correlation with the organic content of these shales has necessitated the suggestion of authigenic anatase being associated with the carbonaceous matter. Porrenga (1967) and Danchin (1970) have noted the enrichment of Ti in separated clay fractions and have also suggested the presence of anatase as Goldberg and Arrhenius (1958) have reported the authigenic presence of this mineral in Pacific pelagic sediments. More detailed analytical and mineralogical studies should be carried out on selected samples and all their separated fractions to determine the sedimentary geochemistry of Ti more exactly and this should throw further light on the distributional

behaviour of the associated elements Cr and Nb. Perhaps electron microprobe studies might detect the presence of Ti and Cr-bearing phases.

As mentioned earlier, the possible use of Cr, V and Cu as environmental indicators should be examined further. Illite-rich unweathered Bokkeveld, Witteberg and non-carbonaceous Ecca samples should be collected and the less than two micron clay fractions analysed for Cr, V and Cu. If the results plotted on a triangular diagram verify marine and non-marine "fields", experimental work on the sorption characteristics of these elements along the lines of Hingston (1964) would be justified. This would include separating pure clay mineral fractions of chlorite, illite, kaolinite and montmorillonite desorbing the trace metal content by mild chemical treatment, and then placing the different clay mineral species in contact with fresh and saline water of various pH's and having trace metal compositions approximating those of fresh-water and sea-water.

The acetic acid soluble fraction of fresh Bokkeveld, Witteberg and Ecca illitic shales should also be analysed with a view to detecting possible differences in soluble trace metal content of not only these elements but of other trace elements as well. These could include the less abundant trace elements such as Ag, As, Sb, Bi and Tl, This approach, which has been used before by workers such as Nicholls and Loring (1962), might also provide a means for differentiating between fresh-water and marine shales.

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