GEOCHEMICAL AND MINERALOGICAL ASPECTS OF THE MOLTENO FORMATION, SOUTH AFRICA

by

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DECLARATION

All work in this thesis is the original work of the author except where specific acknowledgement is made to the work of others.

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ABSTRACT

The Triassic Molteno Formation is a clastic sedimentary sequence consisting of a series of cycles, dominated lithologically by coarse grained sandstones.

Aspects of the petrography have been examined using the conventional petrographic microscope as well as the scanning electron microscope. Both solution and overgrowth features are present not only on the quartz grains but also on certain of the heavy mineral species present. Intrastratal solution of garnet would appear to be a significant feature in the Molteno Formation. Mineralogical examination of the laterally persistent Indwe Sandstone Member indicates no significant variation in heavy mineral content. Evidence from a study of zircon elongation ratios shows the presence of two distinct zircon populations indicating two provenance areas. X-ray diffraction and electron microprobe analysis has identified mineral species characteristic of granites, pegmatitic granite and metamorphic rocks, especially amphibolites. Palaeocurrent data indicates that this source area lay to the south-east; to the south the source area consisted mainly of the Cape Supergroup sediments.

Analysis for Nb, Zr, Y, Sr, Rb, Zn, Mn, Ba, Cu, Ni, Co, Cr, V and Ti for 22 samples from the Molteno Formation, indicates, as expected for a highly arenaceous sequence, a substantial depletion in these trace elements. No consistent variation of trace element concentration occurs with height in the sequence so trace element content may not be used for purposes of stratigraphic correlation. There are indications of trace element variation with geographical position, no doubt a reflection of the contribution of 2 source areas of different compositions. Factor analysis of the interelement correlations has identified 3 factors which influence the trace element content of the Molteno Formation : these are a "heavy mineral" factor, a "pH-Eh" factor and a "clay mineral" factor. These trace factors are ultimately an expression of the source rock composition, the prevailing

climate and a combination of the two. Comparison with the more argillaceous overlying Elliot Formation, indicates that factors influencing geochemical variation in this sequence were far more complex than for the Molteno Formation.

CONTENTS

I INTRODUCTION

A. EARLIER WORK

A.H. Green in 1883 used the term "Molteno Beds" to describe the strata surrounding the village of Molteno. The strata were of particular interest because of the occurrence within them of coal measures. Du Toit in various reports (1903-1911) described and named many units in the Molteno, such as the Indwe Sandstone and the Guba coal. Many of the names are still in use today. Schwarz (1916) described a heavy mineral suite from the Molteno Beds, within which he identified diamonds. Other early reports on the Molteno are provided by Haughton (1924), du Toit (1926), van Eeden (1937) and Stockley (1947). Koen (1955) has tentatively identified the Molteno to be present as far north as the Waterberg coalfield; he has however not compared the heavy mineral suite he obtained with one from the main Molteno area of deposition. In view of the great distance the areas are apart, this attempted correlation must be seen as extremely dubious. Rust (1959) conducted the first detailed analysis of what was by then called the Molteno Stage. He described the stratigraphy, sedimentology and general petrography of the sandstones in the Molteno area.

As a result of renewed interest in the coal reserves of the Molteno, further investigation of the sequence was carried out in the early sixties. One product of this was the work of Ryan (1963). He conducted a study along much the same lines as Rust (1959), but in the Indwe district. Turner (1969-1978) has contributed greatly to the state of knowledge regarding the Molteno, which by then was known as the Molteno Formation (Johnson, 1967). Turner (1975) mapped the Molteno Formation on a regional basis and has been able to define it as a lithostratigraphic unit in terms approved by the South African Code of Stratigraphic Terminology and Nomenclature (1971).

B. REVIEW OF THE SEDIMENTOLOGY AND STRATIGRAPHY OF THE MOLTENO FORMATION

1. Sedimentology

The Molteno Formation consists of a northerly thinning, intracratonic wedge of clastic sediments. Several fining-upwards cycles occur but only the second cycle, the Indwe Sandstone Member, is regionally extensive. Each of the cycles is characterized by,(Turner, 1975(a)) :

a) A basal pebble conglomerate or pebble bed overlying an erosional disconformity of low relief.

b) Grit and coarse sandstone which becomes progressively finer higher in the sequence.

c) This is followed by finer grained sandstone, siltstone and silty shale.

d) Towards the top of a cycle a sequence of shale with occasional thin lenticular coal seams is present.

Most conglomerate clasts in the Molteno Formation fall into the pebble size range (average length of long axis = 16 cm), although boulders up to 76 cm have been recorded (Turner, 1977). The majority of the pebbles are of quartzite but Rust (1959) also records the presence of slates, hornstones and tillite. Ryan (1963) asserting that at least 95% of the clasts were of quartzite, also recorded chert, granite, Fe-slate, vein quartz, hornfels, diabase and quartz felsite pebbles. He found that the heavy mineral suite derived from these quartzite pebbles corresponded to that found by Theron (1962) for the Witteberg quartzites. From this he concluded that the Witteberg Group constituted the source for the majority of the pebbles in the Molteno Formation. Turner (1975(a)) agrees with this interpretation and has recorded the presence of biotite pegmatite clasts in the Molteno Formation.

The arenaceous sediments are of very simple mineralogical compositions consisting principally of quartz, feldspar, micas and rock fragments. They have been classified by Rust

(1959) as lithic sandstones and lithic sub-greywackes, while Ryan (1963) places them in the subgreywacke class. Turner (1975(a)) prefers not to use the term "greywacke" because of genetic connotations inherent in the term, but rather modifies Gilbert's (1955) classification to call them "immature lithic sandstones", the term immature being necessitated by the high clay content.

The finer grained sediments, siltstones, mudstones and shales are similar in composition to the sandstones. The siltstones consist of quartz with minor amounts of feldspar and mica bound in a clay matrix. In the finer grained argillaceous sediment, illite and montmorillonite are the common clay minerals (Turner, 1971). Associated with the finer grained sandstones are various coal seams. These are the Suurkop coal, the Cala Pass coal, the Guba coal and the Ulin coal, Turner (1975(a)). A peak coal production of almost 200 000 short tons of coal per year was reached during the period 1900-1904, but with discovery of the Witbank coals, production rapidly declined. The coals tend to be thin and lenticular and contain shale partings. They are of poor quality, low volatility and have a high ash content; Turner (1971) considers the coal to be autochthonous, i.e. to have formed in situ and he has estimated recoverable reserves to total less than 30 million tons. In view of this low amount and the poor quality of the coal he considers it to be of little economic significance.

Pulsatory diastrophism in the source area is the mechanism by which the well-defined cyclicity (Turner, 1969(c)) of the Molteno Formation may be explained. Rust (1959) states that the second stage of the Cape orogeny was the cause of the Molteno sedimentation. He recognizes a poorly defined "stratigraphic inversion" whereby increasing stratigraphic levels of the Molteno Formation may be correlated with the successively denuded Beaufort, Ecca, Dwyka and Witteberg Groups. Early uplift was concentrated in the south; as the orogeny progressed the axis of uplift shifted eastwards (Turner, 1975(a)). Palaeocurrent evidence lends support to

this statement. Rust (1959) and Ryan (1963) collected data from restricted areas; in both studies the major transport direction was recognized as being northwards. Both authors indicated the possibility of a second subsidiary current being directed westwards. In his regional study, Turner (1975(a)), clear definition of the palaeocurrent directions over the entire basin was obtained. Palaeocurrent data were also collected in the present study and these were found to be consistent with the large numbers of readings taken by Turner (1975(a)). He took approximately 5800 measurements on a total of 540 outcrops. Trough cross-bedding was the feature most commonly measured but sedimentary features such as current lineations, ripple marks, fossil logs and erosion channels were also incorporated into the final synthesis. A consistent direction of sediment towards the north-west is evident (Turner, 1977). By separation of the data so that an arbitrary southern region is defined, Turner (1978) recognizes the existence of a two component flow system. The dominant direction of flow is directed in a northwesterly direction while the subsidiary flow, recognizable in the southern area, is directed in a northeasterly direction. The operation of the two flow components is to a certain extent time-sequential. As has been noted already, earliest uplift occurred in the southern area, this led to a northeasterly directed flow and deposition of the Bamboesberg Member, which is only present in the southern area. With passage of time, as the axis of major uplift migrated eastwards, the northwesterly transport direction became increasingly important until finally it dominated the palaeocurrent trend (Turner, 1977). A certain degree of vertical variability might be expected in the cross-bedding directions. Turner (1975(a)) finds that this is not, in fact, the case. Figure 1 and Figure 2 are from Turner (1977), Figure 1 indicating on rose diagrams the palaeocurrent directions for the basin aggregate, as well as the directions for the basin excluding the southern area, and for the southern area by itself. Figure 2 represents the direction of major sediment transport during the Molteno sedimentation.

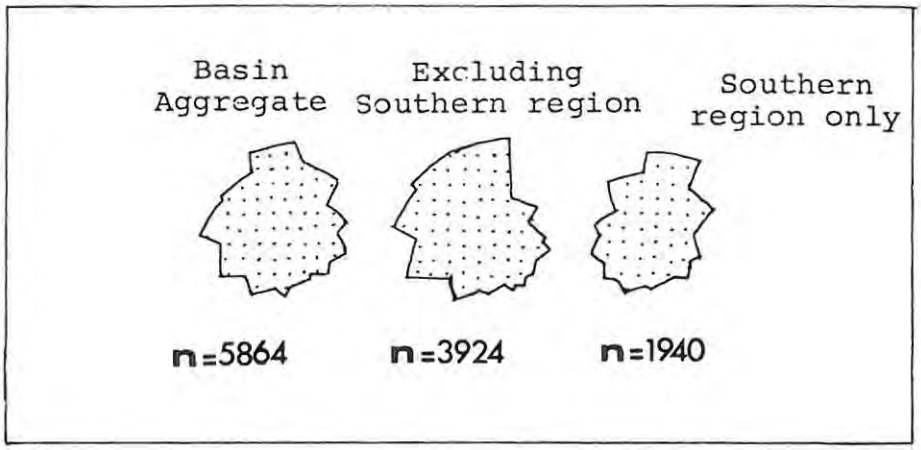


Figure 1 : Rose diagrams indicating palaeocurrent directions for the Molteno Formation (from Turner, 1977).

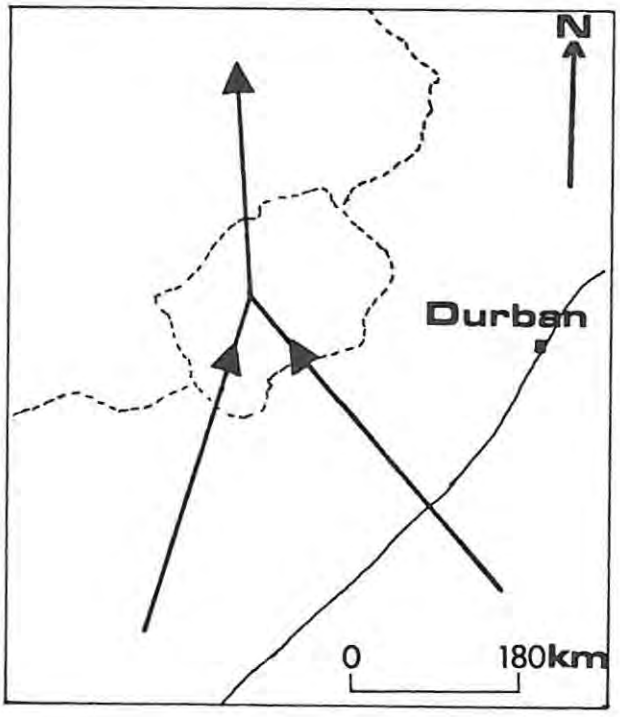


Figure 2 : Directions of major sediment transport during Molteno sedimentation (from Turner, 1977).

2. Stratigraphy

The stratigraphy of the Molteno Formation is dominated by the cyclical character of its sediments. Robinson et al. (1969) divided the Molteno Formation into 3 members : the basal Boesmanhoek Member, the Indwe Sandstone Member and the upper unit, the Kramberg Member. Turner (1975(a)) renames the lowermost unit the Bamboesberg Member. In the present study the divisions proposed by Turner (1975(a)) are used with the exception that the name Kramberg Member is retained for the lithologies above the Indwe Sandstone Member. The basal cyclical unit corresponds to the Bamboesberg Member while the Indwe Sandstone Member constitutes the second cycle. The upper fining-upwards cycles may be collectively grouped into the Kramberg Member. Because the Molteno Formation constitutes a northerly-thinning wedge, a full stratigraphic sequence consisting of all the cycles, is only present in the southerly areas. The Bamboesberg Member wedges out rapidly northwards as do the cycles in the Kramberg Member. In the far north of the basin the only representative of the formation is the second cycle, the Indwe Sandstone Member. Figure 3 shows the generalized stratigraphic relationships in the Molteno Formation.

In the southern part of the basin the lower contact of the Molteno Formation is defined by the base of the Bamboesberg Member. Further north, when the Bamboesberg Member has wedged out, the contact is defined by the base of the Indwe Sandstone Member. Criteria for distinction from the underlying Upper Beaufort are the presence of coarse, gritty sandstones, abundance of large quartzite pebbles, the absence of red shales and the presence of Dicroidium flora. The contact in the field is normally marked by a break in the topographic slope, the sandstones in the Molteno Formation being more resistant than the underlying Beaufort Group lithologies. The contact is often marked by the formation of cliffs and ledges. Indeed the entire Molteno succession is characterized by a terraced type of topography which normally distinguishes it from both the strata above and below.

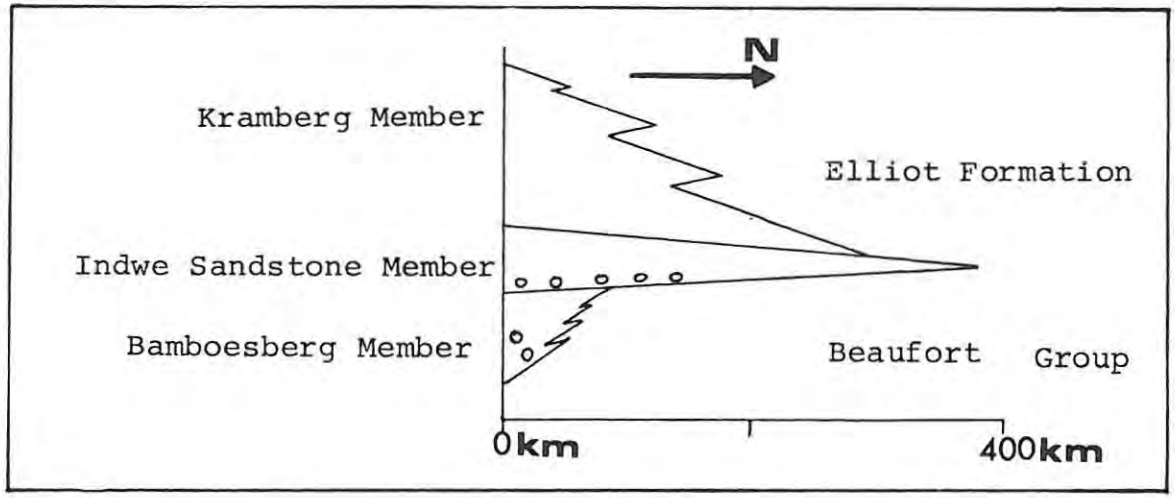


Figure 3 : Generalized stratigraphic relationships in the Molteno Formation (from Turner, 1977).

The Indwe Sandstone Member consists of a sequence of coarse-grained sandstones with occasional thin lenses of finer-grained material also being present. It is in this unit that the highest concentration of pebbles and cobbles exists. Earlier work by du Toit (1903), considered the Indwe Sandstone to be a regionally extensive unit. This idea is contradicted by Turner (1969(b)) but in his later work, Turner (1975(a)), does in fact recognize the Indwe Sandstone Member as a lithostratigraphic marker horizon of regional importance.

Overlying this unit are several further cycles, grouped together as the Kramberg Member. The upper contact with the Elliot Formation is often difficult to define, but according to Turner (1975(a)), the following criteria may be used in making the decision :

a) Reptiles, especially dinosaurs, are very abundant in the Elliot Formation.

b) Red mudstones are common and are laterally and vertically persistent in the Elliot Formation. This criterion is often of dubious value because of localized occurrences in the Molteno Formation of red and purple argillaceous sediments.

c) The Elliot Formation contains no carbonaceous shales or coals.

d) Dicroidium flora is absent from the Elliot Formation.

e) Sandstones, when present, are fine grained in the Elliot Formation compared to the Molteno Formation.

Palaeontological criteria are thus important in the distinction between the two formations. The characteristic flora in the Molteno Formation is, as has already been noted, Dicroidium. The specific flora is not characteristic of a warm, humid environment, but has rather been assigned to a cool temperate climate (Anderson, 1975). There is some controversy regarding the presence of reptile remains in

the Molteno Formation. Stockley (1947), Ellenberger et al. (1967) and Ellenberger (1970) report reptilian fossils from the Molteno Formation. In fact Ellenberger (1970) considers the palaeoclimate to have been hot and wet on the basis of the fossil assemblages present. Turner (1972(a)) regards the stratigraphic interpretations made by the previous authors as being incorrect; rather he assigns the localities to either the underlying Beaufort or the overlying Elliot Formation. This confusion regarding stratigraphic interpretation is a result of the gradation between the finer grained sediments, especially in the case of the Molteno and Elliot Formations. The contact must sometimes arbitrarily be drawn at the uppermost gritty sandstone in the Molteno Formation. In the present study it was found most convenient to use the criterion of colour. The presence of red shales does not necessarily imply the Elliot Formation; nevertheless the lower contact of the Elliot Formation was drawn where the sediments were consistently red. It was found that in most cases this criterion was quite satisfactory.

C. AIMS OF THE PRESENT STUDY

Since the Molteno Formation has been thoroughly examined from a sedimentological and stratigraphical point of view, it was decided to investigate this well-defined unit using geochemical techniques more usually associated with igneous petrology.

Rhodes University is extremely well equipped for geochemical and mineralogical analysis. As well as an X-ray fluorescence and X-ray diffraction facility, an electron microprobe is also in operation.

It was thought that an examination of the trace element concentrations in the Molteno Formation might prove useful. An examination of trace element variation with geographic position could reflect the palaeocurrent directions and thus the influence of the two different provenance areas.

An attempt would be made to see if the Molteno Formation would be amenable to a geochemical stratigraphical correlation, by an examination of the vertical variation in the trace elements. Furthermore, the technique of factor analysis could be used to infer the underlying factors behind the interelement variations. A closer study of some of the mineral phases present might also add to our knowledge regarding the provenance areas of the Molteno Formation.

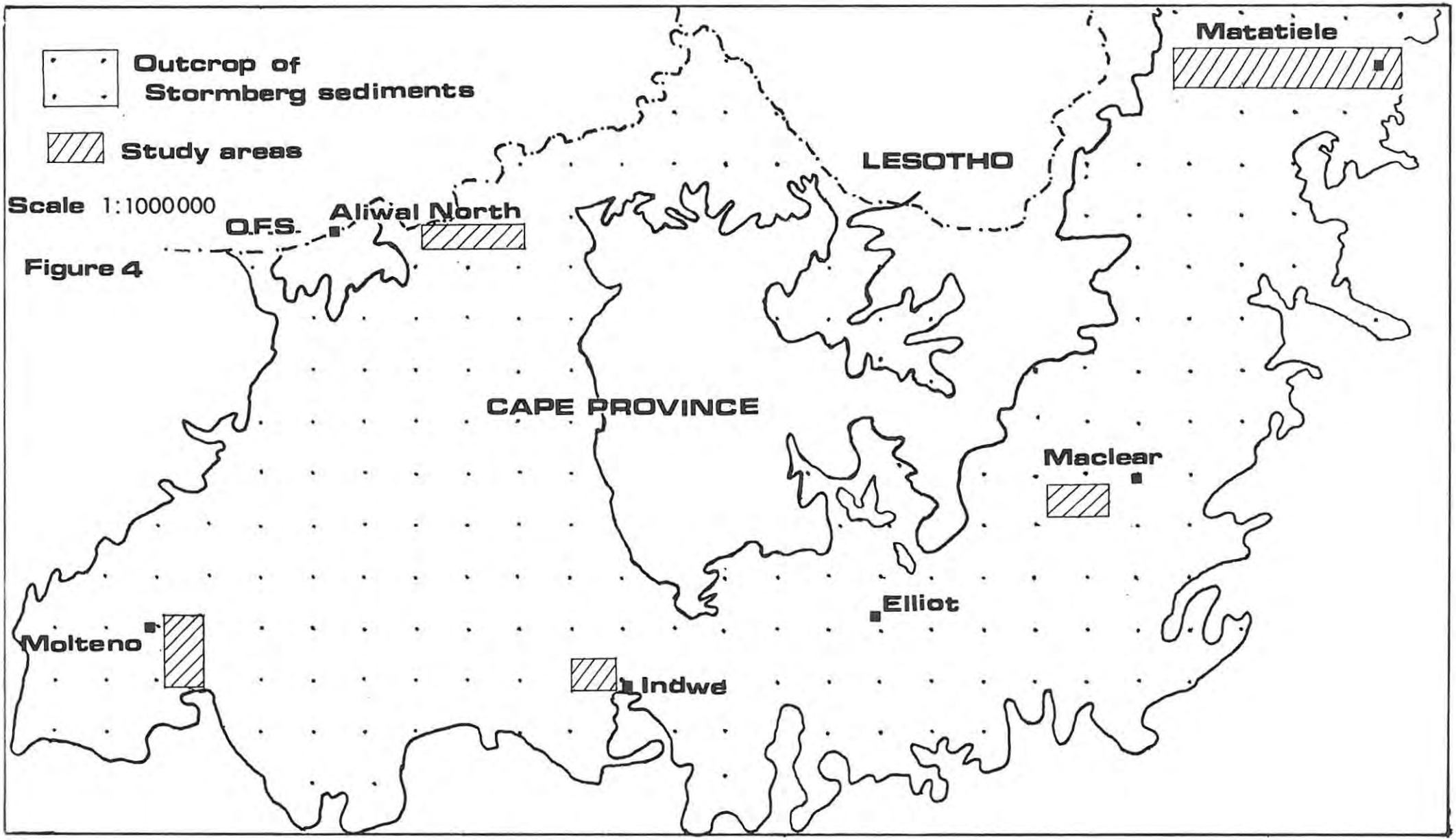
D. FIELD WORK

Field work was carried out during May and November, 1978. As only a limited time was available, collection of samples was confined to five areas. These were chosen so as to give a good geographic spread of the southern half of the Molteno basin. Areas were chosen near to Aliwal North, Indwe, Maclear, Matatiele and Molteno. Figure 4 gives the locations of the study areas and the approximate outcrop of the Stormberg sediments (which comprise the Molteno, Elliot and Clarens Formations).

In the Aliwal North area samples were taken on the farms "Sonnebloem" and "Schoongesig", some 12-14 kilometres to the east of Aliwal North. Samples from the Molteno area were taken from the Boesmanhoek Pass and from the Molteno mountain. Samples from Indwe were taken on the farm "Bannockburn" and from a recent road-cutting to the west of Indwe. All the samples from Maclear were taken on the farm "Brione" while in the Matatiele district they were taken on the farm "Compensation".

E. SAMPLING

By nature of the heterogeneity of sedimentary sequences it is extremely difficult to obtain a fully representative sample suite without resorting to collection of vast numbers of samples. Nevertheless an attempt was made to collect a reasonably representative suite.


Outcrop of
Stormberg sediments
Study areas
Scale 1:1000000
Figure 4
O.F.S.
Aliwal North
LESOTHO
Matatiele
CAPE PROVINCE
Maclear
Elliot
Molteno
Indwe

The Indwe Sandstone Member was adopted as a "base-line" for height measurements. In each of the areas at least one sample was collected from the Indwe Sandstone Member and several from above and below this unit. The stratigraphic heights at which the samples were taken, were recorded relative to the Indwe Sandstone Member using a barometric altimeter. Since atmospheric variations may affect the accuracy of height determinations made in this way, it was necessary to correct for any atmospheric variation by taking readings at a base station at the beginning and end of a traverse. Brief descriptions of the rock units samples and palaeocurrent data were also recorded.

F. ACKNOWLEDGEMENTS

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Finally special thanks are due to Marian and Patricia for the help and encouragement they have given me.

II PETROGRAPHY

Various authors have classified the arenaceous sediments of the Molteno Formation (Rust, 1959; Ryan, 1963; Turner 1975(a)). As a result of the heterogeneity of the Molteno sandstones, the author feels that any attempt to classify them as a whole, would be unwise. In fact the Molteno sandstones vary greatly in composition; orthoquartzites and arkoses are both represented in the sandstone suite.

Five samples of the Indwe Sandstone Member were analysed by X-ray fluorescence methods in order to determine the major element compositions of these very distinctive sandstones. Analytical conditions are given in Appendix A and results of the analyses are presented in Table 1.

TABLE 1 : MAJOR ELEMENT ANALYSES - INDWE SANDSTONE MEMBER

	AJR14	AJR29	AJR54	AJR64	AJR67
SiO_2	93,33	86,86	94,69	97,59	97,11
TiO_2	0,16	0,31	0,44	0,11	0,09
Al_2O_3	3,50	8,36	3,14	1,503	1,34
Fe_2O_3	1,49	1,49	0,35	0,41	1,07
MnO	-	0,08	-	-	-
MgO	0,05	1,15	0,04	-	-
CaO	-	0,10	0,02	0,04	-
Na_2O	0,14	0,01	0,01	-	-
K_2O	0,69	1,65	1,32	0,34	0,38
P_2O_5	-	0,02	-	-	-

Concentrations expressed as percentages

Extremely high concentrations of SiO_2 can be seen to dominate the analyses, making up almost 98% of one sample. Most of the SiO_2 will no doubt be present in the form of quartz but some will be present in feldspar or clays. The analyses for the samples compares favourably with

that given by Pettijohn (1975, p 210) for the "average" orthoquartzite. Since the constituents of sedimentary rocks are non-equilibrium assemblages it is not possible to calculate a "normative" composition from the bulk chemical analyses as in the case of the analyses of igneous rocks. Nevertheless the very high quartz content of the samples is plain.

While much of the quartz is present in the form of original detrital quartz grains, a significant proportion of the quartz may be present as diagenetic overgrowths, from whence comes the "sparkling" appearance of the rocks (du Toit, 1954; Haughton, 1969). The detrital cores are generally subrounded and are seldom seen in mutual contact with other detrital cores. The overgrowths are in optical continuity with the cores; the contact between the two being clearly marked by a thin line of inclusions. Plates 1(a) and 1(b) show quartz grains in various stages of overgrowth. The pattern of overgrowth on the grains in Plate 1(b) is of special interest. This grain appears to have been overgrown twice, each successive overgrowth being marked by a trail of inclusions. The first overgrowth has been rounded to much the same shape as the original detrital core. This implies a period of erosion and transport between the two periods of growth and is direct evidence for derivation from a pre-existing sediment. The early phase of overgrowth would have occurred while the grain was part of the southerly source area; rounding of the overgrowth would have occurred during subsequent transport northwards. The second phase of overgrowth would then have occurred after Molteno sedimentation had ceased and diagenesis commenced. The actual mechanism of quartz overgrowth has been ascribed by Turner (1972(b)) to growth <u>in situ</u> from acidic silica-saturated solutions trapped in the pore spaces at the onset of burial and diagenesis. The alternative mechanisms, pressure solution and replacement he considers to be unlikely.

Further investigation of quartz grain surface textures was carried using a scanning electron microscope, Jeol model JSM-U3 with TV scan accessory. Grains were selected from the Indwe Sandstone Member and mounted on stubs with sellotape adhesive. Prior to examination they were coated with a Pd-Au alloy.

Extensive overgrowth is a ubiquitous feature in the quartz grains examined. In fact none of the original detrital features still appear to be present on the grains. Such diagenetic effects invalidate any modal analysis of sandstone composition (Selley, 1976, p. 98) and make determinations of the palaeoenvironment using the surface features impossible. Solution features, i.e. chemical etch pits, are also present on some of the grains.

Plates 2 and 3 show the development of perfectly smooth quartz crystallographic faces. The grain in the right background shows the presence of triangular etch pits. Plate 4 shows a quartz grain in which a new phase of overgrowth has started. Krinsley and Doornkamp (1973) consider that perfect quartz crystal terminations will only occur when the rate of quartz precipitation is very slow. Under moderate rates of precipitation, the secondary growth takes the form of "plates" which are plastered onto the surface. Plate 5 and Plate 6 show the development of these "plates" and their relationship to the smooth faces. Possible chemical etch pits are also present in Plate 5.

The presence of both growth and solution features on quartz grains is a clear indication of derivation from a diagnetic environment (Krinsley and Doornkamp, 1973).

As has been mentioned the Indwe Sandstone Member contains large numbers of pebbles, most of them being Witteberg quartzite pebbles. One of these pebbles is shown in Plates 7(a) and 7(b). The distinctive interlocking texture, caused by recrystallization of the quartz is evident. The

presence of granitic and pegmatitic clasts in the Molteno Formation has also been mentioned. A note of caution should however be sounded before generalizations regarding the composition of the provenance areas are made on the evidence afforded by the presence of these clasts. While the Witteberg pebbles imply derivation from the Witteberg Group, granitic pebbles do not necessarily imply direct derivation from a granitic source. In the early stages of deposition the sediments of the Lower Karoo Supergroup were a source of detritus to the basin, albeit not a very important source (Rust, 1959). It is therefore possible that some of these granitic and pegmatitic pebbles could have been derived from erratics within the Dwyka tillite.

A common feature in the Molteno Formation is the occurrence of a fine network of rutile needles enclosed within quartz grains. These inclusions are normally oriented parallel to crystallographic directions. According to Friedman and Saunders (1978, p 32) the presence of rutile inclusions in quartz is indicative of derivation of the grains from either quartz veins or granites. Plates 8(a) and 8(b) illustrate this phenomenon.

The degree of weathering shown by the feldspars in the Molteno sandstones is variable. Plate 9 illustrates a relatively unweathered arkose (Sample AJR44), on which only a slight degree of alteration is evident on the plagioclase and microcline feldspar present.

The occurrence of feldspar and the degree of weathering shown is indicative of the maturity of the sediment (Todd, 1968). The maturity of a sediment is a function of both the intensity and the duration of the weathering process. If the intensity of the process is low then an immature product will be formed regardless of the duration of the process. The important factor affecting the intensity of the weathering process would seem to be climatic (Pettijohn, 1975). A cold climate would tend to retard the chemical processes operative during weathering and so immature

products may be transported away from the source. The duration of the process is determined largely by the relief of the source area since erosion is a function of relief. Rapid erosion is promoted in a source area of high relief; under these conditions soil-forming processes lag behind transportation processes so much, unweathered material may be transported away. The presence of feldspar in the Molteno Formation therefore implies erosion under cold climatic conditions in an area of high relief. The association of cold climatic conditions with areas of high relief is quite well known.

Whether all the alteration of the feldspar took place in the source area is doubtful. Ryan (1963) reports no difference in the degree of alteration of the feldspars at depth and at surface. This could imply that either all the weathering did in fact take place prior to deposition, or it is possible that the sandstones were permeable to such a degree that the feldspars would be equally altered at depth and at the surface. Turner (1975(a)) expresses contradictory viewpoints on this matter. On the one hand (Turner 1975(a), p 253) he states that the feldspar grains have not been affected by diagenetic alteration on modern outcrop weathering; on the other hand (p 292) he states that weathering of feldspar is a post-depositional feature. Hofmeyr (1971) concludes that clay minerals are principally formed in the weathering environment and not in the environment of deposition. It would seem to the writer that alteration of the feldspar to clay minerals has occurred both in the source area and after deposition. Some of the feldspars have undergone total alteration to clays. These clasts are often 2-3 mm in diameter; it does not seem conceivable that they could have survived transport without being destroyed, so it is suggests that alteration of these large grains occurred <u>in situ</u> after deposition.

Another characteristic of many of the sandstones in the Molteno Formation, especially in the Indwe Sandstone Member, is the pronounced reddish-brown colouration produced by

secondary iron minerals. The colouration may be restricted to the surface layer or may penetrate through the rock. According to Turner (1975(a)) the colouration is due to the presence of limonite.

A petrographic examination of the siltstones present in the sample suite revealed an interesting feature. Sample AJR61 contained quite significant amounts of apatite and garnet. Apatite is not present in the Molteno Formation according to Rust (1959); it is certainly uncommon as it was only observed in this one sample (see Plate 10).

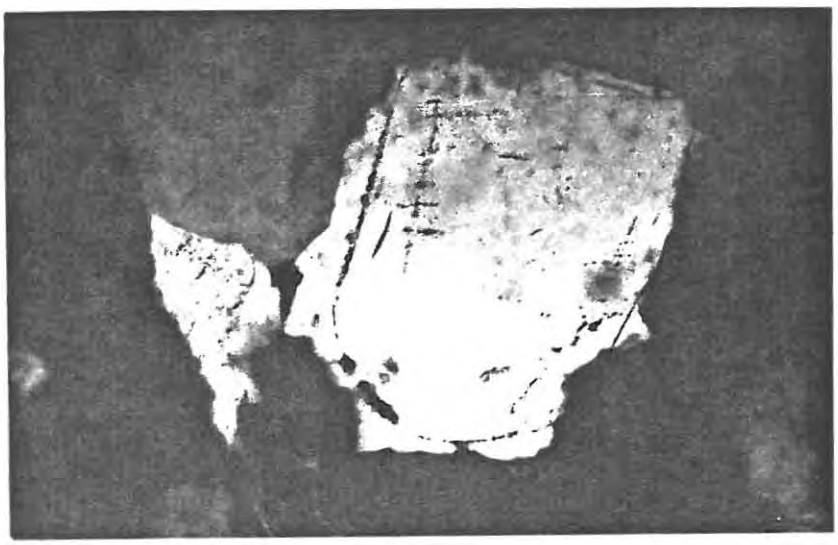


PLATE 1(a) : Rounded quartz overgrown by authigenic silica. Boundary delineated by a line of inclusions. Sample AJR64. Cross polars.

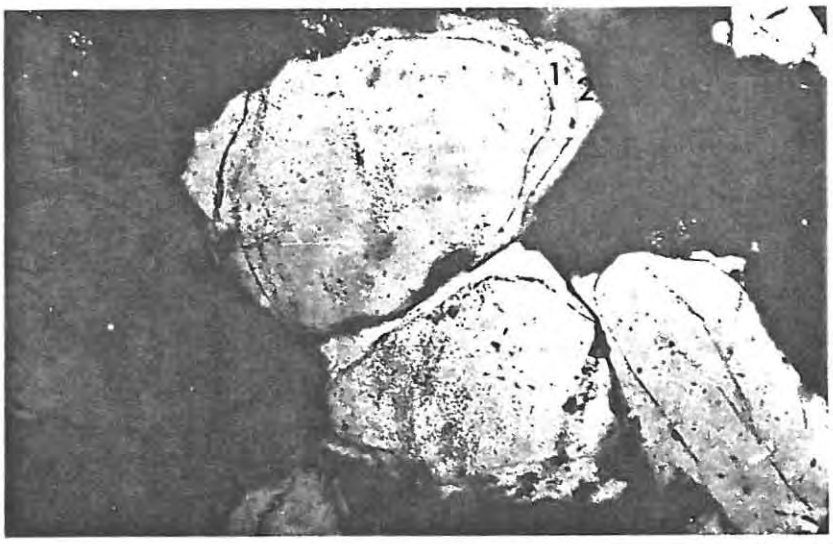
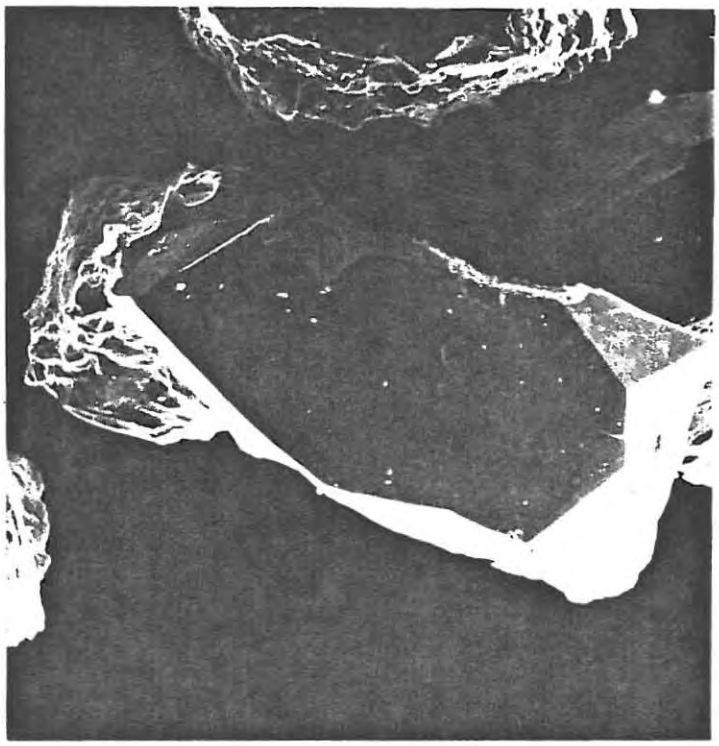
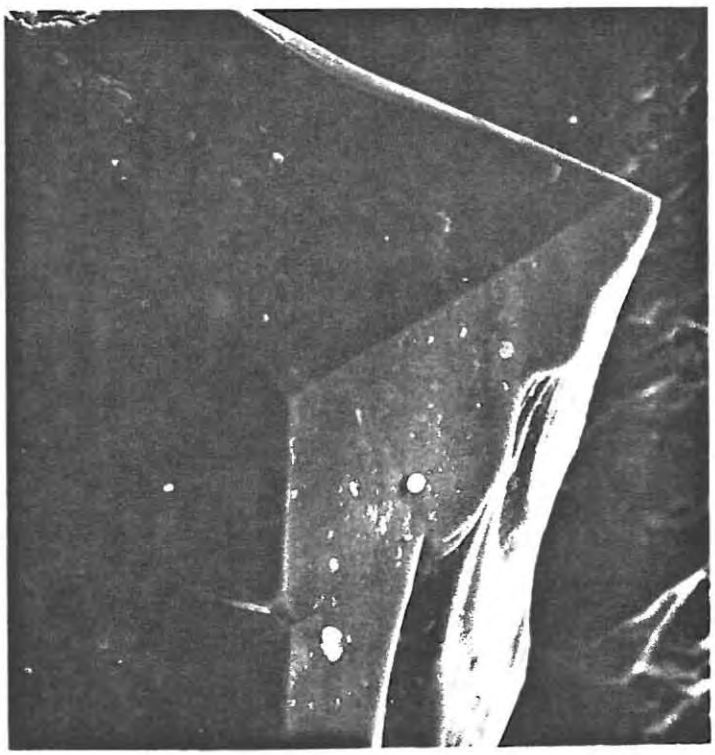


PLATE 1(b): Rounded quartz grain which has undergone 2 cycles of overgrowth (numbers). Sample AJR64. Cross polars.



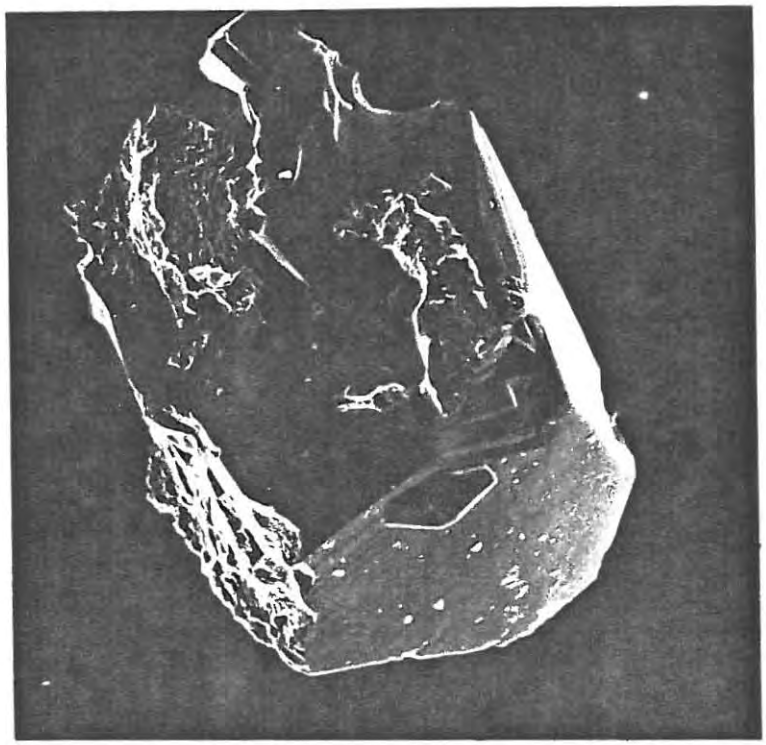
x 230

PLATE 2 : Same as above at higher magnification. Note etch pits on the grain in the background.



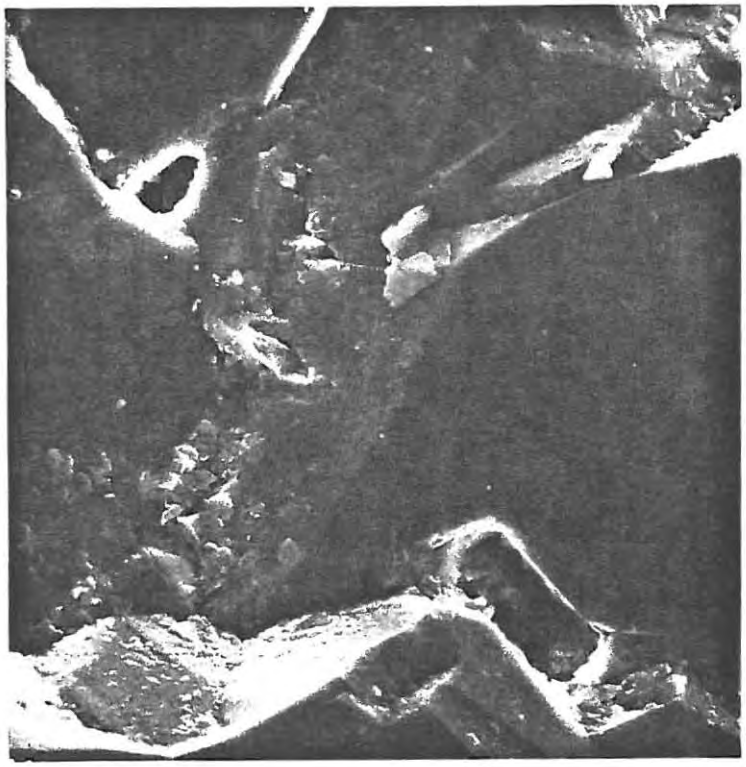
x 1000

PLATE 3 : SEM micrograph showing overgrowth on quartz.



x 300

PLATE 4 : Overgrown quartz with second phase of overgrowth commencing.



x 1600

PLATE 5 : Note presence of silicate "plates" and 2 possible etch pits.

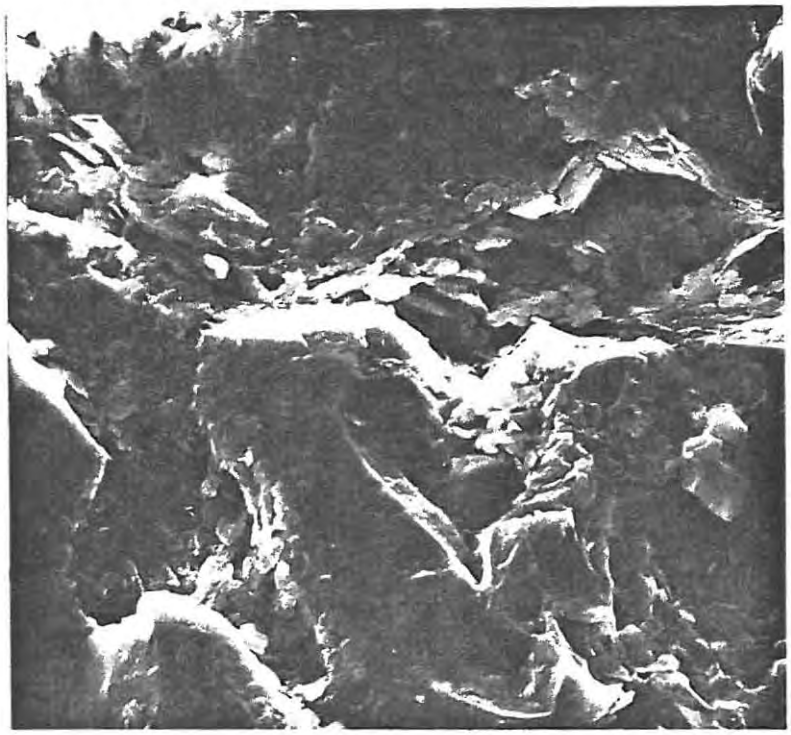


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PLATE 6 : Detail of "plates" showing their relationship to the smooth overgrowth.

PLATE 7(a) : Witteberg quartzite pebble consisting mainly of quartz with microcline also present. Plane polarized light.

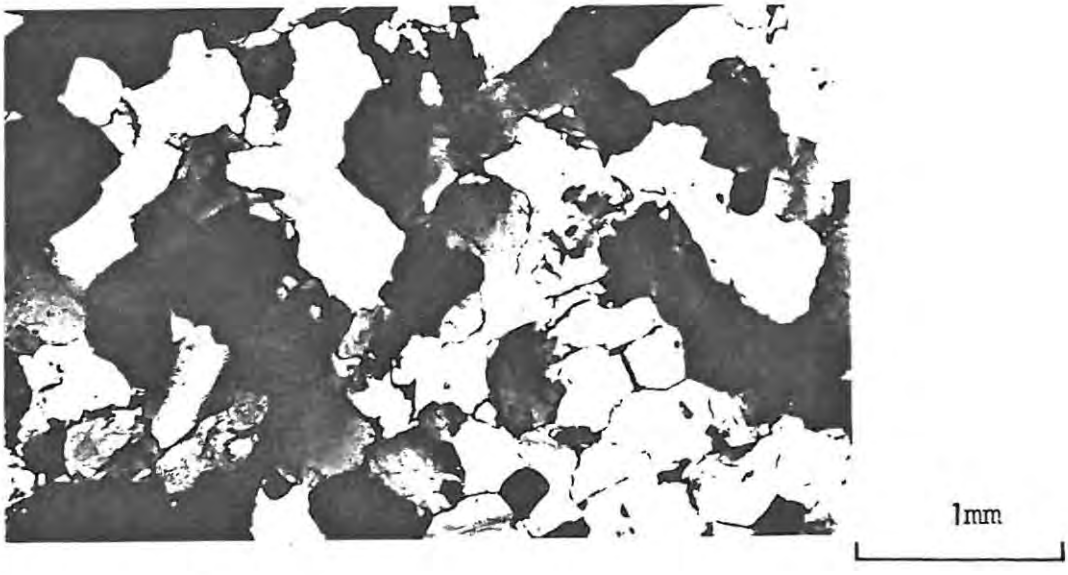


PLATE 7(b) : Same as above. Cross polars.

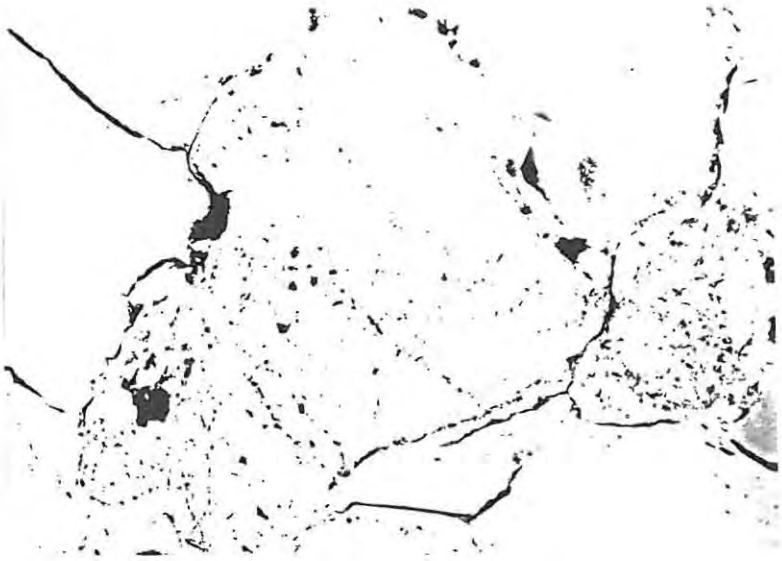


PLATE 8(a) : Inclusions of rutile in quartz. Note alignment parallel to certain directions. Sample AJR62. Plane polarized light.

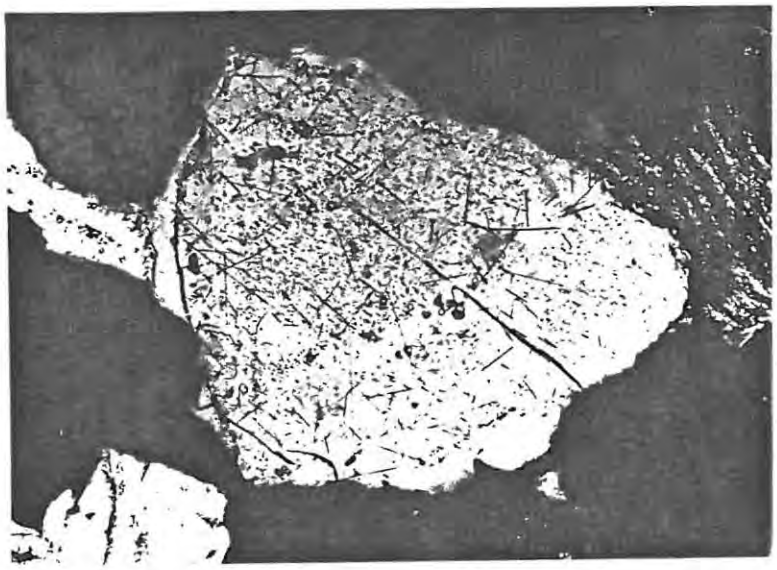


PLATE 8(b) : Same as above. Cross polars.

PLATE 9 : Arkose (Sample AJR44). Note microcline (mic), plagioclase (plag) and angular quartz (qtz). Cross polars.

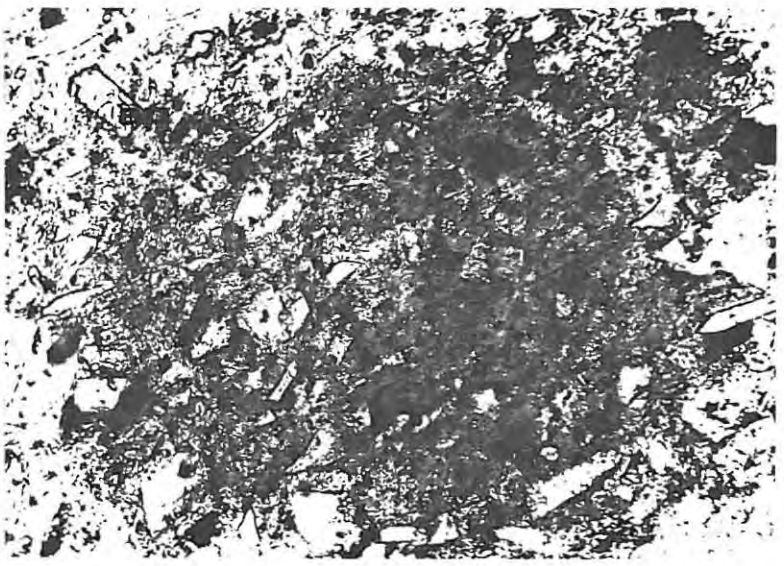


PLATE 10 : Siltstone (AJR61). Note presence of grains of apatite (ap). Plane polarized light.

III HEAVY MINERAL STUDIES

A. INTRODUCTION

Heavy mineral studies have long been used in sedimentary petrology in order to infer the composition of the source rocks of a sediment. The presence of certain minerals is diagnostic of the particular type of source or provenance, e.g. the presence of kyanite in a sediment would imply derivation from a high grade metamorphic provenance area. Other minerals such as tourmaline may be derived from several different types of source terrain. In such a case varietal features of the mineral, such as composition, colour, form, can serve as an indication of provenance area. More useful perhaps than the presence of certain minerals is the presence of certain mineral associations. Table 2 lists the detrital mineral suites characteristic of certain rock types.

It is possible that a sediment be derived from more than one type of source area. Recognition of this may be afforded by the presence of more than one mineralogical province in the sedimentary sequence in question. A mineralogical or sedimentary province has been defined by Edelman (1933, reported in Suttner, 1974) as "a group of distinctive, homogenous sediments which constitute a natural unit by age, origin and distribution ... a three dimensional body characterized by a distinctive suite of light and heavy minerals". More than one mineralogical province may exist in the same sedimentary basin depending on the number of distinct source areas which contributed detritus to the basin. An illustration of a case where a sedimentary sequence contains two distinct mineralogical provinces and a hybrid province is shown in Figure 5.

Province A would be derived from source area A, province B from source area B, while the hybrid province is derived from a mixing of detritus from the two areas. The Gulf of Mexico is an example of a basin which consists of several distinct mineralogical provinces (Davies and Moore, 1970).

TABLE 2 : DETRITAL MINERAL SUITES CHARACTERISTIC OF SOURCE ROCK TYPES (FROM PETTIJOHN (1975) p. 487)

Reworked sediments	
Barite	Leucoxene
Glauconite	Rutile
Quartz (especially with worn overgrowths	Tourmaline, rounded
Chert	Zircon, rounded
Quartzite fragments (orthoquartzite type)	
Low-rank metamorphic	
Slate and phyllite fragments	Quartz and quartzite fragments (metaquartzite type)
Biotite and muscovite	
Feldspars generally absent	Tourmaline (small pale brown euhedra carbonaceous inclusions)
Leucoxene	
High-rank metamorphic	
Garnet	Quartz (metamorphic variety)
Hornblende (blue-green variety)	Muscovite and biotite
Kyanite	Feldspar (acid plagioclase)
Sillimanite	Epidote
Andalusite	Zoisite
Staurolite	Magnetite
Acid igneous	
Apatite	Zircon, euhedra
Biotite	Quartz (igneous variety)
Hornblende	Microcline
Monazite	Magnetite
Muscovite	Tourmaline, small pink euhedra
Sphene	
Basic igneous	
Anatase	Leucoxene
Augite	Olivine
Brookite	Rutile
Hypersthene	Plagioclase, intermediate
Ilmenite and magnetite	Serpentine
Chromite	
Pegmatite	
Fluorite	Muscovite
Tourmaline, typically blue (indicolite)	Topaz
Garnet	Albite
Monazite	Microcline

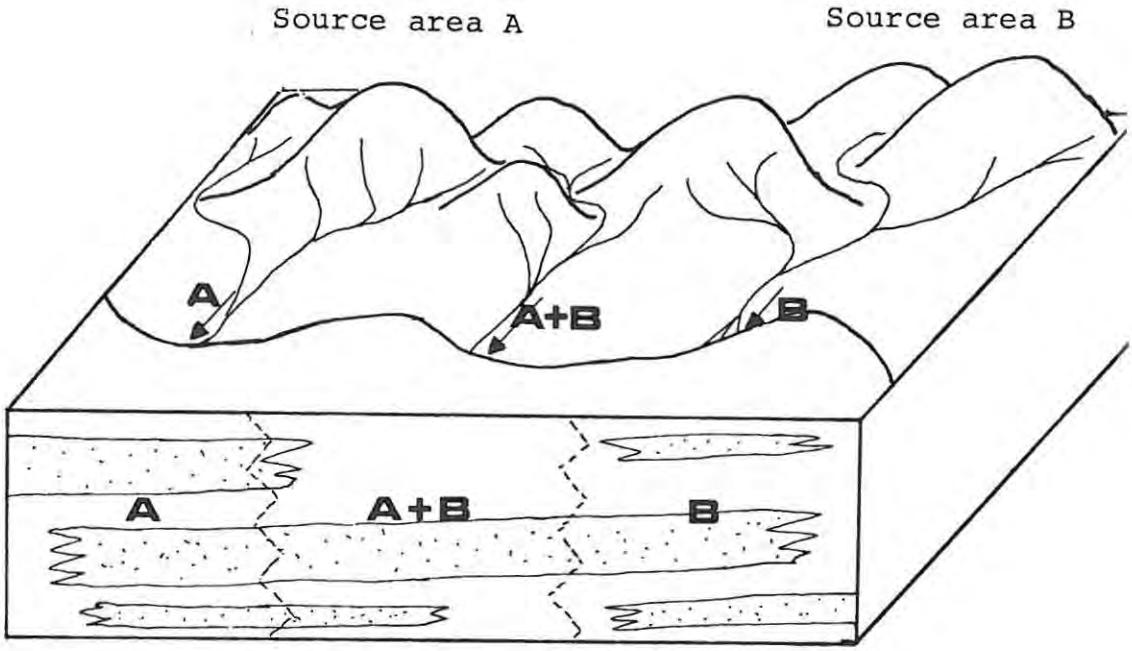


Figure 5 : Schematic block diagram illustrating the formation of two distinct mineralogical provinces in a single sedimentary unit (from Suttner, 1974).

Heavy minerals have also been used for the purpose of stratigraphic correlation. If heavy mineral zones are the result of progressive denudation and unroofing, so that the rocks being eroded change in composition with time, then the different heavy mineral zones present in the sediment may in fact be used for the purposes of stratigraphic correlation. Milner (1962) lists many studies of this type; Koen (1957), Theron (1970) and Theron (1972) have also applied the technique. If intrastratal solution is of general rather than local significance, as believed by Blatt and Sutherland (1969) and Pettijohn (1975) then correlation using heavy mineral

zones is invalid. Intrastratal solution implies that heavy mineral zones would only represent mineral stability zones. Pettijohn (1975, p 495) lists several criteria for recognition of intrastratal solution :

a) The presence of etched grains or grains with a hacksaw or cockscomb character (these might in fact represent pre-depositional features).

b) Microstylolitic contacts between grains.

c) An abundance contrast between the minerals in a concretion and the minerals in the matrix within which it occurs.

d) Pronounced differences in the heavy mineral suite between sandstones and the associated cogenetic shales.

Hubert (1962) considers intrastratal solution to be unimportant while Theron (1970) concludes that even if it had been important in his study, he would expect the same degree of corrosion to have taken place throughout the study area so in this way the relative abundances of the minerals would not have changed.

Heavy mineral studies also provide a means of estimating the maturity of a sediment. The presence of unstable, chemically reactive minerals, such as olivine or pyroxene, would indicate the sediment to be very immature, in much the same way as a high abundance of unweathered feldspar does. A sediment which consists of only very resistant detrital minerals would be considered to be far more mature (presuming the source areas for the two sediments to be of the same composition). Hubert (1962) has defined a quantitative index, the ZTR index. The ZTR index is the percentage of the combined zircon, tourmaline and rutile among the transparent, nonmicaceous detrital heavy minerals. Because of their high chemical and mechanical stability these are the phases, together with quartz and chert, which will be concentrated as the sample becomes progressively more mature.

Theron (1970) uses a modification of the ZTR index where instead of examining the entire unsieved sample, only a specific size fraction is analysed, in his case the -200 + 400 mesh fraction.

B. APPLICATION TO THE PRESENT STUDY

Two different provenance areas have contributed detritus to the Molteno Formation (Rust, 1959; Ryan, 1963 and Turner, 1975(a)). The southerly source area was a sedimentary provenance while that to the south-east predominantly granitic in character (Turner, 1975(a)). A study of the heavy mineral suite from different geographic areas within the Molteno Formation might enable recognition of different mineralogic provinces reflecting the presence of the two provenances of different composition. To avoid differences in the heavy mineral suite caused by vertical variation it was decided only to examine the heavy mineral suite from a single laterally persistent unit. The Indwe Sandstone Member fulfils this qualification. Since the grain size and porousity of the unit does not appear to vary greatly with geographic position it was assumed that if intra-stratal solution had taken place, it would have done so to the same extent throughout the basin. Further information regarding the provenance compositions could also perhaps be obtained by an examination of ZTR ratios, zircon elongation ratios and the exact composition of certain of the mineral species present.

C. SEPARATION TECHNIQUES

Heavy mineral separation, i.e. separation of those minerals with a specific gravity greater than 2,9 was achieved using a two-stage process. This is described in some detail since it was developed by experimentation and proved a simple, yet very efficient technique. The initial stage is a primary concentration using a superpanner while the second stage entails further concentration using heavy liquid.

Disaggregation of the individual grains is made difficult by the presence of a silica cement in the Indwe Sandstone Member. As a result the acid treatment suggested by Carver (1971) is not effective, so, instead, the method suggested by Theron (1970) is adopted. The samples were crushed using a steel mortar and pestle, care being exercised to ensure that the samples are struck squarely without a grinding motion. An inherent danger is that fragmentation of the heavy mineral grains may take place. Since the degree of fragmentation would depend on physical characteristics such as hardness, cleavage and grain size rather than on relative mineral abundances, the actual counts of a fragmentation prone mineral may be greatly exaggerated if crushing leads to excessive breakage of grains. As excessive force was not required to crush the samples, it was considered that fragmentation, if present, would be minimal. Subsequent optical examinations supported this contention.

A potent factor affecting the facility with which mineral grains are separated is the range of grain sizes present. It is well known that large grains of low specific gravity are hydraulically equivalent to smaller grains of high specific gravity (Rubey, 1938, reported in Carver, 1971). Accordingly it is important to restrict examination of a disaggregated sample to a particular size fraction. Although this practice is in general usage a standard size fraction has not been accepted. Koen (1955) and Theron (1972) suggest use of the -200 mesh sample (smaller than 74 microns), Rust (1962) in his study of the Molteno Formation used the size range less than 149 microns while Turner (1975(a)) examined the 74 to 200 micron class. Carver (1971) considers the 125-250 micron range to be a useful compromise. In the present study an initial examination was conducted on both the 125-250 micron and 63-125 micron ranges. It was found that the 125-250 micron class contained a larger suite of heavy minerals and also gave a better separation, and was consequently adopted as the most suitable size range for the study.

The disaggregated sample was then sieved for approximately 30 minutes and the retained grains washed in dilute hydrochloric acid in order to remove iron oxide staining from the grain surfaces. This procedure facilitates optical examination and does not destroy any important heavy minerals except apatite, which according to Rust (1959) is not present in the Indwe Sandstone Member or for that matter in the Molteno Formation.

Initial separation of the samples was carried out using a superpanner. Detailed conditions for separation will not be given since effective utilisation of the machine only comes with practice. The variables adjusted will, however, be briefly described :

a) Speed of "knocking" - this was adjusted to approximately $^1/_3$ full speed.

b) Amount of "knocking" - this was adjusted to the maximum available.

c) Lateral movement - nil at the inflow position and approximately half at the outflow position.

These three variables were kept constant throughout the separation; the following two variables, which appear to be the most critical, are constantly adjusted until a good "tail" is achieved.

a) Rate of water flow - this is adjusted several times during a separation, but is kept to fairly small volumes.

b) Angle of tilt of the pan - initially the pan is tilted at approximately 10 degrees to the horizontal. The angle is then slowly lessened until final separation is achieved.

The manipulation of the latter two variables is the key to quick and successful separation; a long process of trial and error often occurs before this can be achieved.

The "tail" of heavy minerals was extracted from the pan by the simple expedient of sucking up the grains using an ordinary pipette. A fair proportion of quartz grains would unfortunately also be sucked up but this was thought preferable to leaving heavy mineral grains behind. Secondary concentration was then achieved by use of heavy liquid. There are two standard laboratory techniques for separating heavy minerals and as Carver (1971) points out there is no essential difference between the two. In the simpler of the techniques, gravity settling is achieved normally in a battery of glass funnels. The centrifuge method, on the other hand, increases the speed of separation by effectively increasing the influence of gravity. Gravity settling methods are slower than centrifuge methods but have the advantage that actual physical recovery of the heavy fraction is simpler. In the more elegant centrifuge method, which was adopted in this study, actual physical recovery of the heavy fraction after the separation may be difficult. The problem is to avoid recontamination of the heavy fraction with the suspended light mineral fraction. Blatt and Sutherland (1969) suggest using a pipetting technique while Carver (1971) gives details of partial freezing techniques which he considers to be the most effective. Theron (1970) constructed a rather complex mechanism with which to effect recovery. A rather simple device was used in the present study, consisting of a glass tube fitted inside the normal centrifuge tubes. The lower end of the inner tubes were provided with an exit orifice 2-3 mm in diameter and the external diameter of the inner tubes was such that they just fitted inside the centrifuge tubes. Each tube would be approximately $^{3}/_{4}$ filled with heavy liquid and 2 grams of samples placed in the inner tube. After separation the lighter fraction would remain in the inner tube while the heavy fraction would have exited into the outer tube through the lower orifice. By blocking the mouth of the inner tube, it could be removed from the outer tube, thus effecting physical separation of the two fractions. Figure 6 illustrates the design of the tubes and the method of separation.

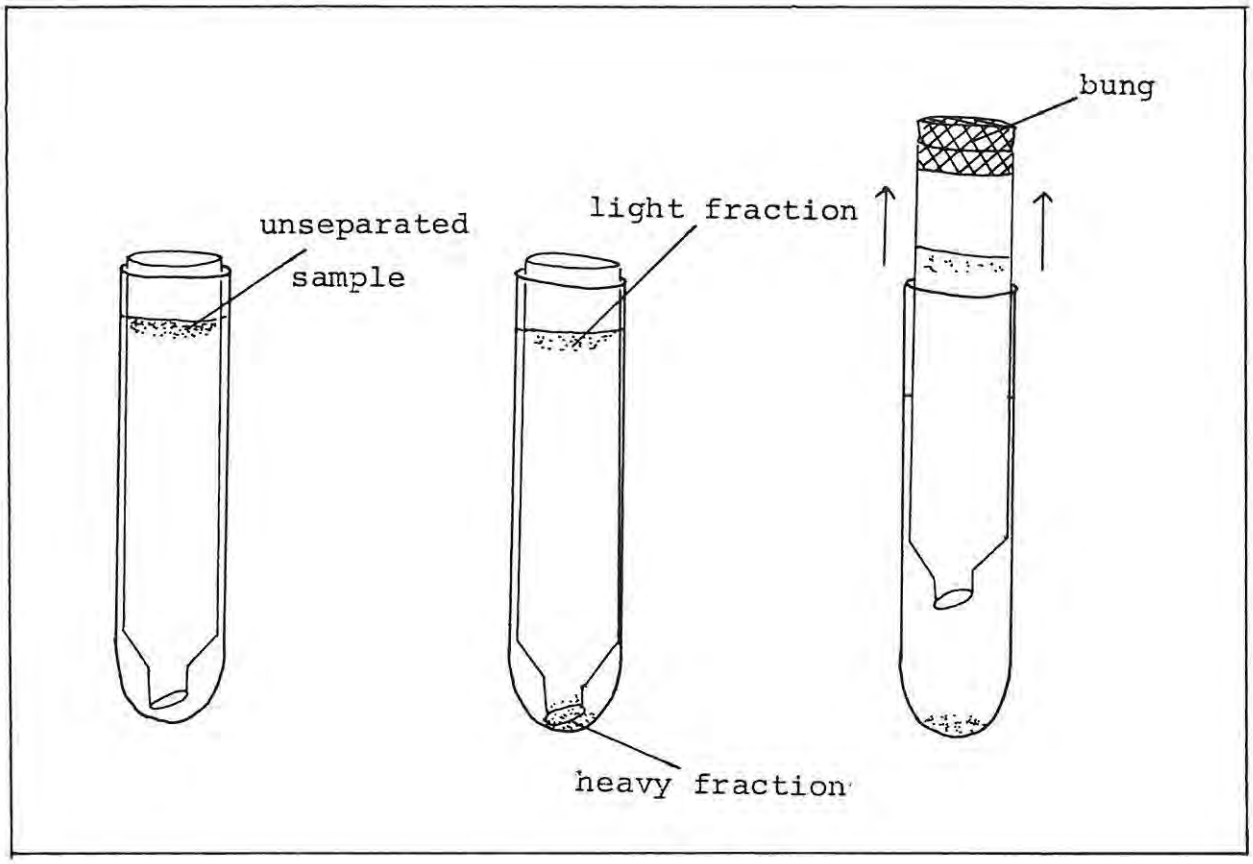


Figure 6 : Design of inner centrifuge tubes and method of physical separation of the 2 fractions.

Tetrabromoethane ($C_2H_2Br_4$, specific gravity = 2,97) was the heavy liquid used and it was found that a total separation could be achieved after 10 minutes centrifuging at 3 500 rpm. The liquid containing the heavy minerals is filtered and the heavy minerals retained on the paper washed with acetone.

Before optical examination of the suite, the opaque phases present were separated from the non-opaques using an

electromagnetic separator. With the following operating conditions

Forward tilt = 25^{o}
Sideways tilt = $5\text{-}10^{o}$
Current = 0,55 - 0,65 amperes

it was found that the opaque phases would separate. At lower currents the garnets present would also have separated, so these would then be combined with the rest of the non-opaque suite.

D. HEAVY MINERAL CONTENT OF THE INDWE SANDSTONE MEMBER

The non-opaque heavy mineral suite present in the Indwe Sandstone Member is extremely simple and represents an ultrastable assemblage. It consists almost entirely of zircon, tourmaline and rutile; garnet may or may not be present. Five samples were examined, one from each of the study areas. The sample from the Aliwal North area (AJR29) contained a very sparse heavy mineral crop and has thus not been included in the quantitative analysis. This relative paucity is presumably a reflection of the distal position occupied by Aliwal North in respect to the source areas. Examination of a finer fraction from this area might reveal a higher percentage of heavy minerals.

Before orthodox optical examination of the grains, an identification exercise using X-ray diffraction techniques was performed. Grains thought to be garnet, rutile and tourmaline were selected. X-ray diffraction would, it was hoped, provide a simple and quick method of positive identification of these minerals and more specifically, the varietal types present.

While the actual identification technique is simple, a specialized instrument, the Gandolfi camera, must be used. A grain of the mineral to be identified is stuck on the end of a fibre (using Alcolin cold glue) and this is then mounted in the Gandolfi 180 mm camera. Correct orientation of the

grain may prove tricky at first but becomes routine with practice. A cobalt tube operated at 55 kV and 30 mA provided the primary radiation source and a fine collimator was employed. Exposure times were limited to 3½ hours. A problem inherent in the Gandolfi technique is that intensities recorded on the film will often bear little or no relationship to those obtained using the Debye-Scherrer camera. A direct consequence of this is a degree of difficulty in indexing the lines correctly and identifying the mineral; nevertheless use of the Fink index makes location of the correct JCPDS card reasonably certain.

The minerals tourmaline (variety dravite) and garnet (variety pyrope) were identified as well as the three polymorphs of TiO_2, rutile, anatase and brookite. A comparison of the d-spacings obtained with those listed on the JCPDS cards is given in Appendix B.

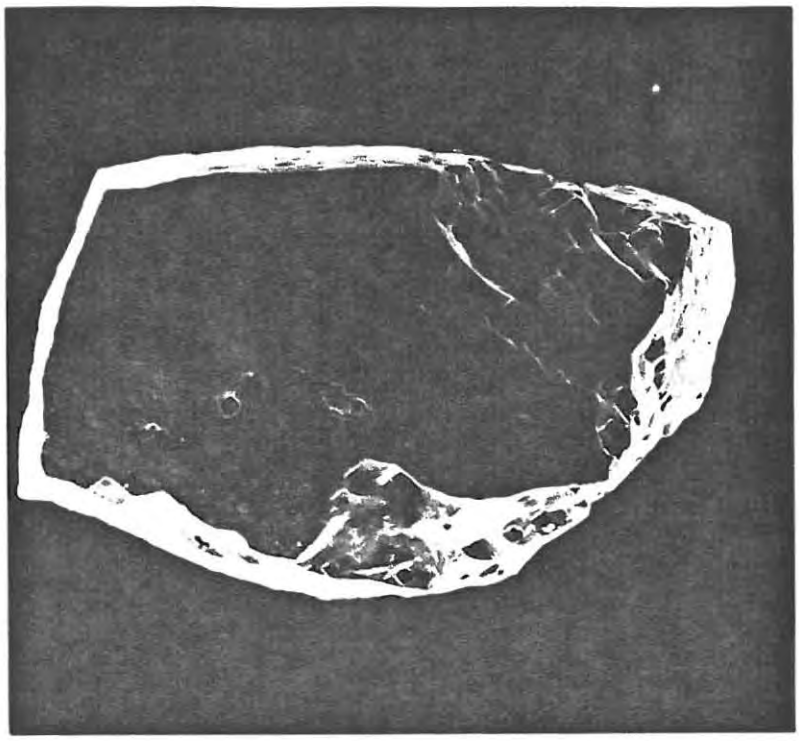
Garnet

The presence of garnet in the Indwe Sandstone Member, and for that matter in the Molteno Formation itself, poses a problem. Koen (1955) describes garnet as being extremely rare or absent from the Molteno Formation. On the other hand, both Rust (1959) and Ryan (1963) found garnet to be an abundant phase in the heavy mineral suite. Theron (1970) reported garnet as being depleted in the Molteno Formation to such an extent that he suggested this be used as a criterion to distinguish the Molteno Formation from the underlying Beaufort Group. Turner (1975(a)) supported the findings of Rust (1959) and Ryan (1963) and in fact found garnet to be the most abundant of the heavy minerals. He suggested that the previously recorded inconsistencies might be explained in terms of the differing grain sizes analysed. This suggestion does contain some merit but is not the total answer to the inconsistencies found. In the present study all the samples analysed were of the same grain size but only one (AJR67) was found to contain garnet. A possible solution to the problem is suggested by Carroll

(1957), who has ascribed variations in heavy mineral abundances between geographically adjacent samples to a combination of the effects of hydraulics and chance variations. In this way the distribution of any particular phase may be extremely irregular even in a single unit. Another possible explanation is that of intrastratal solution. As has been noted earlier, there is considerable debate concerning the efficiency of intrastratal solution. A scanning electron microscope study was undertaken to determine if there was any evidence for intrastratal solution of the garnets. To obviate any solution effects which might have been caused by cleaning the grains in hydrochloric acid, another crop of heavy minerals was obtained; these were not treated with acid. The garnets were separated using the electromagnetic separator.

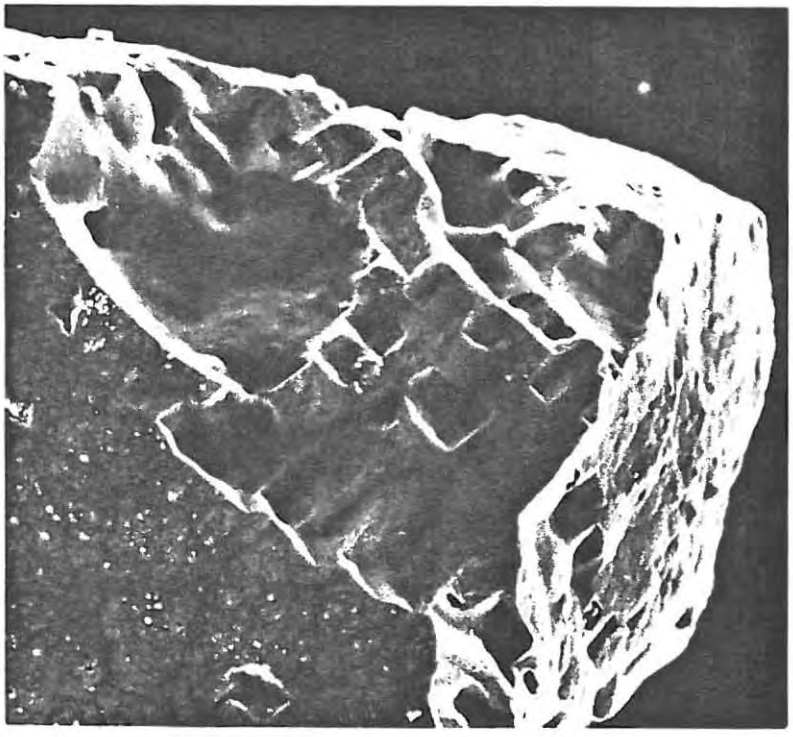
There is considerable debate regarding what constitutes solution features on garnets. Bramlette (1929), Rahmani (1973) and Gravenor (1979) consider a "faceted" appearance on garnet grains to be the result of etching leading to solution of the garnet. Simpson (1976) has noted, on the other hand, that surface features on garnets may be divived into two distinct morphological types to which he assigned different interpretations. One group of surface features he called "hillocks" (the "facets" referred to by earlier workers) and the other group "pits". The first feature he ascribed to authigenic overgrowth while the latter he considered to be the result of solution. Garnets could be unaltered, overgrown and etched, if both facets and etch pits appeared on the same grain or if the overgrowths were worn, an idea of the geological history of the grain could be obtained.

The garnets investigated from the Indwe Sandstone Member have clearly been etched, with an abundance of the quadrilateral etch pits being present on the grains. Plates 11(a), (b) and (c) are successive enlargements of the same grain showing the presence of these pits. Plate 12 shows a garnet on which the solution process has proceeded to



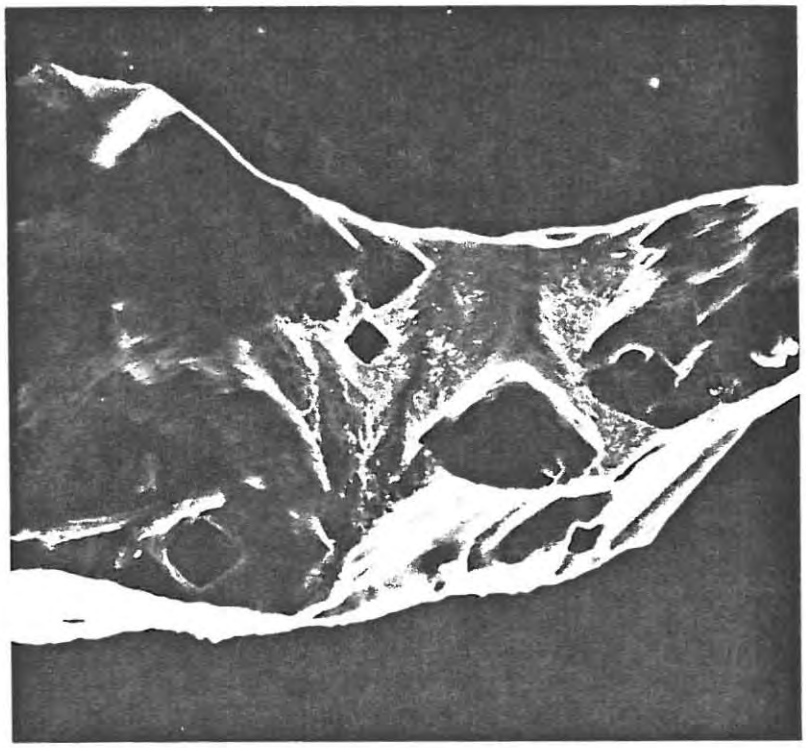
x 250

PLATE 11(a): SEM micrograph of garnet showing the presence of etch pits.



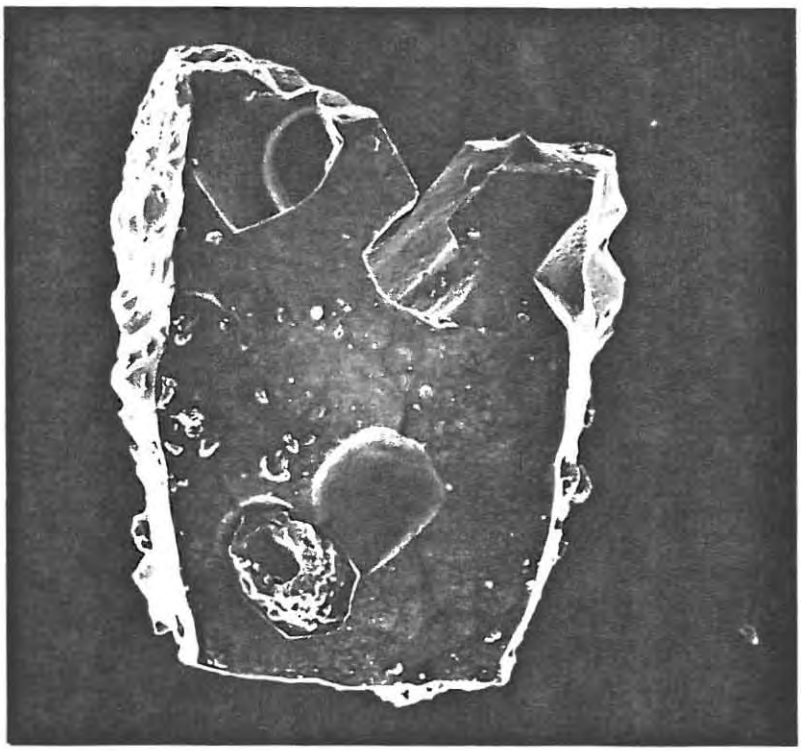
x 650

PLATE 11(b): As above at higher magnification. Note the suggestion of layers or facets.



x 1000

PLATE 11(c) : Detail of pits.



x 250

PLATE 12 : SEM micrograph showing extreme development of etch pits to the point where solution has cut right through the grain.

such an extent as to have dissolved holes right through the grain. There is also a slight suggestion of overgrowth on the first of these grains. This is especially noticeable in Plate 11(b) where an indication of different facets or layers may be seen. Simpson (1976) has also reported the presence of both of the features in the same grain. Presumably they result from a period of solution following a period of overgrowth suggesting, perhaps, that either the grain was exposed to two fluids of different composition sequentially in the same rock, the first leading to overgrowth, the second to solution, or possibly more likely, the overgrowth occurred during an earlier sedimentary cycle. The absence of garnet from samples from the same lithology may therefore be as a result of intrastratal solution in those areas. Potter (1968) believes this to be often the case with garnets in sediments.

Overall, garnet occurs as angular to subangular grains (see Plate 13) easily distinguished microscopically from the other phases by the isotropic character of garnet. On the basis of optical properties, Turner (1975(a)), has assigned the garnets of the Molteno Formation to the almandine-spessartite group. He does not state the optical criteria he uses and since physical properties (such as density, Heinrich (1965)) are also necessary for an estimation of the chemical composition of garnets, his identification might be considered speculative. The Mg-rich garnet, pyrope, has been identified using XRD methods; further investigation was undertaken in order to establish the exact chemical composition of the garnets.

14 garnets selected from sample AJR67 were analysed using the electron microprobe. The instrument used is a Cambridge Mark V Electron Probe Micro-analyser and was operated at 20 kV accelerating voltage with a specimen current of 3 x 10^{-8} amps. All specimens were carbon coated prior to the analysis. Raw data were collected using the Bence-Albee correction routine (1968). Full results for the 14 grains analysed are given in Table 3. With the exception of two

garnets (Nos. 1, 11), the MnO content of the garnets is very low. Essentially their compositions may be described using the three end-members almandine ($Fe_3 Al_2 Si_3O_{12}$), pyrope ($Mg_3 Al_2 Si_3 O_{12}$) and grossularite ($Ca_3 Al_2 Si_3 O_{12}$). The compositions of the garnets (plotted as normalized molecular percentages of FeO, MgO and CaO) are presented in Figure 7. Most of the garnets contain equivalent molecular percentages of FeO and MgO; three garnets seem to form a group with higher FeO. The Ca (grossularite) component is variable but is generally low. The garnets may thus be assigned to the almandine-pyrope class of garnets but there is a component of the grossularite molecule in some of them. Since XRD methods are not able to distinguish the exact chemical composition of minerals in which there is extensive solid solution, it is considered likely that the pyrope garnet identified by XRD methods is probably a member of these MgO-FeO garnets. Two garnets with high MnO also indicate the presence of a spessartite component.

The presence of almandine-pyrope garnets suggest derivation from amphibole bearing metamorphic rocks while grossularite garnets are generally derived from contact metamorphic rocks. Spessartite-almandine garnets are characteristic of pegmatites, some granites and low grade schists (Heinrich, 1965).

Tourmaline

Tourmaline occurs as irregular and angular grains with a few subrounded grains also being present. The grains are pleochroic in various shades of yellow, green and brown. X-ray diffraction has identified the Mg-rich tourmaline, dravite, which is characteristic of metasomatically altered carbonate rocks (see Plates 14, 18).

Rutile

Two types of rutile are present, a very deep brown, almost opaque variety and a lighter, yellow-brown variety. The grains are generally subequant to prismatic in shape; some

TABLE 3 : ANALYSES OF 14 GARNETS - MOLTENO FORMATION

(Weight percentages)

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Cr_2O_3	Total
1	38,68	0,01	22,14	10,21	11,82	6,55	11,35	0,03	100,94
2	37,79	0,03	22,21	32,18	0,64	7,02	1,1	0,02	101,03
3	38,71	0,04	22,79	26,42	0,37	11,55	1,67	0,04	101,62
4	38,74	0,19	22,49	22,43	0,61	8,4	8,97	0,03	101,9
5	38,38	0,08	22,72	21,56	0,42	7,12	11,13	0,00	101,43
6	39,59	0,06	22,74	25,67	0,36	0,39	5,05	0,01	102,9
7	39,76	0,02	23,31	24,67	0,41	13,06	1,65	0,03	102,94
8	40,03	0,03	23,37	24,08	0,25	14,23	0,83	0,01	102,87
9	37,6	0,08	21,57	32,34	0,95	2,61	6,89	0,54	102,61
10	40,39	0,02	23,11	24,95	0,46	12,84	1,13	0,12	103,05
11	38,71	0,02	21,49	20,13	7,53	7,3	6,92	0,01	102,16
12	39,85	0,15	23,33	22,94	0,45	12,85	3,02	0,08	102,7
13	38,14	0,2	22,39	32,56	1,09	7,0	1,1	0,01	102,33
14	39,48	0,007	22,48	25,53	0,04	9,35	5,05	0,04	102,4

(Totals are high probably as a result of difference in thickness of carbon coating between standards and samples, since they were coated at different times).

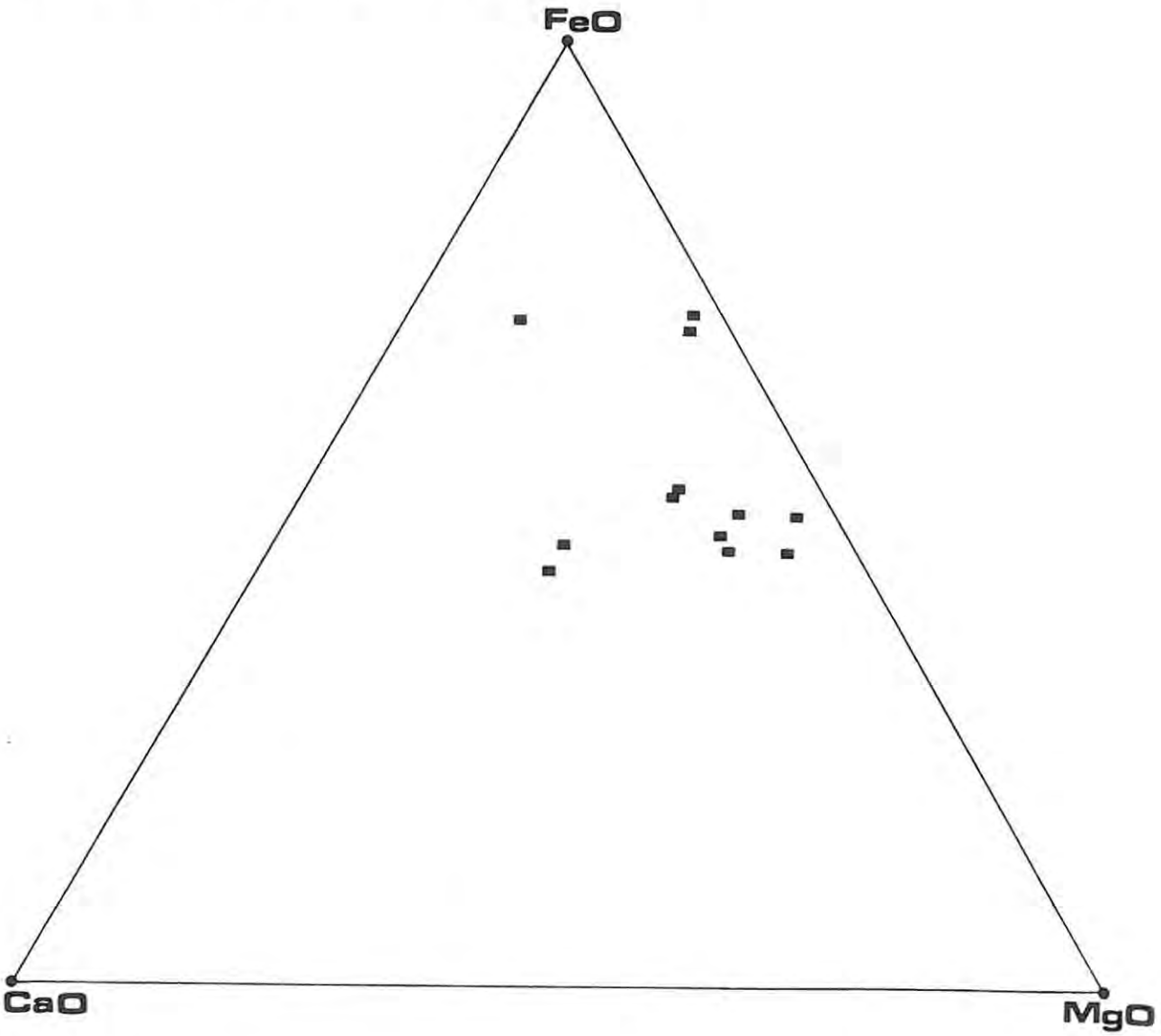


Figure 7 : Garnets from the Molteno Formation plotted in terms of FeO, MgO and CaO end members.

are rounded while others may be angular (see Plate 14).

The other two titanium dioxide polymorphs, anatase and brookite, have been identified. Anatase has been identified in the sample from Aliwal North (AJR29) and is undoubtedly authigenic in origin, possibly an alteration of ilmenite. Plates 15(a) and 15 (b) show the typical tetragonal bipyramidal crystal form of anatase. Plate 16 shows another grain which has undergone extensive overgrowth. Brookite has been identified from sample AJR67. This, too, presents a striated crystal form which would not have survived transport and is probably also authigenic (see Plate 17).

Zircon

The majority of the grains are colourless and many are zoned. Grain shapes range from extremely elongate to highly spherical. Inclusions of rutile needles, opaque phases and cavities are found in some of the grains (see Plates 14, 18, 19(a) and 19(b)).

The morphology of zircon grains has been used by several authors (Poldervaart, 1950; Wyatt, 1954; Spotts, 1962; Marshall, 1966) for purposes of correlation and differentiation of lithologies. The most widely used parameter is that of elongation ratio which is defined as :

Elongation ratio = length of zircon/width of zircon

Zircons from igneous rocks tend to consist mainly of sharply terminated prismatic euhedra with elongation ratios between 2 and 3, (Theron, 1970). Sedimentary zircons, on the other hand, due to processes of abrasion and attrition, tend to be rounded and have low elongation ratios (less than 2). It might be expected that the elongation ratio of zircons in a sedimentary sequence would be inversely proportional to the distance from the source area. Furthermore, well sorted sediments will be characterized by a unimodal elongation ratio distribution (Theron, 1970). The degree of maturity of a sediment is also reflected in the elon-

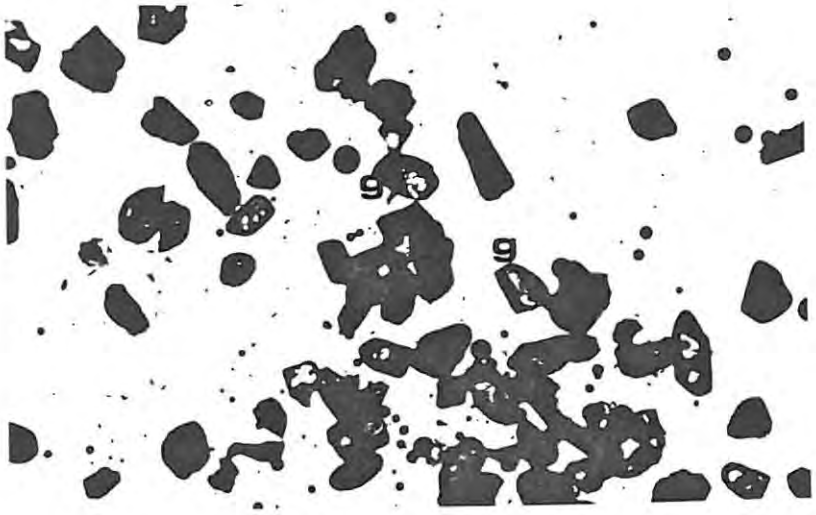


PLATE 13 : Heavy mineral concentrate (AJR67) showing presence of garnet (g). Plane polarized light.

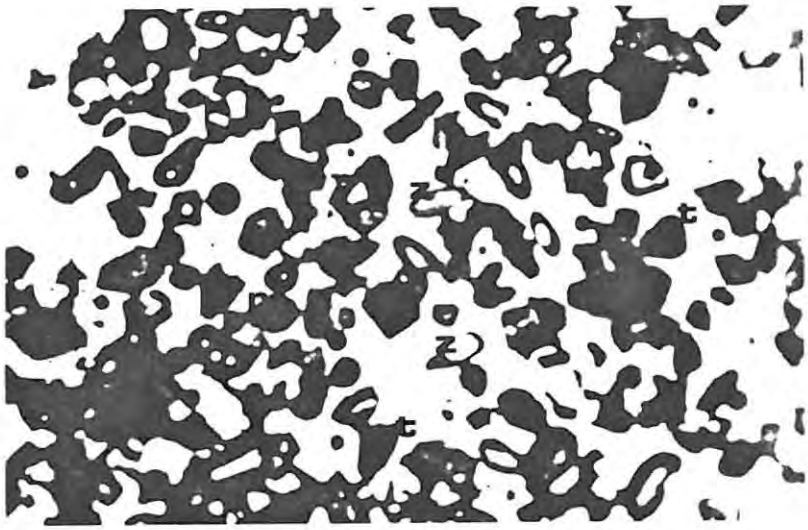
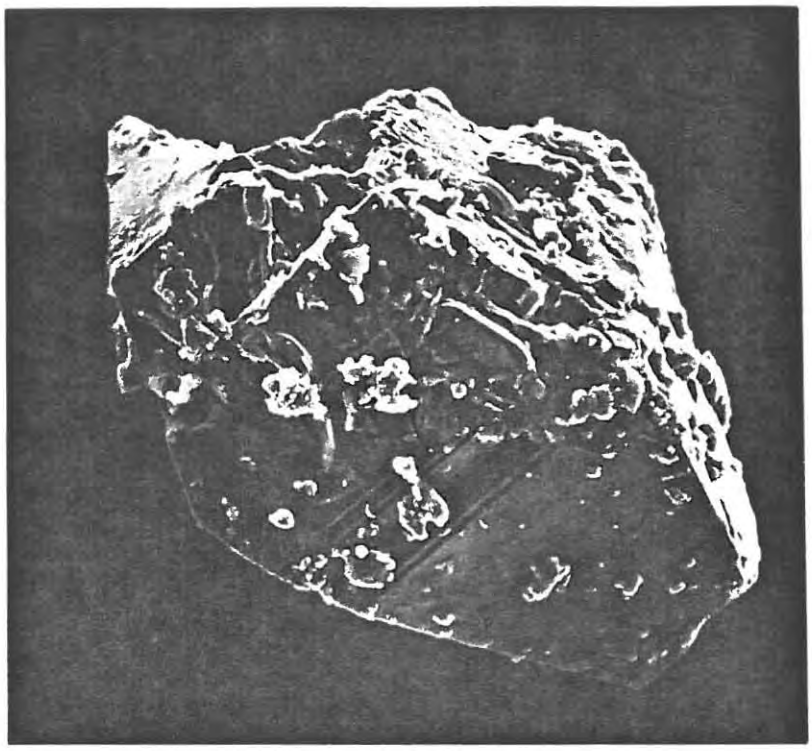
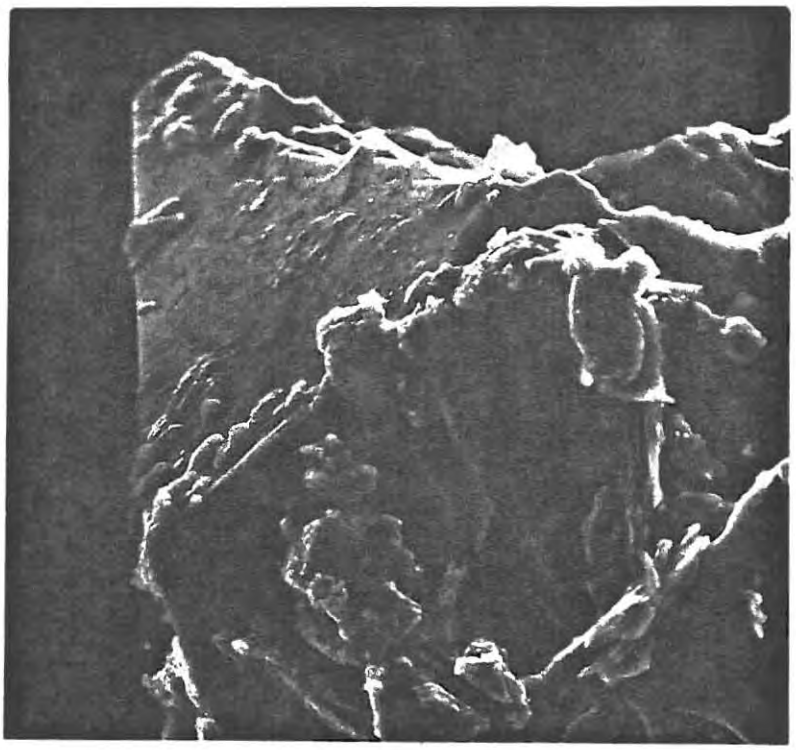


PLATE 14 : Heavy mineral concentrate (AJR54). Zircon (z), mainly clear and rounded, tourmaline (t) and rutile (r), are all present.



x 400

PLATE 15(a): Authigenic anatase showing tetragonal bipyramidal form.



x 1300

PLATE 15(b): Detail of above.

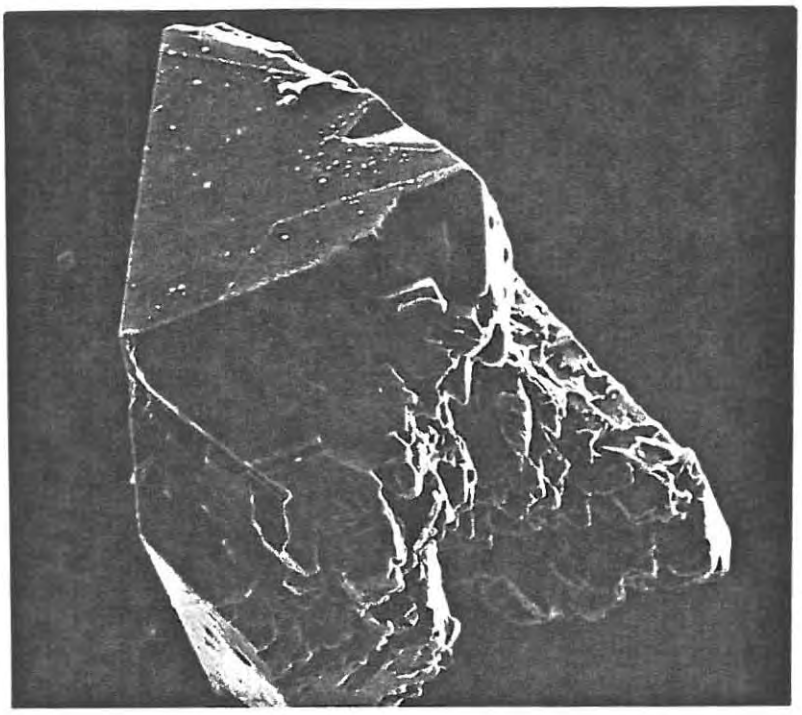


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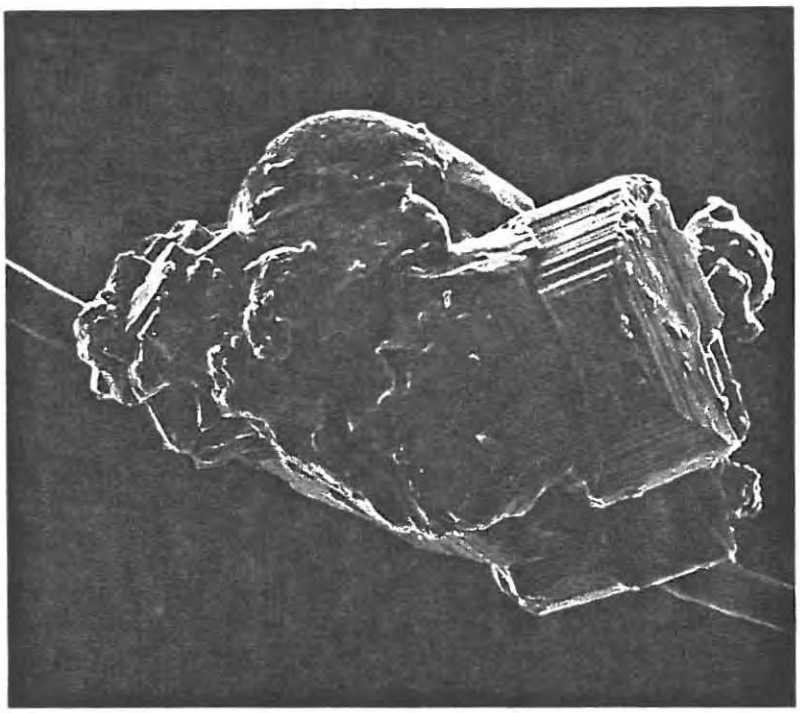
PLATE 16 : Anatase displaying sharp pyramidal faces and edges. No rounding is evident.



x 300

PLATE 17 : SEM micrograph of brookite showing striated faces.

PLATE 18 : Sample (AJR14) showing precence of very clear zircons. Note the sharp zircon euhedra (z). Tourmaline (t) and rutile (r) are also present. Plane polarized light.

PLATE 19(a) : Elongate euhedral zircon with slightly rounded terminations. Plane polarized light.

PLATE 19(b) : Detail of above with sub-stage condensor in place. Note inclusions present.

gation ratios of the zircons. Immature sediment would still contain elongated idiomorphic grains and the mean elongation ratio would be high; while in immature sediment, which has undergone two or more cycles of erosion, very few idiomorphic grains would remain and the elongation ratio would be low.

A variation in zircon elongation ratios could therefore be expected in the Molteno Formation reflecting derivation of the zircons from two different source areas. The zircons from samples closer to the granitic source would perhaps have a higher average elongation ratio while those from nearer the sedimentary source would be expected to have lower elongation ratios.

Zircon grains were examined from samples AJR14, 54, 64 and 67. Using a micrometer eyepiece the long axes of the grains and an axis perpendicular to the long axis were measured along regularly spaced traverses. Approximately 200 grains were measured in each slide and the elongation ratios calculated. These were then sorted into class intervals and the mean and standard deviation calculated for each sample (see Table 4). From this it can be seen that there is no systematic variation in elongation from west to east. Examination of the histograms of the data (see Figure 8) yields further information. Again, while there is no systematic variation from sample to sample, a bimodal distribution is evident, especially in samples AJR64, 54 and 67. This suggests that the zircon population of the Indwe Sandstone Member is derived from two different provenance areas. The grains with elongation ratios $< 1{,}3$ being derived from the sedimentary source area and the more elongate grains being derived from the granitic source.

An interesting relationship is that between the elongation of the grain and its size. Poldervaart (1955) considers that an inverse relationship occurs between the two, while Turner (1975(d)) states that for the Molteno Formation, the smaller the grain size the less the elongation of the grain. The long axes of 160 zircon grains from the present study

TABLE 4 : FREQUENCIES OF ZIRCON ELONGATION RATIOS

(class interval 0,15)

Class Interval	AJR14	AJR67	AJR64	AJR54
1,0-1,14	26	26	34	30
1,15-1,29	28	27	26	16
1,30-1,44	26	16	29	27
1,45-1,59	29	33	28	27
1,60-1,74	19	20	21	22
1,75-1,89	15	12	13	17
1,90-2,04	10	14	14	12
2,05-2,19	8	9	9	10
2,20-2,34	3	8	8	12
2,35-2,49	4	5	5	6
2,50-2,64	5	4	4	4
2,65-2,79	3	2	2	1
2,80-2,94	3	3	3	1
2,95-3,09	1	1	1	3
3,10-3,24	2	2	2	2
3,25-3,39	3	2	2	1
3,40-3,55	1	1	1	1
Ratios >3,55	12	6	6	5
n	199	181	207	195
mean	1,850	1,699	1,702	1,767
Std. deviation	1,95	1,86	1,99	1,84

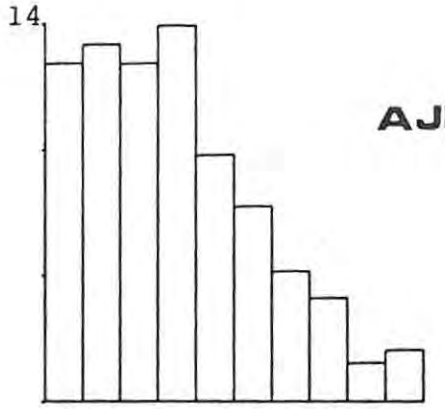
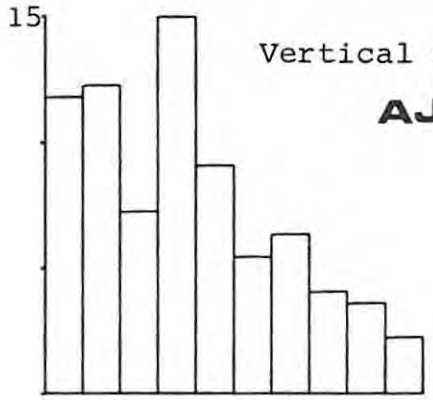
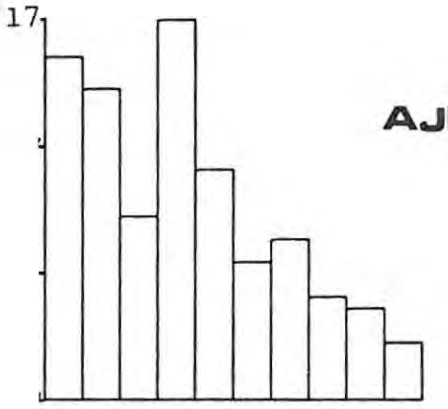


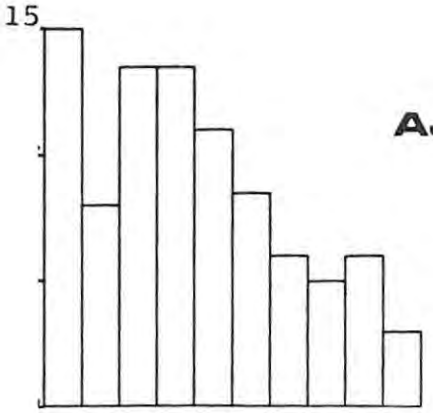
Figure 8 : Histograms showing frequency distribution of zircon elongation ratios.

Horizontal axis = elongation ratio (class interval = 0,15)

Vertical axis = percentage frequency







were plotted against their respective elongation ratios (see Figure 9). The relationship observed by Turner (1975(a)) appears to hold and the relationship is significant at the 99% confidence level.

Opaque oxides

Opaque oxides make up to 30 percent of the total heavy mineral assemblage. Apart from ilmenite and magnetite, secondary iron minerals such as goethite are also present.

ZTR index

The percentage abundances of zircon, tourmaline, rutile and garnet in samples AJR14, 54, 64 and 67 are shown in Table 5(a). Approximately 600-700 grains were counted in each slide. It was thought that there might be a systematic variation in the heavy mineral content between samples from different areas. Similarly a change in the ZTR index would also reflect the influence of the different source areas, a high ZTR index being expected close to the sedimentary source. As can be seen from Table 5(b), the ZTR index is 100% for 3 of the samples. This is a result of the very simple non-opaque suite present. Recognition of 2 separate mineralogical provinces (Suttner, 1974) is also not possible. Z/Z+T, Z/Z+R, R/T ratios and the amounts of Z+T have been calculated (see Table 5(b) and also show no systematic variations although there is a suggestion of increase in Z+T eastwards.

A greater sample density would probably be required before any significant variation in ratios becomes detectable.

TABLE 5(a): HEAVY MINERAL COMPOSITION, INDWE SANDSTONE SAMPLES

(opaques excluded)

Sample No.	AJR14	AJR67	AJR64	AJR54
Zircon	34	42	40	52
Tourmaline	9	7	9	19
Rutile	57	27	51	29
Garnet	-	24	-	-

Figures are percentages of total non-opaques
Approximate n = 650

TABLE 5(b)

ZTR index, $\frac{Z}{Z+T}$ ratio, $\frac{Z}{Z+R}$ ratio, $\frac{R}{T}$ ratio, Z+T for Indwe Sandstone samples

Sample No.	AJR14	AJR67	AJR64	AJR54
ZTR	1,00	0,76	1,00	1,00
$\frac{Z}{Z+T}$	0,79	0,86	0,82	0,73
$\frac{Z}{Z+R}$	0,37	0,61	0,44	0,64
$\frac{R}{T}$	6,33	3,86	5,67	1,53
Z+T	43%	51%	49%	71%

west → east

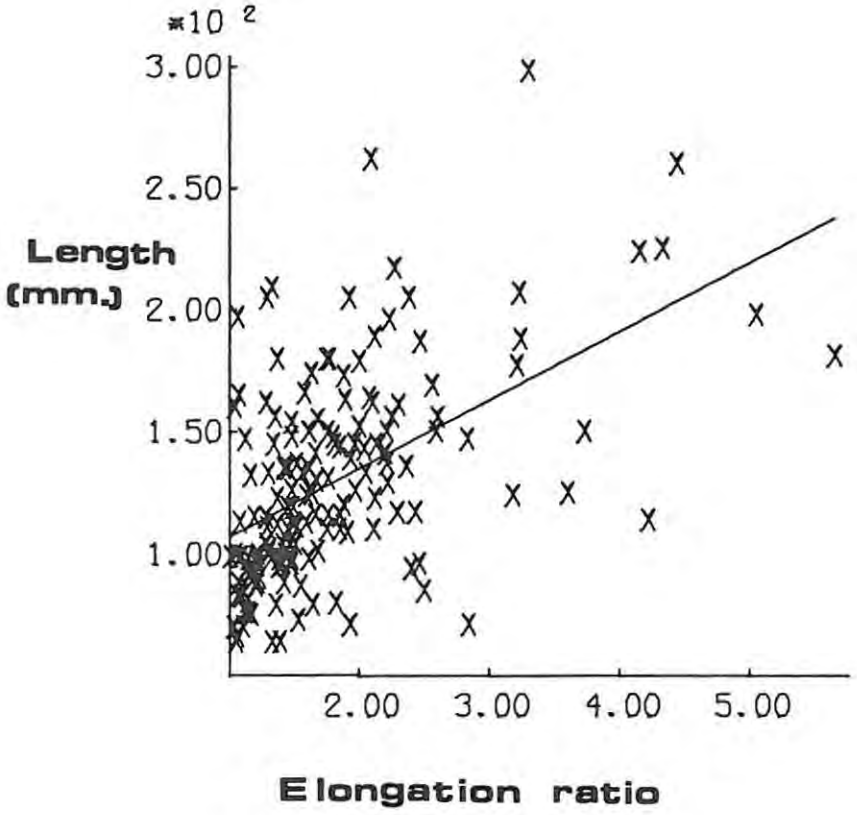


Figure 9 : Plot of elongation ratios vs. lengths of zircon grains.

IV TRACE ELEMENT GEOCHEMISTRY

A. INTRODUCTION

The concentrations of 14 trace elements were determined in 22 samples of Molteno Formation and in 7 samples of Elliot Formation. The elements Nb, Zr, Y, Rb, Sr, Co, Cr, V and Ti were analyzed using X-ray fluorescence spectrometry at Rhodes University. Analytical techniques and analytical conditions are described in Appendix A. The elements Mn, Ba, Zn, Cu and Ni were analyzed by the Anglo-American Research Laboratories. Mn and Ba were determined by semi-quantitative spectrographic analysis, while Zn, Cu Ni were analyzed by Atomic Absorption.

Discussion will concentrate on the Molteno Formation; data for the Elliot Formation will only be presented for comparison purposes at the end of the chapter.

B. TRACE ELEMENT BEHAVIOUR IN SEDIMENTS

Trace element data for sedimentary rocks are relatively scarce compared to those available for igneous rocks; still less is the use of trace element content of sediments to elucidate problems of genesis, source and correlation of sediments. It is considered, however, that the trace element concentrations in sediments may be as useful to the sedimentologist as the trace element concentrations of "hard" rocks to the igneous petrologist.

The trace element content of clastic sedimentary rocks will depend on the proportions of four types of mineral :

a) Heavy detrital minerals such as zircon, rutile, tourmaline and garnet.

b) Light detrital minerals such as quartz and feldspar.

c) Clay minerals such as illite and kaolinite.

d) Precipitated minerals such as calcite and the Fe-Mn oxides and hydroxides.

The total trace element concentration will be dependent on the amount of the various minerals present as well as the amount of the trace elements that they actually contain. Some of the trace elements will be held in the lattices of host minerals, such as potassium in alkali feldspar, others will be present in the form of discrete minerals, such as zirconium in zircon. A summary of the expected trace element behaviour relevant to sedimentary rocks follows :

Niobium

Pentavalent Nb has an ionic radius of 0,72Å (all ionic radii quoted are from Whittaker and Muntus (1970), radii are given for the most likely co-ordination of the ion) when in octahedral co-ordination. On the basis of ionic size niobium may be expected to substitute for Ti, Sr, Zr, Mo and W. Nb may form its own minerals, mainly oxides but these are extremely rare. The tendency of Nb to proxy for Zr and Ti leads to its concentration in the heavy detrital minerals. Some Nb may be taken into solution on weathering and subsequently be scavenged by Fe-Mn hydroxides or adsorbed by clay minerals (Van de Kamp et al., 1976).

Zirconium

The ionic radius of tetravalent zirconium is 0,80Å. This combination of ionic size and ionic charge leads to the formation of the mineral zircon ($ZrSiO_4$) rather than its substitution for other cations. Erlank et al. (1978), however, consider that Zr may proxy for elements such as Fe and Ti. The bulk of zirconium in a sediment will be in the form of detrital heavy minerals, mainly zircon, with much lesser amounts perhaps present in ilmenite, rutile or garnet. Nicholls and Loring (1962) have suggested that zirconium may proxy for Al^{3+} in clay minerals. Degenhardt (1957) has reported values of 80 ppm Zr in kaolinite, 100 ppm in illite and 140 ppm in montmorillonite. Hofmeyr (1971) and Cosgrove (1973) also indicate that significant amounts of Zr may be contained in clay minerals.

Yttrium

Trivalent yttrium with an ionic radius of 0,98Å is slightly smaller than Ca and can thus be expected to substitute for it. There are no common Y minerals; rather Y will be found in Ca-bearing mineral phases such as calcite, apatite and garnet (Rankama and Sahama, 1952).

Strontium

Sr^{6+} has an ionic radius of 1,21Å, intermediate in size between calcium and barium. Sr would therefore be expected to enter the plagioclase and K-feldspar lattices. Replacement of Ca in calcite and apatite could also be predicted.

Rubidium

Potassium is very similar in size to rubidium; consequently potassium is often replaced by rubidium in K-feldspar and in micas. Van der Kamp et al. (1976) reports that illite readily holds rubidium in its lattice.

Zinc

The behaviour of zinc is to a certain extent unpredictable. Zinc does form sulphide ores such as sphalerite, these are however uncommon in sediments. The ionic radius of Zn is similar to that of Fe^{2+} and Mn^{2+} and will replace them in a variety of minerals. Magnetite, ilmenite and garnet may all contain zinc. It is also found in the chlorite group minerals and may be fixed by the highly absorbing clay minerals of the montmorillonite and kaolinite groups as well as by precipitated ferric iron oxides. Van der Kamp et al. (1976) consider the majority of zinc in sediments to be held by clays.

Manganese

Mn forms oxide minerals such as pyrolusite and cryptomelane. As a result of the valencies and ionic radii of Mn it may substitute for ferric iron. Some Mn may be found in garnets; greater amounts will be present in the form of Fe-Mn oxides and hydroxides.

Barium

Ba^{2+} has an ionic radius of 1,44Å. It forms an essential component of the minerals barite ($BaSO_4$) and celsian, a feldspar ($Ba\ Al_2Si_2O_8$). Since its ionic radius is close to that of potassium it will proxy for K^+ in K-feldspar and in micas. Ba is adsorbed by montmorillonite, kaolinite and illite. Hydrous iron and manganese oxides will also adsorb barium (Puckelt, 1972).

Copper

Since the ionic radius of Cu^{2+} is similar to that of Fe^{2+}, Cu^{2+} will proxy for ferrous iron. Substitution of Cu in most common rock-forming minerals may therefore be expected. Minerals such as magnetite, ilmenite, garnet, mica and plagioclase may all contain low amounts of Cu. Higher concentrations can be expected in clays and Fe-oxides.

Nickel

Ni^{2+} is intermediate in size between Fe^{2+} and Mg^{2+} and can consequently be expected to substitute for iron in spinels. In sediments the bulk of Ni will be presented in magnetite and ilmenite.

Cobalt

Co^{2+}, due to the similarity in ionic size with nickel, will in part mimic the behaviour of Ni. The ease with which Co substitutes for Fe^{2+} and Mg^{2+} is not as great as that of Ni but it will nevertheless be found in small amounts in ilmenite and magnetite.

Chromium

Cr will replace ferric iron to a large degree; Ti and Mg are also replaced by Cr. Consequently the detrital minerals holding Cr will be those such as magnetite, pyrope, uvarovite, ilmenite and rutile.

Vanadium

V^{3+} is slightly larger than Cr^{3+}, and will readily enter Fe^{3+} and Ti^{4+} sites. Ilmenite and magnetite will act as hosts to V. According to Landergren (1969), V will be absorbed by the montmorillonite and chlorite groups of clay minerals.

Titanium

Ti^{4+} forms an essential constituent of the titanium dioxide minerals (rutile, brookite and anatase) and ilmenite. Ti^{4+} may proxy for Fe^{3+}, Al^{3+} and Mn^{3+}; substitution will occur in andradite garnets and in micas. Titanium is also an abundant constituent of clays, especially illite and kaolinite (Degens, 1965).

C. RESULTS

Results of the analyses for the 22 samples of Molteno Formation are presented in Table 6. The localities of these samples and their stratigraphic height in the succession are shown in Figure 10. Summary statistics relating to the number of cases for each element, the mean, standard deviation and range of the concentrations are given in Table 7. For comparison purposes average trace element concentrations of sandstones and shales as given by Marchant and Moore (1978) are also presented in Table 7.

As has been related in the section on sampling, an attempt was made to collect a representative lithological sample of the Molteno Formation. The samples are in the main classified as sandstones but samples AJR45, AJR60 and AJR61 are fine grained argillaceous sediments. Comparing the values obtained in the present study with those for average sandstones and shales (Table 7) it can be seen that:

a) Zirconium and barium are enriched in the Molteno sediments relative to the average values for sandstones and shales.

TABLE 6 : TRACE ELEMENT ANALYSES - MOLTENO FORMATION

	Nb	Zr	Y	Sr	Rb	Zn	Mn	Ba	Cu	Ni	Co	Cr	V	Ti
AJR1	8	320	20	62	61	41	600	1000	9	5	17	23	39	5100
AJR2	8	321	23	46	66	58	250	750	12	10	14	23	44	4600
AJR14	3	122	8	39	20	25	180	400	10	2	2	6	13	1900
AJR17	8	225	25	73	86	77	400	650	3	9	19	16	39	4400
AJR26	13	446	35	56	112	94	200	1500	15	27	16	44	63	8300
AJR29	5	137	14	31	69	11	150	900	15	12	3	14	25	3300
AJR35	8	530	18	50	69	31	300	900	10	11	10	14	26	4600
AJR37	13	705	33	44	72	48	250	900	14	14	13	30	45	7500
AJR44	8	168	18	492	145	62	600	3000	9	13	10	15	66	5200
AJR45	15	234	28	106	180	63	120	900	16	9	6	36	54	6700
AJR48	4	151	9	6	23	x	x	x	x	x	5	12	14	2100
AJR51	4	364	28	106	74	42	350	850	7	14	8	29	61	6400
AJR54	8	34	13	25	36	4	80	700	2	4	2	2	9	2000
AJR58	8	337	13	80	73	14	180	900	2	4	6	24	19	2000
AJR60	11	328	44	103	112	x	x	x	x	x	8	26	39	6000
AJR61	17	120	123	286	129	33	180	3000	3	4	6	1	8	2000
AJR62	2	146	6	30	20	36	80	320	7	5	3	2	6	5100
AJR63	9	277	26	58	78	47	350	1500	12	18	15	22	53	5200
AJR64	2	83	6	7	17	4	90	350	2	5	2	4	8	1400
AJR65	13	472	36	56	140	30	80	650	3	5	4	21	45	6450
AJR67	2	115	6	10	15	11	100	400	2	7	5	13	13	1200
AJR77	9	277	26	58	78	47	350	1500	12	18	15	22	53	5200

All analyses expressed in parts per million

x = analyses not available

Zn, Mn, Ba, Cu, Ni - Analyses courtesy of Anglo American (Zn, Cu, Ni - Atomic Absorption Analysis, Mn, Ba - Spectrographic analysis)

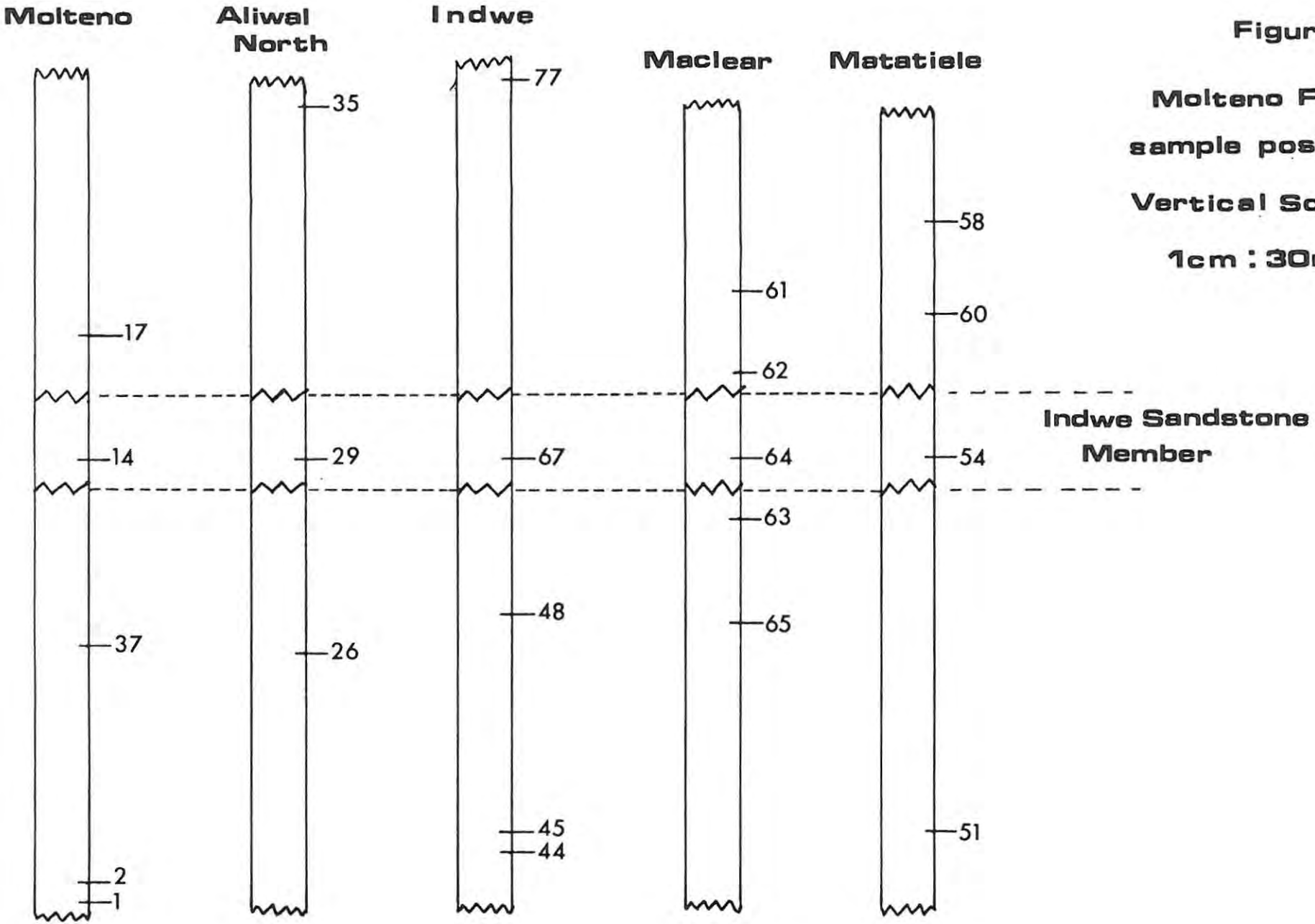


Figure 10

Molteno Fm. – sample positions

Vertical Scale

1cm : 30m

TABLE 7 : SUMMARY STATISTICS - MOLTENO FORMATION

Element	N	Mean	Std. Deviation	Range	Ave. Sandstone	Ave. Shale
Nb	22	8,0	4,3	2-17	Not avail.	11
Zr	22	264,2	167,5	34-705	216	192
Y	22	19,3	11,6	6-123	15	30-38
Sr	22	97,1	123,9	6-492	20	300
Rb	22	74,8	45,9	20-180	46	164
Zn	20	34,8	25,6	4-94	30	95
Mn	20	216,4	164,7	80-600	200-540	850
Ba	20	935,0	77,0	320-3000	316	546
Cu	20	7,0	5,4	2-16	25-30	39
Ni	20	8,5	6,3	4-27	2	68
Co	22	8,2	5,3	2-19	0,3	19
Cr	22	17,3	11,8	2-44	35	90
V	22	2,7	19,7	8-66	12-79	98-260
Ti	22	4393,2	2159,4	1200-8300	1500	4600

All values expressed in parts per million. Values for average sandstone and average shale taken from a compilation by Marchant and Moore (1978).

b) Yttrium, strontium, rubidium, zinc, manganese, nickel, cobalt, vanadium and titanium have concentrations intermediate between the average concentrations for sandstones and shales.

c) With respect to the average values for sandstones and shales, both cobalt and chromium are depleted in the Molteno sediments, relative to average sandstones and shales.

Histograms showing the frequency distribution of the elements are presented in Figure 11. Chayes (1954) suggests the use of a class interval for histograms of $^1/_3$ of the standard deviation of the sample distribution but it was considered more convenient to use a class interval of approximately maximum value/six. Since the number of cases was low (maximum n = 22) the histograms are in some cases very irregular; no definite assumptions can be drawn regarding the distributions of elements such as V, Zn, Rb and Y. Some elements do exhibit a fairly smooth recognizable pattern. The frequency of Zr, Sr, Mn, Ba, Co and Cr show positively skewed distributions. This is a common feature of trace element distributions in most rocks (Spencer, 1966; Stephens et al., 1975).

1. Variations in trace element concentrations with stratigraphic height

The variation of element abundance with stratigraphic height is illustrated in Figure 12. The plots must be interpreted with care because successively higher samples were often collected at considerable distances apart. As a result it is possible that differences due to lateral variations may confound the differences due to vertical variation. Nevertheless it was felt that some meaningful relationships might emerge. Polynomial regression curves of degree 1 have been drawn through the data and correlation coefficients calculated. As can be seen from the plots there is no very pronounced "straight line"

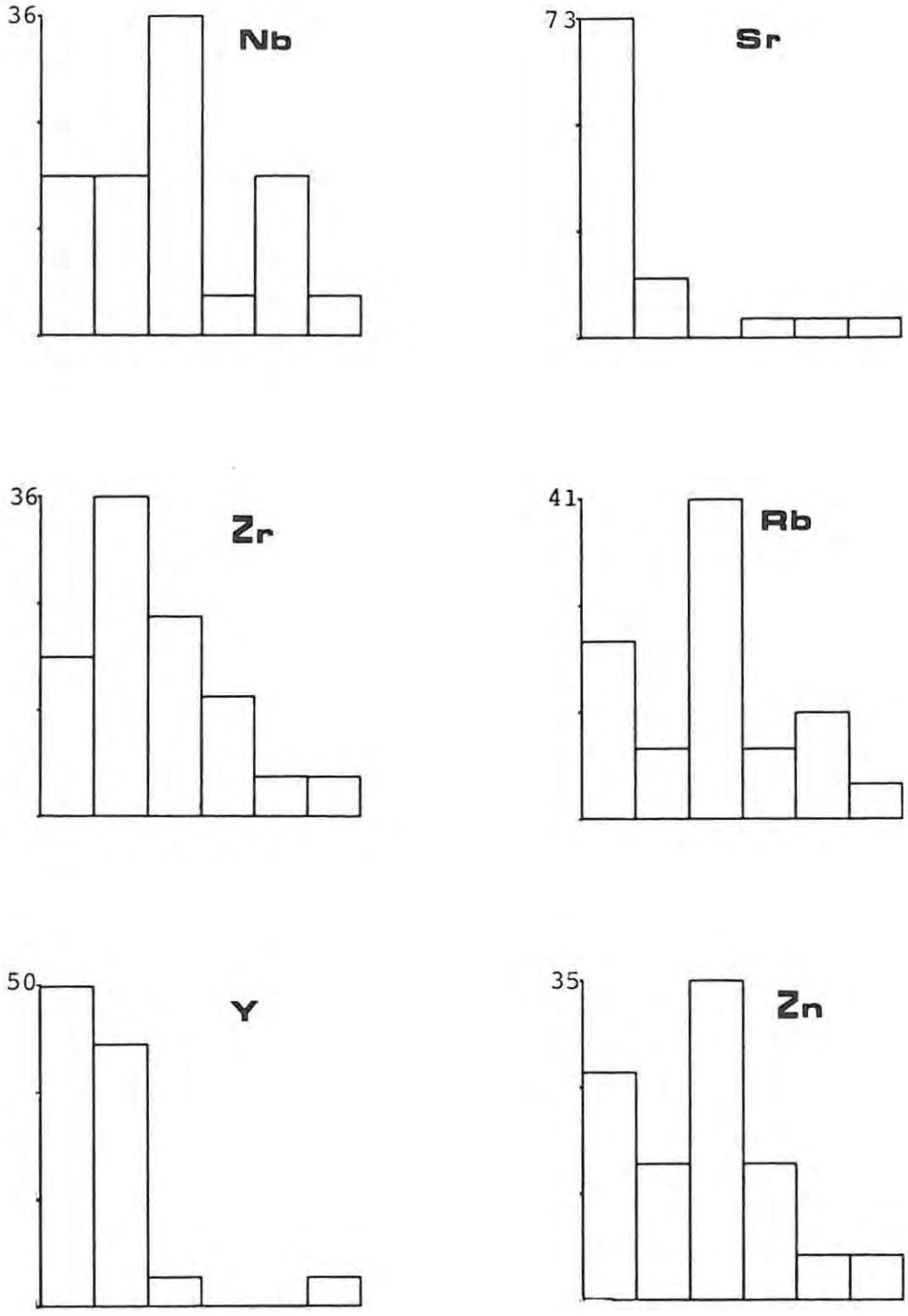
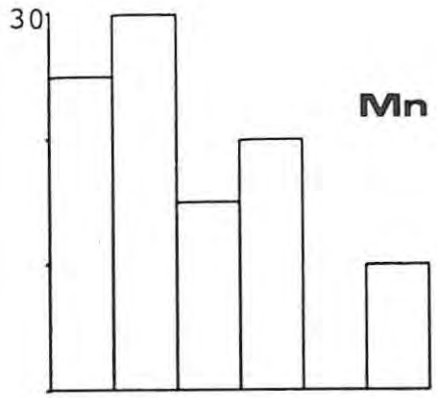
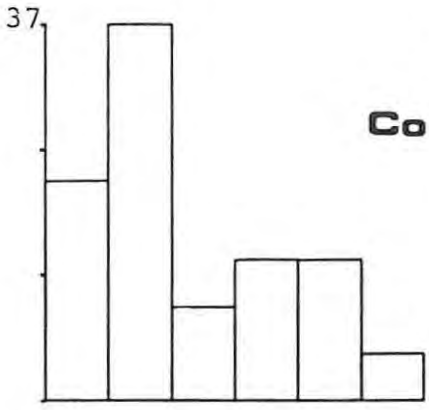


Figure 11 : Histograms showing percentage frequency of elements analysed.

Horizontal axis = concentration in parts per million.

Vertical axis = percentage frequency.


30
Mn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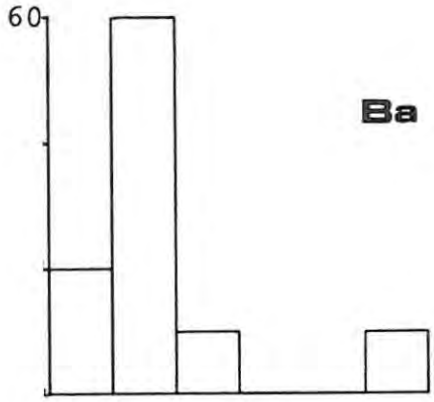
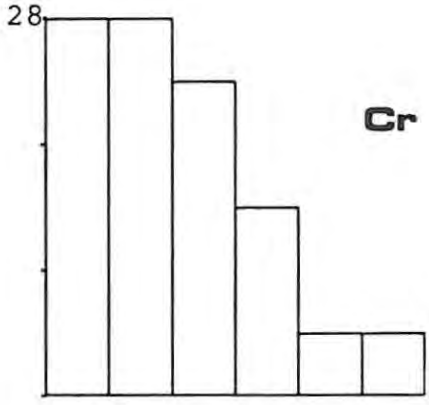
Co


60
Ba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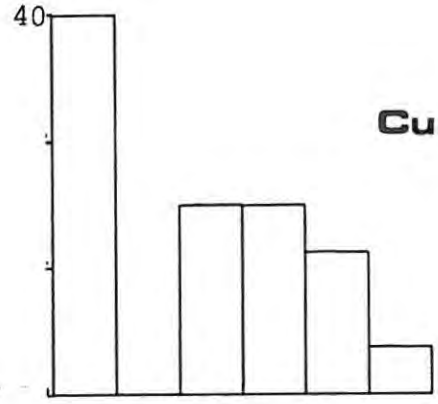
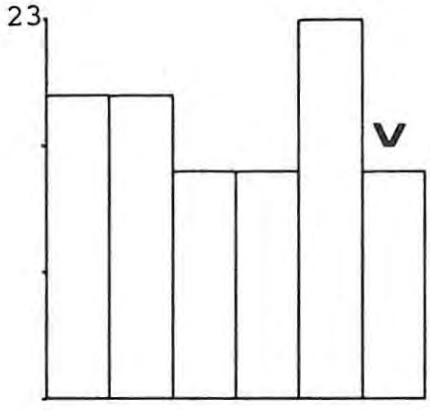
Cr


40
Cu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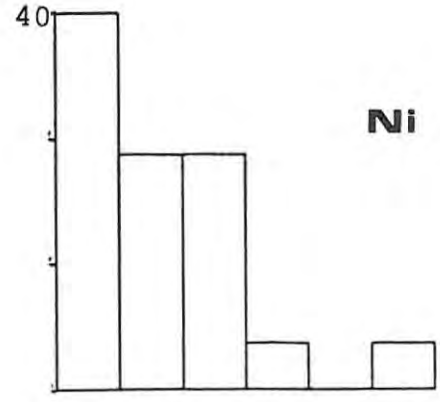
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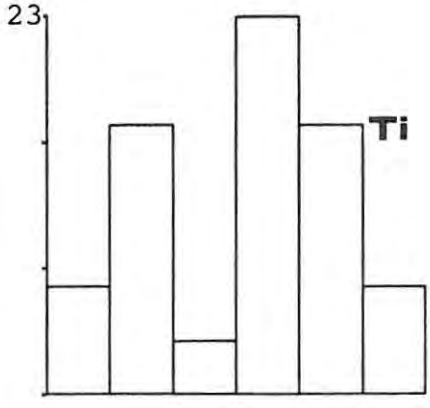
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Ti

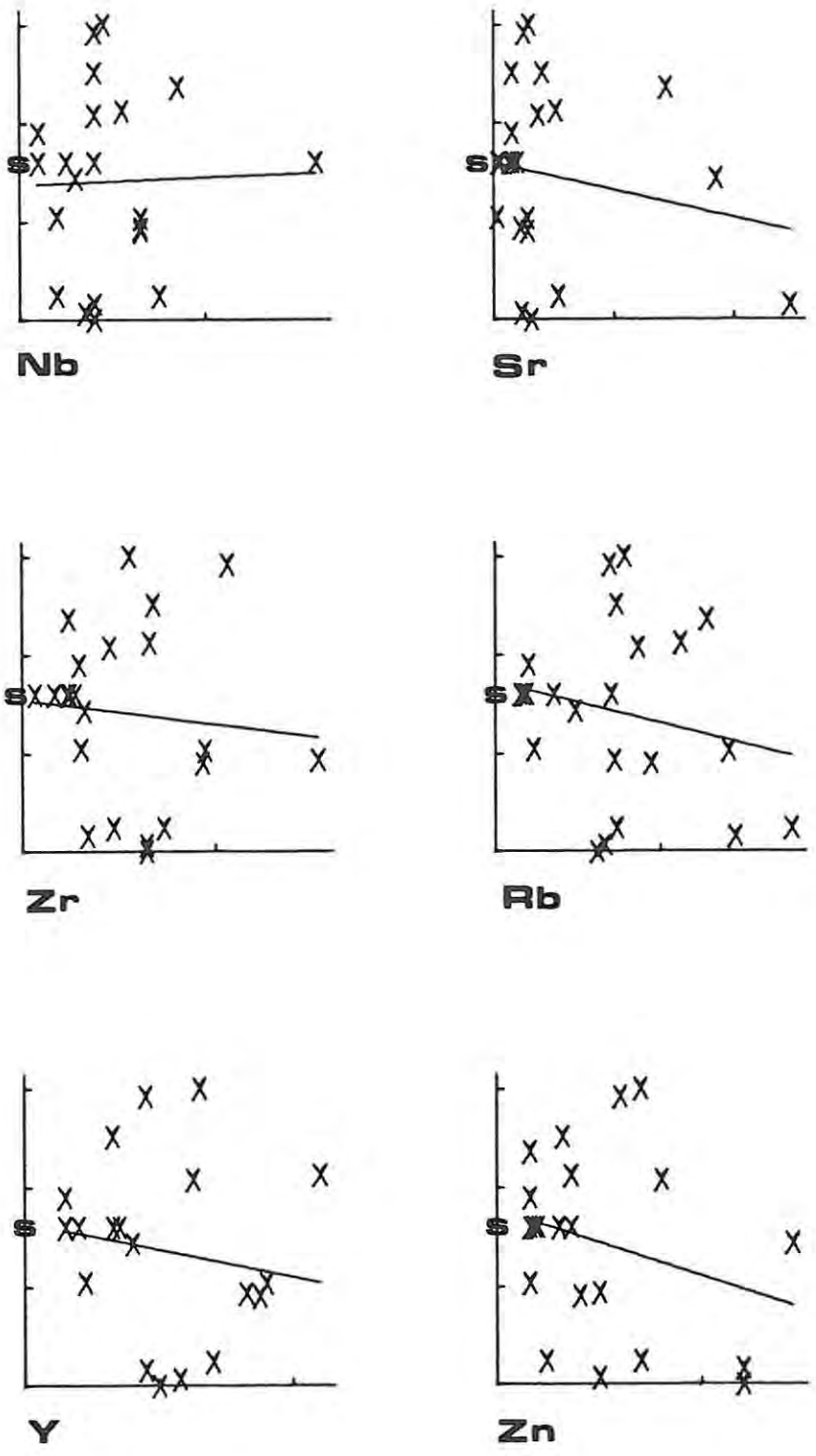
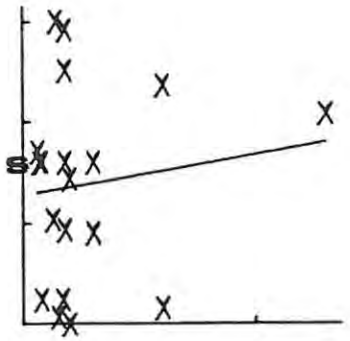


Figure 12 : Variation in trace element concentrations with height, Molteno Formation ("s" marks height of the Indwe Sandstone Member).

Vertical axis = height in metres (maximum = 500m)

Horizontal axis = concentration in parts per million



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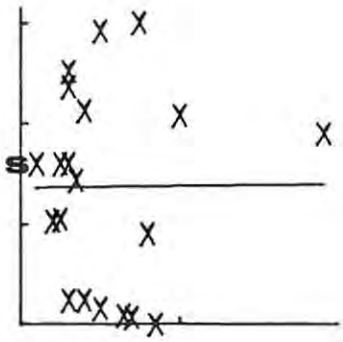
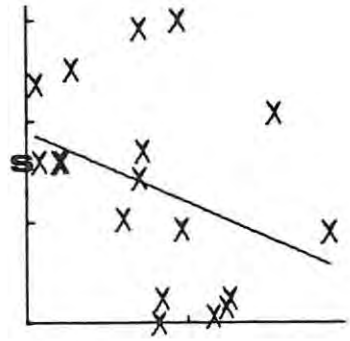


Co



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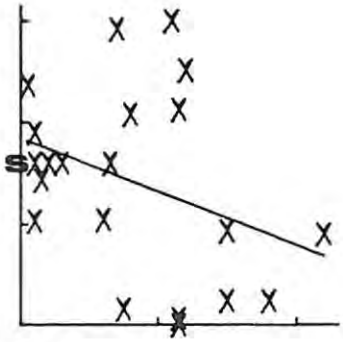

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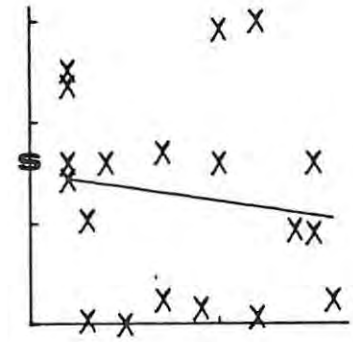

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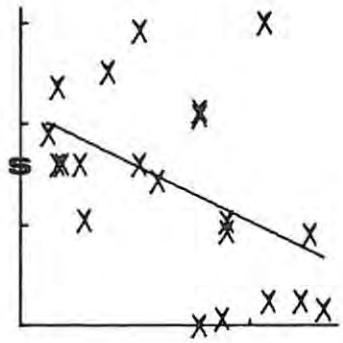

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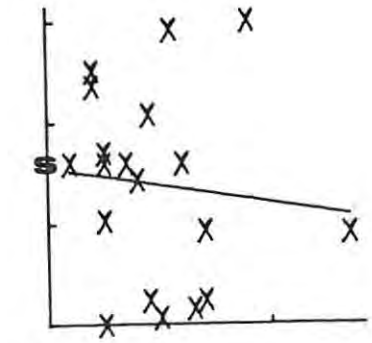
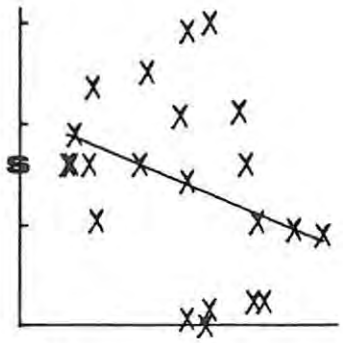


Mn



Ti

relationship between stratigraphic height and trace element concentration. The Student's t-test has been applied to the correlations found to determine whether any of the relationships are statistically significant. Tabulated values were obtained from Pearson and Hartley (1972). The 95% confidence level is only satisfied by one relationship, that of vanadium, which shows a decrease in concentration with stratigraphic height. The rather low confidence level of 90% has been applied to the remainder of the relationships and it is found that titanium, chromium and copper all show significant decreases at this level.

Perhaps more important than these rather dubious relationships is the marked depletion of certain elements in the samples of Indwe Sandstone (AJR14, 29, 54, 64, 67) relative to the lithologies above and below them. This is especially evident for zirconium, yttrium, strontium, manganese, chromium and cobalt. This depletion could be due to two causes :

a) The Indwe Sandstone Member has a much higher quartz content than the lithologies above and below it; consequently the initial concentrations of trace elements would be expected to be lower.

b) The Indwe Sandstone Member is very coarse grained and extremely porous. It is possible therefore that even if the trace element concentration had been "normal" initially, it has since been lowered by weathering and leaching of the unit.

To sum up, there are probably no useful geochemical variations with respect to stratigraphic height in the Molteno Formation with the possible exception that the Indwe Sandstone Member is depleted in certain trace elements.

2. Variations in trace element content with geographic position

The Molteno Formation consists of sediment derived from two source areas (Turner, 1975(a)). The southern source area consisted of sedimentary rocks while the

area to the south-east was mainly granitic in character. It could have been expected that these different provenance areas would result in different suites of minerals being present depending on which of the source areas was dominant in a particular area. It was found in Chapter 3 that relative to geographic location of the samples, no significant variation in the heavy mineral suite occurred. This is probably partly due to the extremely impoverished suite that exists. Trace element data will reflect not only the contribution due to the presence of heavy minerals but is also a reflection of the other types of minerals present. It was considered that samples taken closer to the granitic source area might be enriched or depleted in certain elements relative to samples taken closer to the sedimentary source area.

In order to separate the effect of stratigraphic height on the geographic position, the sample suite was divided into 3 groups :

a) The Indwe Sandstone Member,

b) Samples from below the Indwe Sandstone Member - the Bamboesberg Member,

c) Samples from above the Indwe Sandstone Member - the Kramberg Member.

The trace element geochemistry of the 3 groups was then compared relative to their geographic positions. The problem of defining geographic positions relative to the influence of the different source areas is difficult. The exact location of the two areas is unknown and furthermore, even if the location were known, the pattern of inflow into the basin would in all probability be extremely complex. It was decided to plot geographic position in an arbitrary fashion such that the positions are plotted as being certain distances eastwards of the most westerly sample area, Molteno. The arbitrary positions are :

Molteno area	0 km east
Aliwal North area	36 km east
Indwe area	86 km east

Maclear area	175 km east
Matatiele area	250 km east

In view of the small number of areas available for comparison, as well as the arbitrary fashion in which geographic position relative to source area influences has been defined, it was decided not to try and derive statistically significant variations. It was hoped nevertheless that some variations with respect to geographic position would be evident.

Five of the relationships investigated do in fact show a degree of systematic geochemical variation with geographic position. In Figure 13(a) it can be seen that the Zr content of the Indwe Sandstone Member decreases in an easterly direction, i.e. in the direction of the granitic source. This is not, as one would expect at first, an anomalous situation. While zircon, in which the majority of zirconium is contained, is very common as an accessory mineral in granites, it is a resistate mineral and tends to become enriched in sediments relative to granitic rocks (Marchant and Moore (1978) report the average granite as containing 175 ppm Zr and the average sandstone as 216 ppm). Consequently a lower content of Zr in sediments closer to the granitic source area can be expected. This decrease eastwards is at odds with the heavy mineral data (Chapter III), where it was seen that the amount of zircon in the sample from the Molteno area was lower than for the samples from the more easterly areas. This discrepancy may be explained in two ways :

a) In the heavy mineral analysis only the size range 125-250 microns was examined. This obviously does not contains all the zircon in the rocks.

b) While most of the zirconium will be held in the mineral zircon, a significant proportion may be held by clay minerals as has been discussed previously.

In the samples from below the Indwe Sandstone Member (the Bamboesberg Member), both cobalt (Figure 13(b)) and nickel (Figure 13(c)) decrease eastwards. A sympathetic decrease in the amounts of magnetite/ilmenite eastwards is probably the

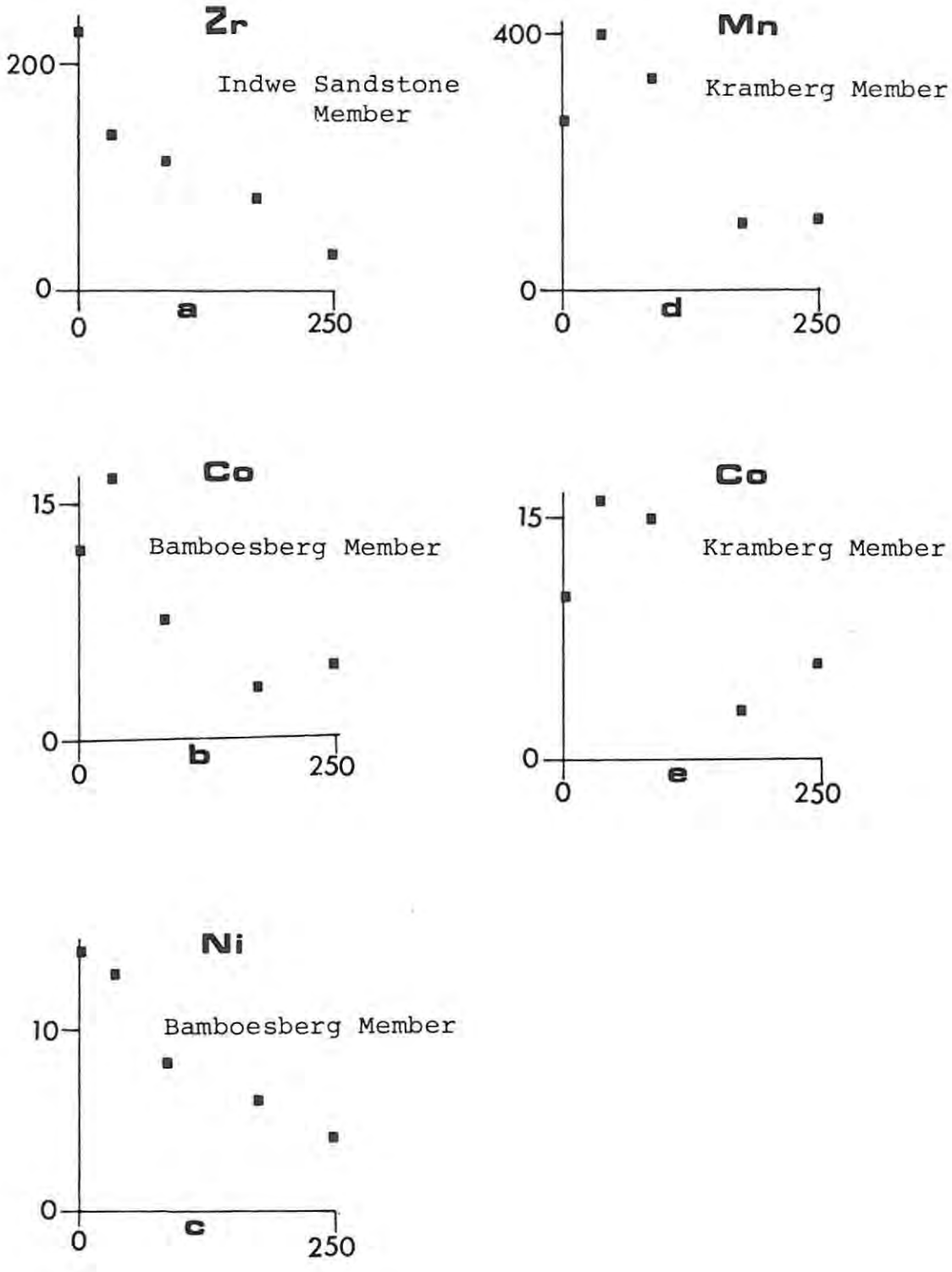


Figure 13 : Variations in trace element concentrations with geographic position.

Vertical axis = concentration in parts per million.

Horizontal axis = distance eastwards of Molteno in kilometres

source of this variation. However, no petrographic evidence for this can be presented; it is also noticeable that other elements held in opaque detrital phases are not affected by a similar decrease. In the Kramberg Member (above the Indwe Sandstone Member) manganese and cobalt show overall decreases eastwards (Figure 13(d) and Figure 13(e)). The variation in Mn is possibly due to a decrease in Fe-Mn oxides and hydroxides eastwards. There is some supporting evidence for this, because as has been mentioned amounts of goethite were seen in AJR14 and AJR29, but not in the samples from further eastwards. Of course much of the oxide-hydroxide phase present in the Molteno sandstones is present as a surface coating on the quartz grains. Qualitative differences in the amount of surface coating are not evident. The decrease in the cobalt concentrations is probably due to variation of the magnetite/ilmenite content of the rocks.

It can be said therefore that while the approach adopted in this section was not rigorous, a clear indication that there are systematic geochemical variations with geographic position has been obtained.

3. Interelement variations

A measure of the degree of the linear relationship between two variables is expressed by r, the correlation coefficient. Because the correlation coefficient is a ratio, it is a dimensionless number; r may vary from -1 through 0 to +1. Where r = +1 there is perfect sympathy between x and y, i.e. x and y have a direct linear relationship. If r = -1, the relationship shows perfect antipathy and where r = 0, there is no linear relationship between the two variables.

In a given type of rock, the correlation coefficient may thus be taken as a measure of the geochemical coherence between the two elements (Rankama and Sahama, 1959). A matrix of correlation coefficients for the 14 elements analysed has been calculated and is presented in Table 8.

TABLE 8 : CORRELATION COEFFICIENT MATRIX - MOLTENO FORMATION

	Nb	Zr	Y	Sr	Rb	Zn	Mn	Ba	Cu	Ni	Co	Cr	V	Ti
Nb	*	0,46	0,50	0,25	0,82	0,42	0,06	0,49	0,26	0,24	0,34	0,47	0,42	0,59
Zr	0,46	*	0,69	-0,16	0,33	0,38	0,20	-0,01	0,38	0,44	0,51	0,69	0,54	0,62
Y	0,50	0,69	*	-0,05	0,55	0,40	0,11	-0,11	0,28	0,39	0,50	0,78	0,78	0,85
Sr	0,25	-0,16	-0,05	*	0,45	0,26	0,44	0,74	-0,08	0,08	0,07	-0,16	0,30	0,10
Rb	0,82	0,33	0,55	0,45	*	0,50	0,21	0,55	0,31	0,29	0,27	0,53	0,66	0,58
Zn	0,42	0,38	0,40	0,26	0,50	*	0,56	0,45	0,59	0,72	0,72	0,54	0,71	0,53
Mn	0,06	0,20	0,11	0,44	0,21	0,56	*	0,55	0,34	0,40	0,67	0,18	0,53	0,26
Ba	0,49	-0,01	-0,11	0,74	0,55	0,45	0,55	*	0,25	0,40	0,25	0,00	0,33	0,15
Cu	0,26	0,38	0,28	-0,08	0,31	0,59	0,34	0,25	*	0,68	0,35	0,52	0,52	0,43
Ni	0,24	0,44	0,38	0,08	0,29	0,72	0,40	0,40	0,68	*	0,55	0,58	0,68	0,56
Co	0,34	0,51	0,50	0,07	0,27	0,72	0,67	0,25	0,35	0,55	*	0,55	0,63	0,49
Cr	0,47	0,69	0,78	-0,16	0,53	0,54	0,18	0,00	0,52	0,58	0,55	*	0,79	0,70
V	0,42	0,54	0,78	0,30	0,66	0,71	0,53	0,33	0,52	0,68	0,63	0,79	*	0,79
Ti	0,59	0,62	0,85	0,10	0,58	0,53	0,26	0,13	0,43	0,56	0,49	0,70	0,79	*

(All correlation coefficients >0,38 are significant at the 95% confidence level).

With one exception, the values are based on the maximum number of comparisons possible in the data set, so for the majority of the elements n = 22. Concentrations of Zn, Mn, Ba, Cu and Ni were not available for 2 of the samples (AJR48, AJR61). Sample AJR61 has anomalously high yttrium (123 ppm), nearly 3 times as high as the next highest value. It has already been noted in the section on petrology, that this sample contained significantly high amounts of garnet and apatite; the presence of these two calcium-bearing phases is probably the reason for such a high Y value. In order to prevent this one very high, anomalous value from disrupting the correlation coefficient pattern it has been omitted from the calculations of the matrix.

Correlation coefficients are somewhat limited in the amount of information they can convey. Two totally different patterns of distributions may give the same correlation coefficient, and in this way incorrect interpretations may be drawn. Figure 14(a) & Figure 14(b) illustrate this effect.

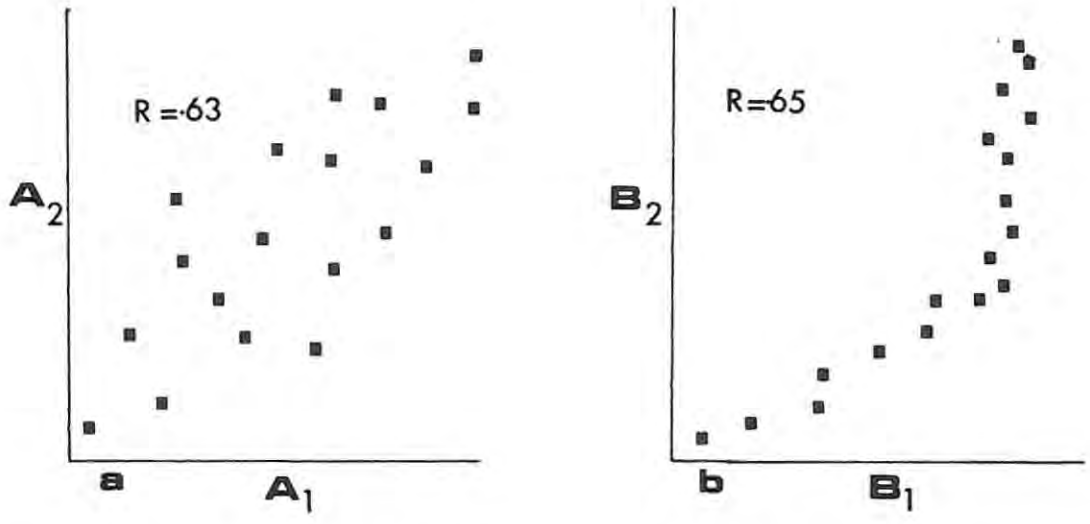
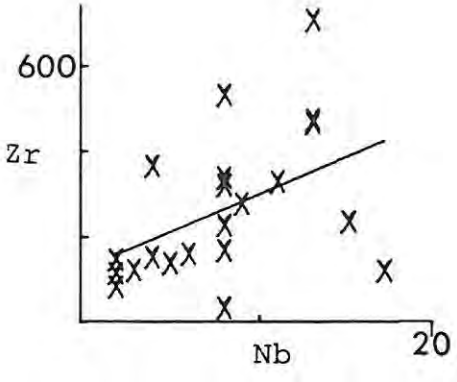


Figure 14(a) and 14(b) : Example of 2 different relationships for which approximately the same correlation coefficient holds.

While the correlation coefficients are approximately the same, the actual relationships are totally different. Interelement variation diagrams have therefore been plotted for those elements that show significant correlations (at 95% confidence level); these are presented in Figure 15. Observation shows that there are no statistically significant negative correlations but 57 statistically significant correlations do exist.

The correlation matrix can be used to designate covariant groups of elements. Those with the highest correlation coefficients will either be those elements which occur in the same mineral, or which occur in separate but covariant minerals. Element pairs such as copper and nickel, cobalt and vanadium, and chromium and vanadium would be expected to have high correlation coefficients because they do occur in the same minerals. The nature of the groups of highly correlated elements and the relationship between them can be used to induce the factors which influence the element correlations. However in a situation where a large number of variables are to be compared, and where there are possibly several underlying factors, the interpretive task is made extremely complex. As can be seen from the interelement variation diagrams, very few of the "best-fit" lines would pass through, or even close to, the origin. Granted a certain degree of experimental error, this nevertheless implies that few if any of the correlated pairs are always found together in the same mineral(s). This has already been indicated in the section of trace element behaviour; elements tend to occur in more than just the one type of mineral (e.g. in detrital minerals as well as clay minerals). Furthermore, the presence of the different types of mineral may be a function of different factors. In order to obviate the complex problem of identification of the coherent groups, a technique which allows for simultaneous consideration of the relationships between many variables has been adopted. This is the technique of factor analysis.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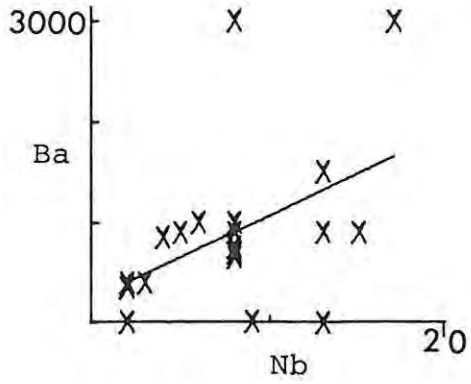
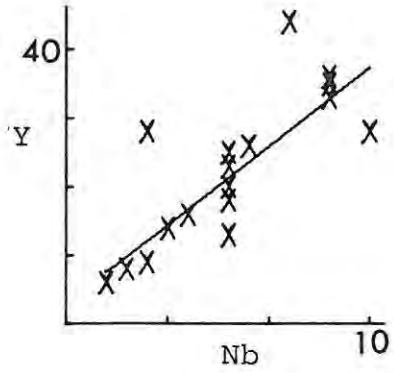
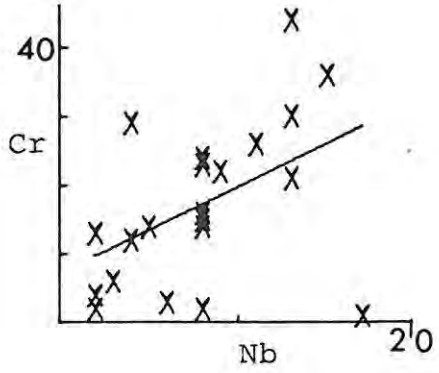
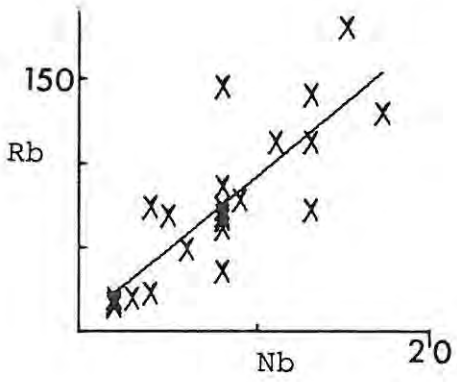
Zr
Nb
20


3000
Ba
Nb
20


40
Y
Nb
10


40
Cr
Nb
20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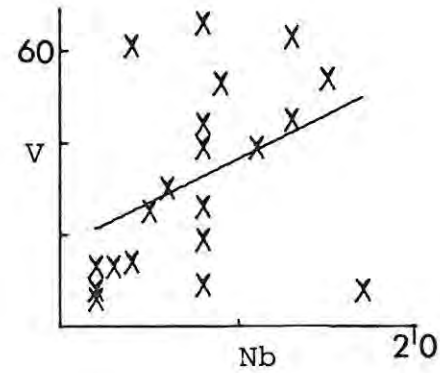
Rb
Nb
20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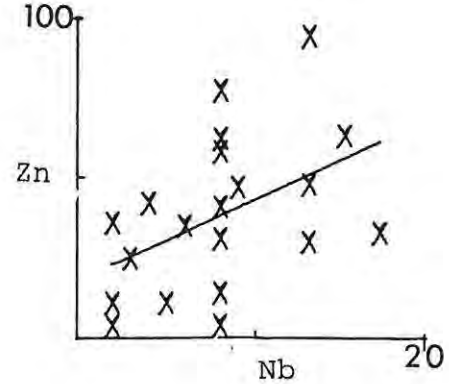
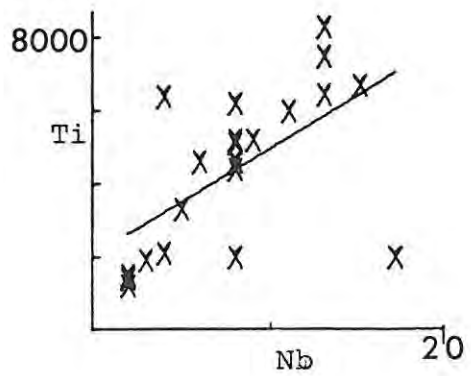
V
Nb
20


100
Zn
Nb
20


8000
Ti
Nb
20

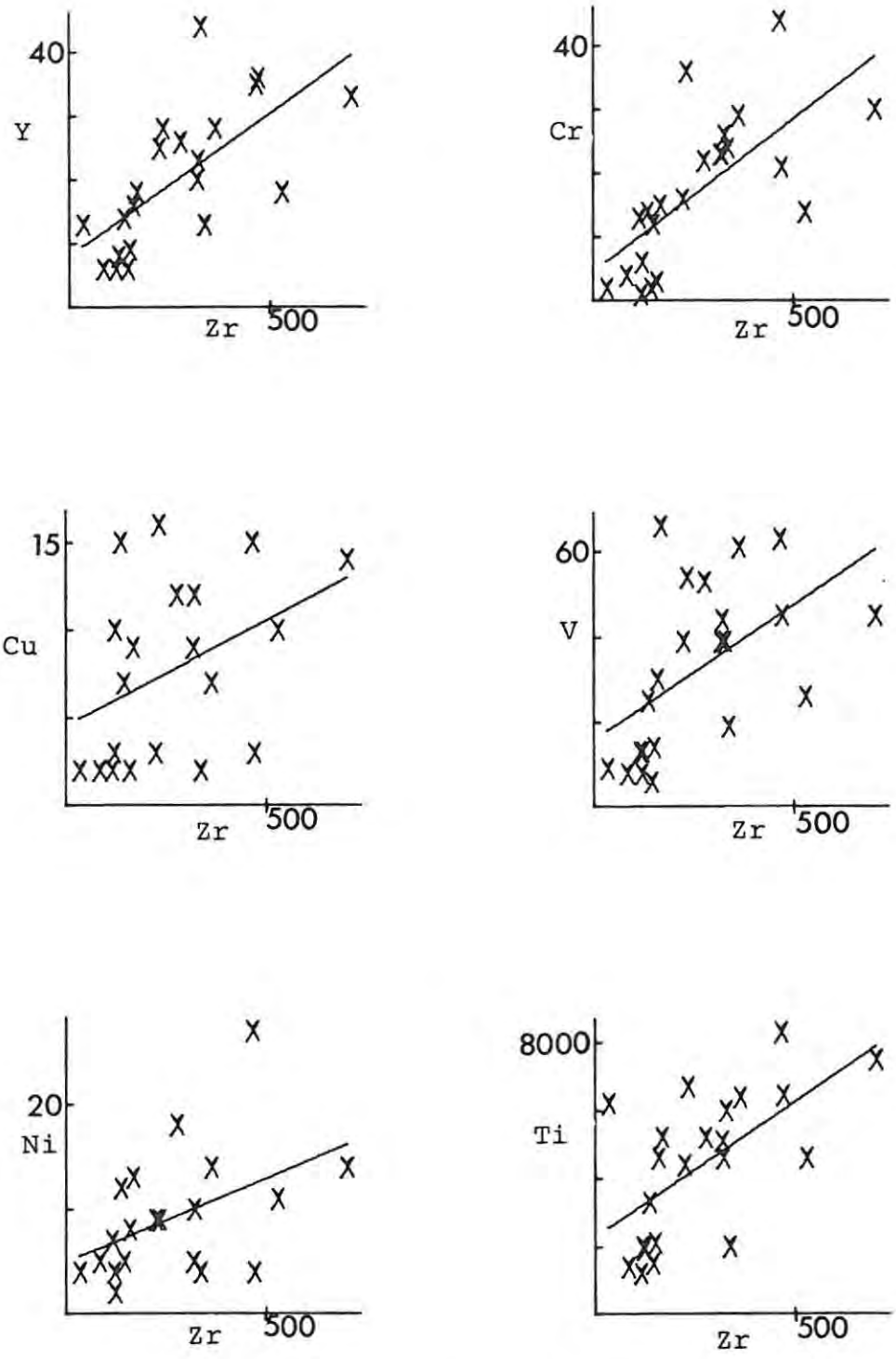
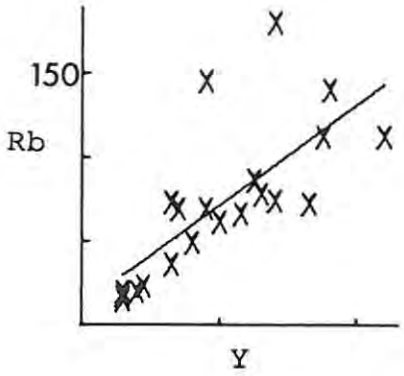
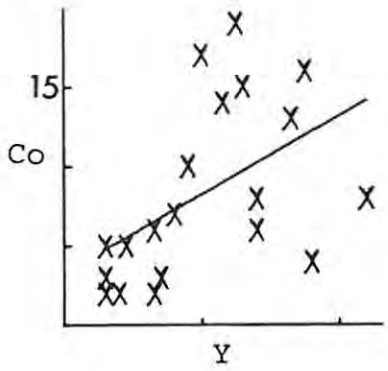
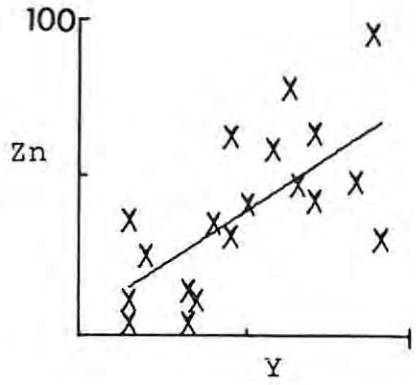
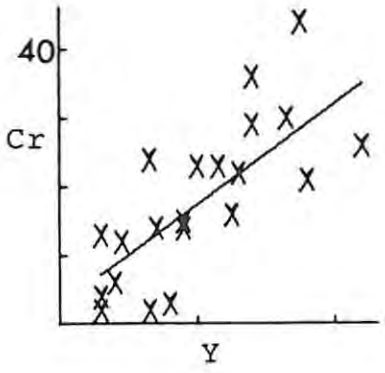


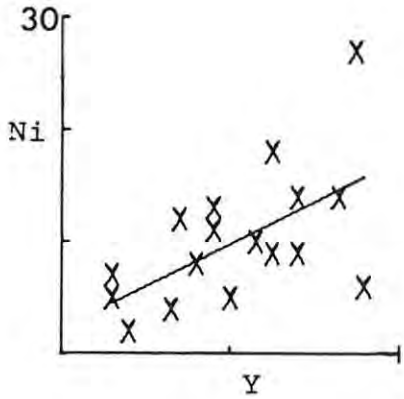
Figure 15 (cont.)

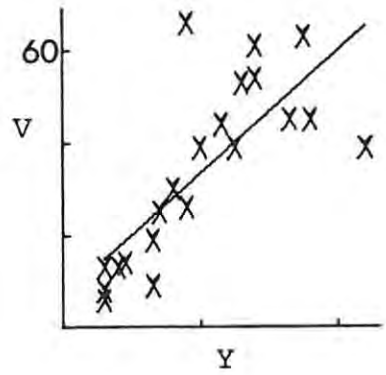












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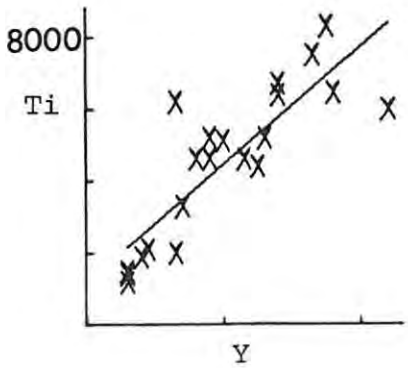

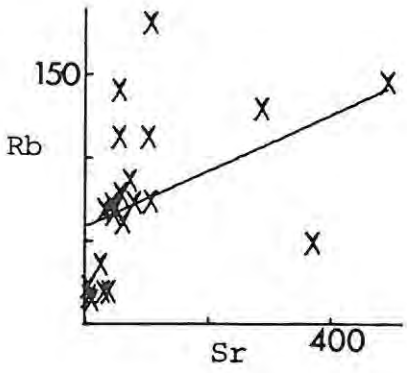

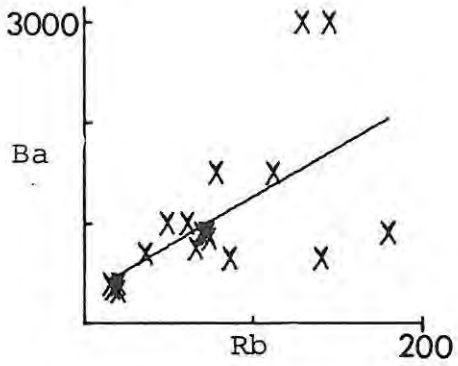

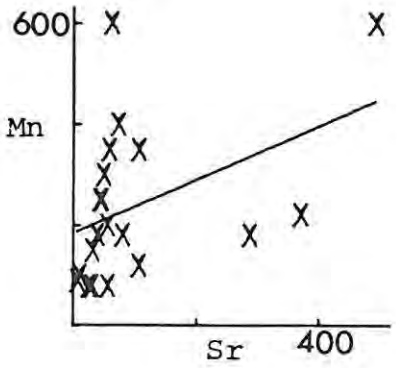

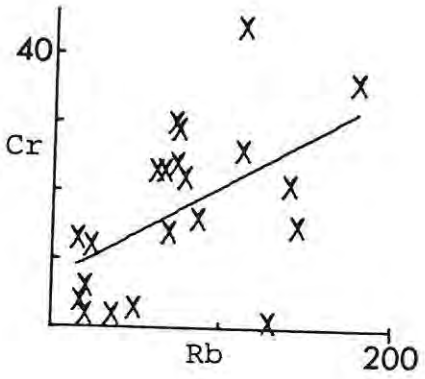

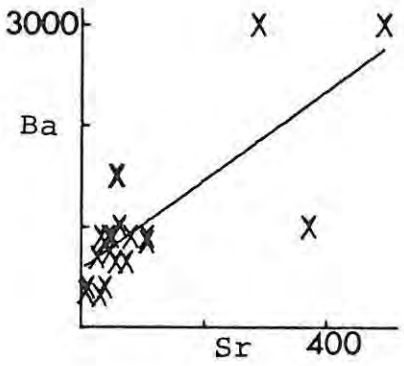

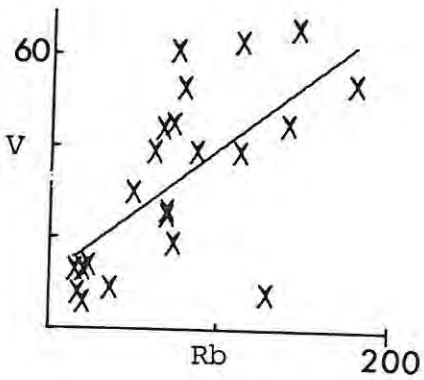

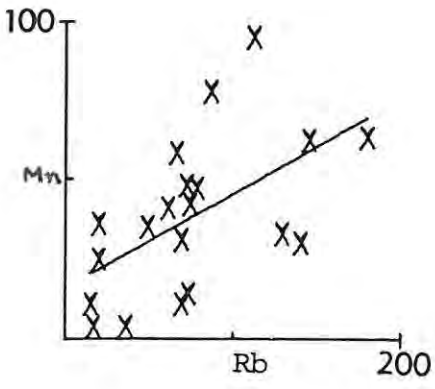

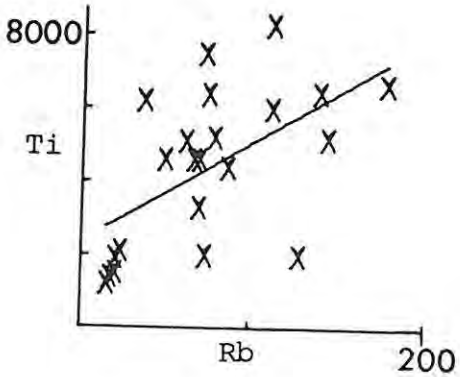

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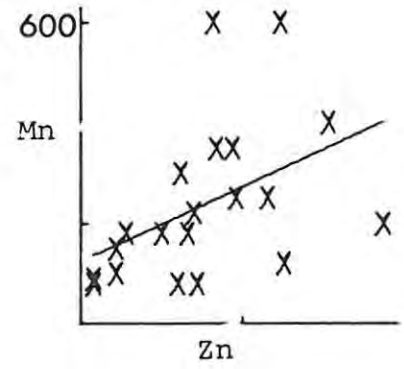
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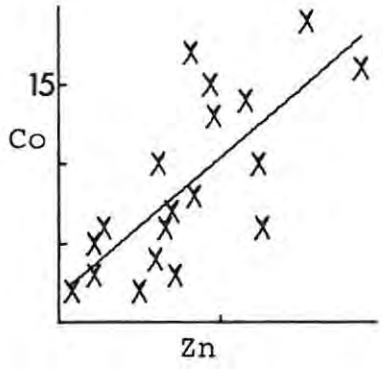
Mn
Zn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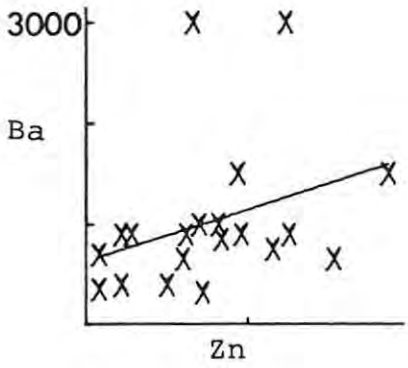
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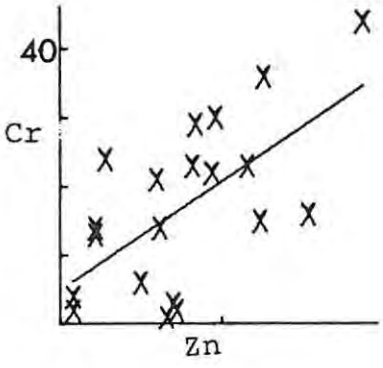
Ba
Zn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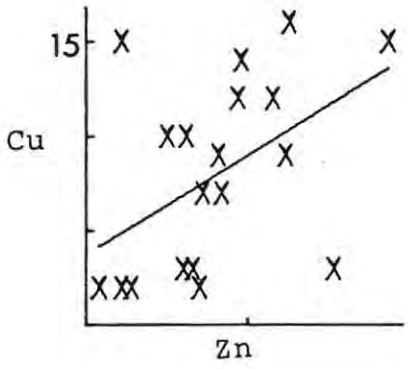
Zn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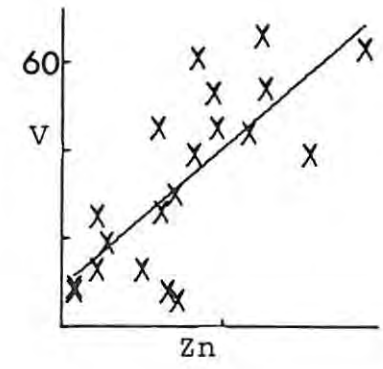
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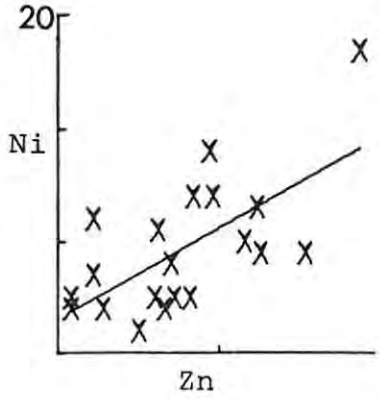
V
Zn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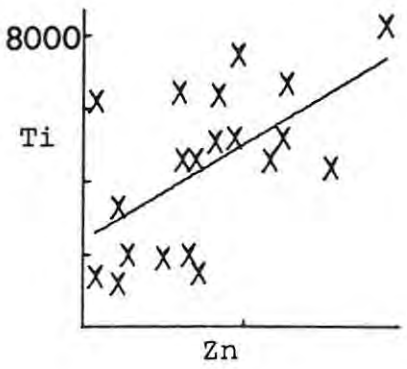
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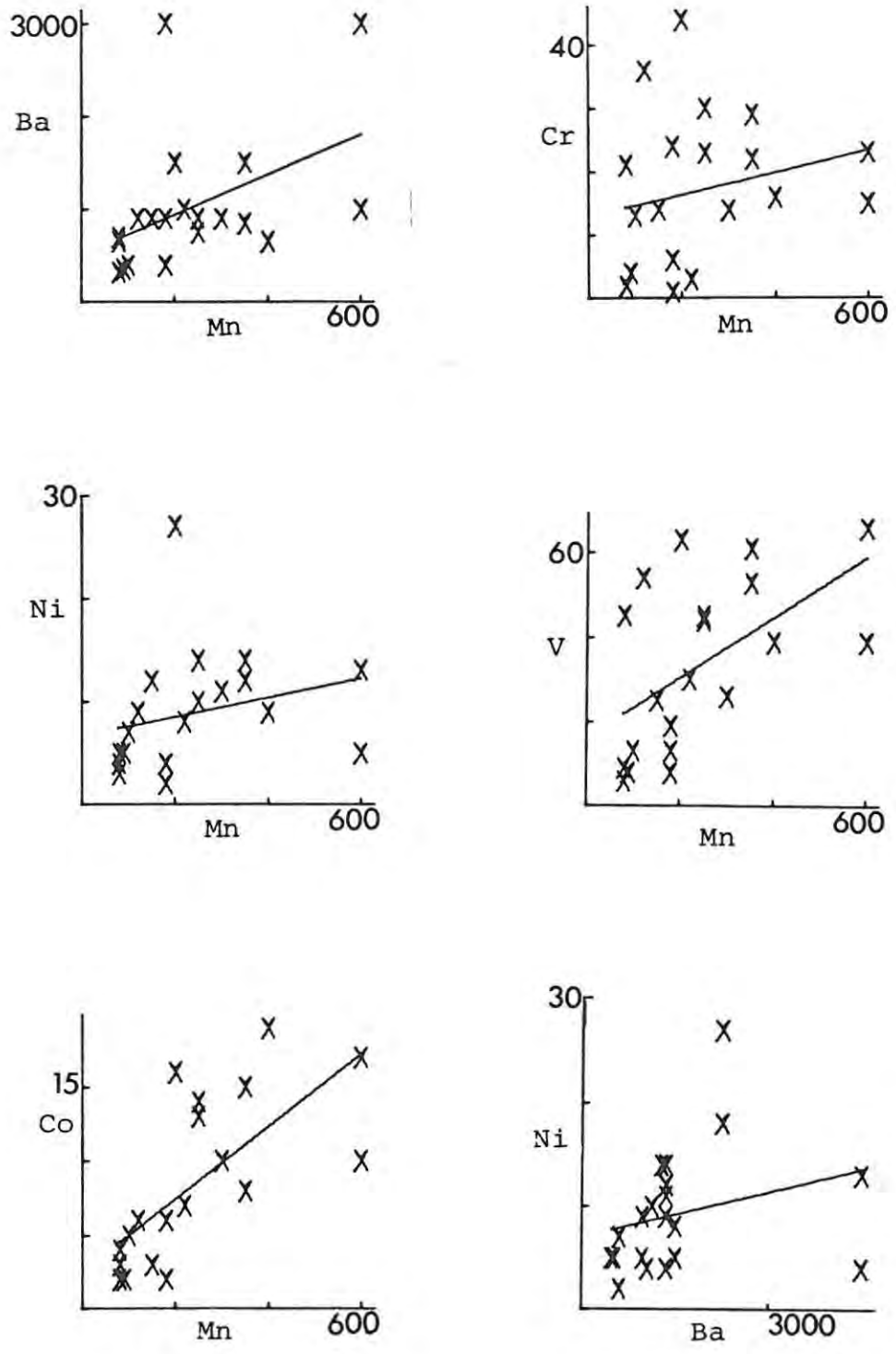
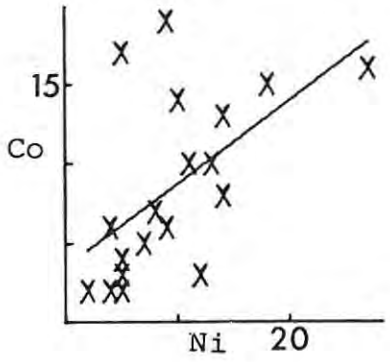


Figure 15 (cont.)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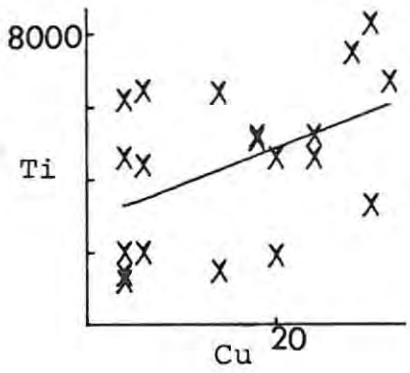
Co
Ni
20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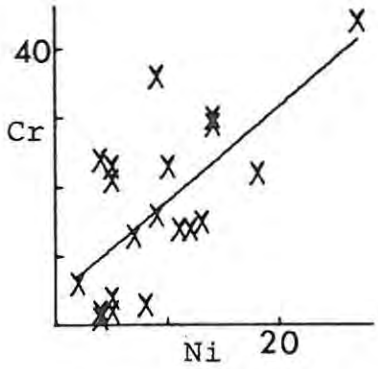
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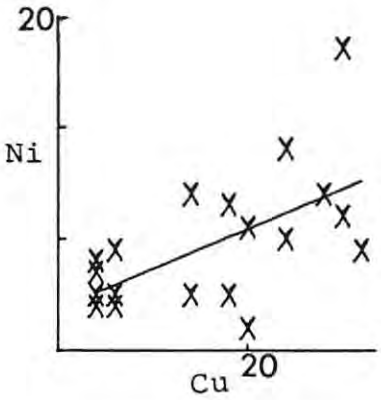
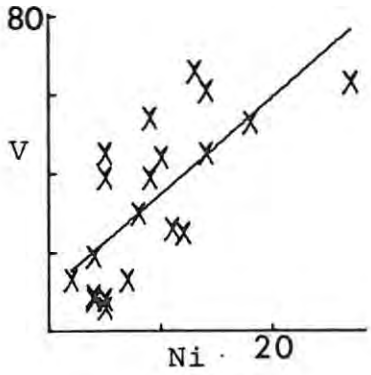
Ni
20


20
Ni
Cu
20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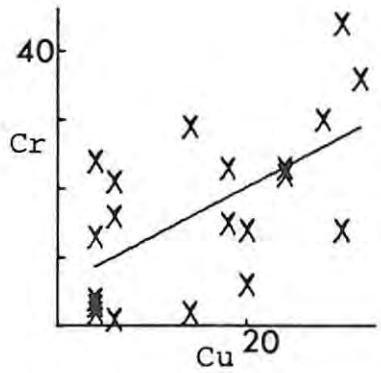
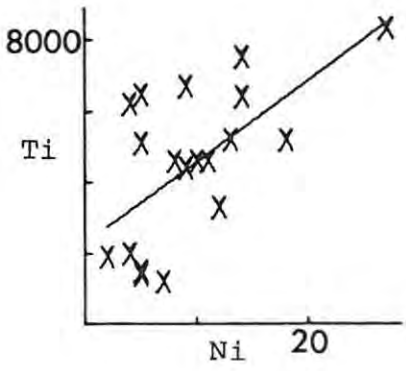
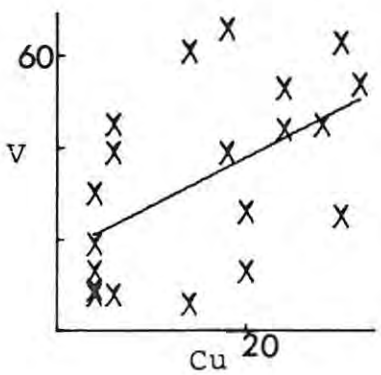
V
Ni
20


40
Cr
Cu
20


8000
Ti
Ni
20


60
V
Cu
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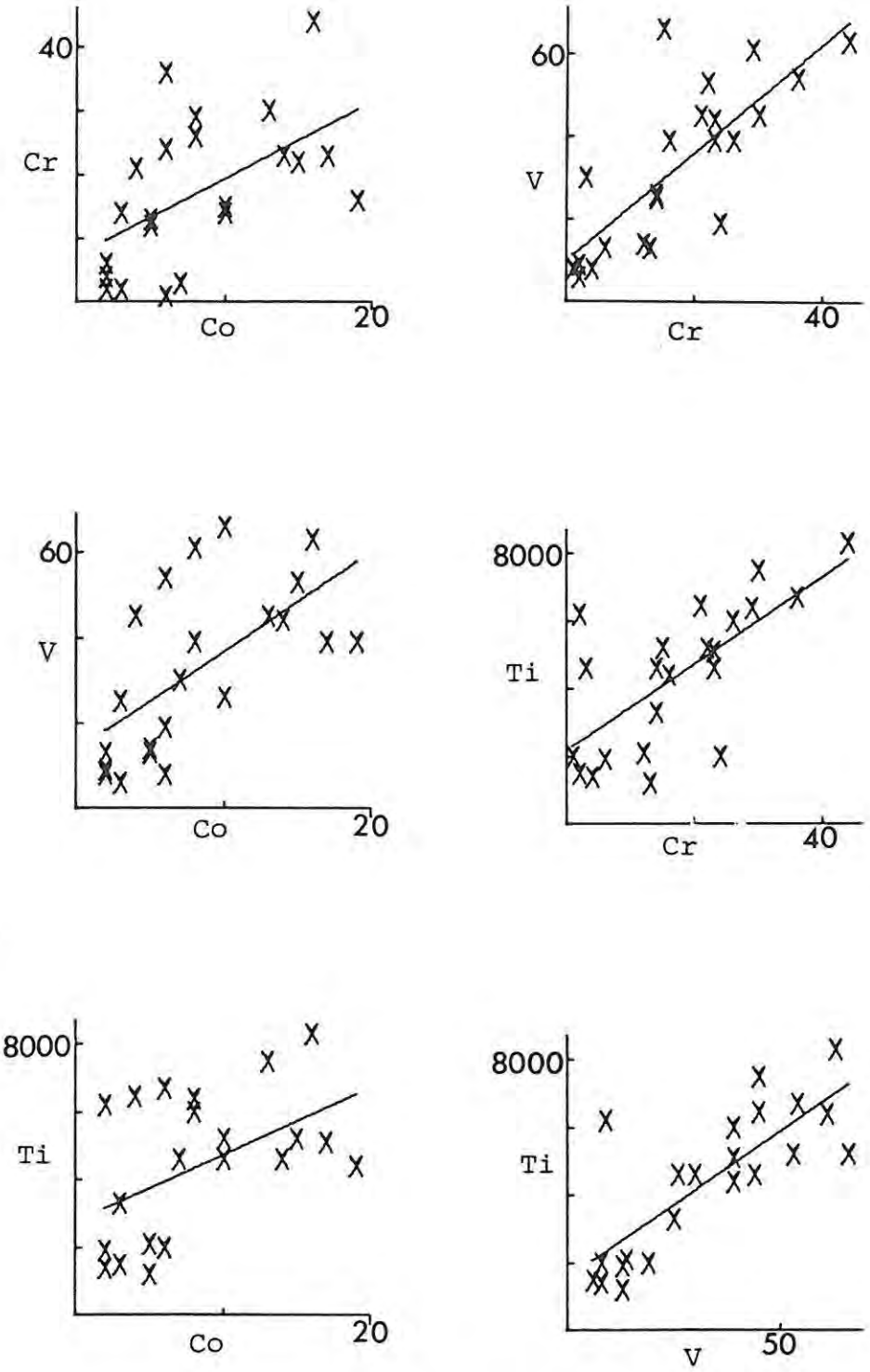


Figure 15 (cont.)

4. Factor Analysis

In igneous and metamorphic rocks the distribution of elements is normally determined by equilibrium physical and chemical processes that are relatively well understood. In sediments the distribution of elements is determined to a large degree by non-equilibrium processes making prediction of the distribution of elements more difficult.

Nevertheless the element distribution in sediments is characterized by the occurrence of geochemically coherent groups of elements, i.e. by groups of elements that under given conditions will behave in the same manner. The composition of these groups will be determined by certain underlying processes or fundamental FACTORS. Spencer et al. (1968) consider the distribution of elements in sediments to be largely governed by the following factors :

a) The compositions of the source rocks.

b) The environmental conditions at the site of weathering.

c) The nature of the depositional process.

d) The environmental conditions at the site of deposition.

e) The nature and activity of the biomass at the site of deposition.

f) Tectonic and volcanic events during the weathering-transportation-deposition cycle.

g) Diagenetic processes.

They go on to say that the only independent factors are the composition of the source rocks and the climate. These two factors will interact with the tectonic and volcanic events to control the environmental conditions at the depositional site and the nature of the transportation process. Even tectonic and volcanic events are not entirely independent because the nature and composition of rocks occurring in

similar tectonic provinces show a correlation with those provinces. To put it another way, one would not expect to find volcanic events occurring in sedimentary source areas.

One way to identify the chemical grouping of elements controlled by the interaction of these factors is to use the statistical technique of factor analysis. With this technique it is possible to :

a) locate groups of coherent elements in a complex data matrix;

b) measure the extent of influence of the different groups.

With this knowledge, and a knowledge of the composition of the groups it is then possible to infer the complex interacting causes that underlie element distributions in sediments.

Various authors have applied the technique of factor analysis successfully to the geochemistry of sediments. Thus Spencer (1966) identified 5 factors that influenced the geochemistry of a Silurian graptolite band. These were an ion-exchange factor, a scavenging factor, a sulphur diagenesis factor, an Eh-pH factor and a detrital factor. Spencer et al. (1968) named a carbonate factor, a quartz dilution factor, an Eh factor, an authigenic degraded illite factor and a montmorillonite factor in their study of sediments in the Gulf of Paria. Saager and Esselaar (1969) recognised 3 factors in their study of the Basal Reef in the Orange Free State. These were a physical and chemical factor (shown by a grouping of S, Ni and Co), a detrital factor (shown by Ag, Au and U clustering) and a precipitation factor (shown by a high loading for Cu). Other applications of factor analysis are those by Hirst and Kaye (1971), Cosgrove (1973), Saager and Sinclair (1974), Herbosch (1974) and Mackin and Owen (1979).

a. Factor analysis : theory

Factor analysis was first developed as a statistical technique by experimental psychologists in the 1930s and 1940s. Essentially factor analysis aims to reduce the observed relationships between many variables to simpler relationships among fewer variables. Given a data array, factor analytical techniques enable identification of any underlying pattern of relationships which would allow the data to be rearranged or reduced to a smaller set of underlying variables which can be taken as the factors accounting for the observed relationships in the data set.

In factor analysis the relationship within a set of m variables is regarded as reflecting the correlation of each of the variables with p mutually uncorrelated underlying factors where $p < m$. Variance in the m variables is derived from variance in the p underlying factors but in addition a contribution is made by unique sources which independently affect the m variables. The p variables are known as common factors while the independent factor is a unique factor. Factor analysis attempts to fit the model

$$Z_{ij} = a_{i1} F_{1j} + a_{i2}F_{2j} + a_{i3}F_{3j} + \ldots a_{im}F_{mj} + a_{i}U_{ij}$$

where

Z_{ij} = value of the ith variable in the jth sample

F = common factor

m = common factors (that is factors that are common to two or more variables under study)

U = specific factor for a specific gravity

a = factor weight on loading necessary to express the original data in the terms of new factors.

Davis (1973) points out that "Factor analysis commonly is regarded as a deep and mysterious methodology of great complexity. Analysts are sharply divided on the topic, both as to the validity of the factor model and the utility of the technique. Nevertheless factor analysis is a very

powerful and useful technique especially when dealing with a large mass of complex relationships".

b. The Mechanism of Factor Analysis

Cattell (1965) gives a thorough, if somewhat mathematical, review of factor analysis. A "geological" approach to factor analysis is well presented by Davis (1973).

Factor analysis is not in fact a unitary concept, but subsumes a variety of procedures with various alternatives being available in the course of the analysis. A brief review of the three basic steps in factor analysis will now be given :

(i) The calculation of a correlation coefficient matrix

Factor analysis interprets the variance-covariance matrix obtained from a collection of multivariate observations. Since in many cases the variables are not directly comparable it is necessary to convert them to some standardized form. This is simply achieved by the use of a correlation coefficient matrix which is nothing more than the covariance matrix of standardized data.

Geochemical data tends to be positively-skewed, or expressed another way, lognormally distributed (Spencer, 1966; Joyce, 1976; Mackin and Owen, 1979). Parametric statistics, such as factor analysis are not applicable to non-normal data distributions; fortunately this problem may be overcome by the transformation of raw data to log values. This has the effect of causing the data to resemble a normal distribution and parametric statistics may thus be employed.

The two major alternatives available at this point are Q-mode and R-mode factor analysis. In Q-mode factor analysis the relationship between the different samples is examined on the basis of all the variables. The object of Q-mode analysis is to arrange a suite of samples into a meaningful order so that the interrelationships between the

samples may be deduced. An nXn matrix of correlations between samples is created. Examples of the technique are given by Imbrie and van Andel (1964), Nicol et al. (1969) and Saager and Sinclair (1974). R-mode factor analysis is the more common of the two techniques and is based on the correlations between variables on the samples examined. An nXn matrix of variable correlations is created.

(ii) The computation of the initial factor matrix

The first step in the computation of an initial factor matrix is the extraction of eigenvectors and eigenvalues from the data matrix. The concepts of eigenvectors and eigenvalues are not difficult; a short explanation of how they are derived now follows (from Davis, 1973) :

In a bivariate data collection such as in Figure16(a), where variance of X_1 is 20,3 and variance of X_2 is 24,1 and the covariance between the two is 15,6, the variances may be represented by plotting them on the same pair of co-ordinates, as in Figure 16(b). The variance and covariance of the data may then be represented as two vectors (Figure 16(c)). or by a 2 x 2 matrix :

$$\begin{bmatrix} 20,3 & 15,6 \\ 15,6 & 24,1 \end{bmatrix}$$

The elements in such a matrix can be regarded as defining points lying on an m-dimensional ellipsoid of which the orientation of the principal axes yield the eigenvectors of the matrix while the lengths of principal axes are the eigenvalues, see Figure 16(d). Eigenvectors and eigenvalues can be calculated for the simple matrix above using matrix algebra. Solution of the characteristic polynomial for the matrix and of the associated simultaneous equations gives the length of the first principal axis, or eigenvalue, as 37,9 and the associated eigenvector $I = \begin{bmatrix} 0,66 \\ 0,75 \end{bmatrix}$ which means that for every 0,75 units the principal axis slopes

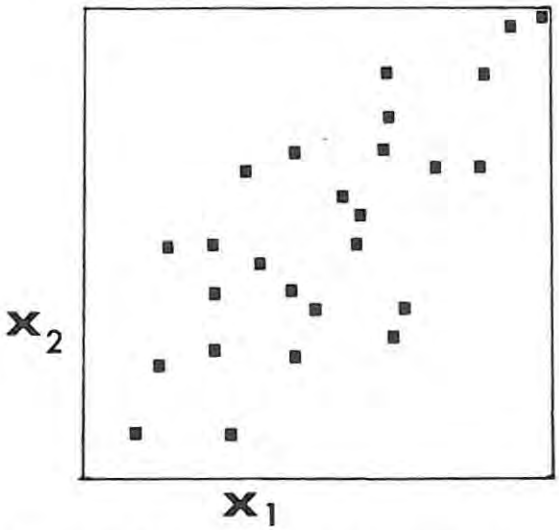


Figure 16(a) : Bivariate data set.

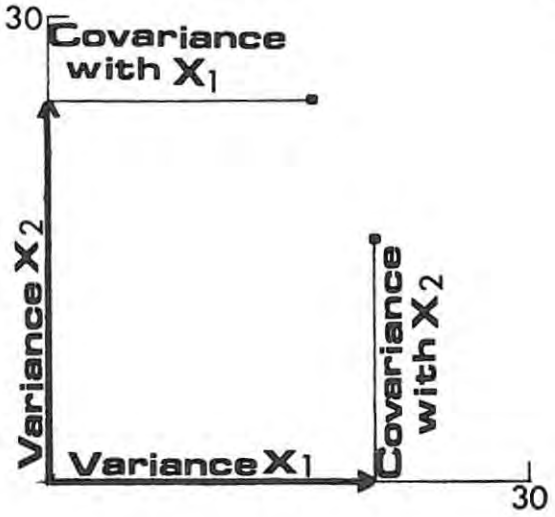


Figure 16(b) :

Plots of variances and covariances as co-ordinates.

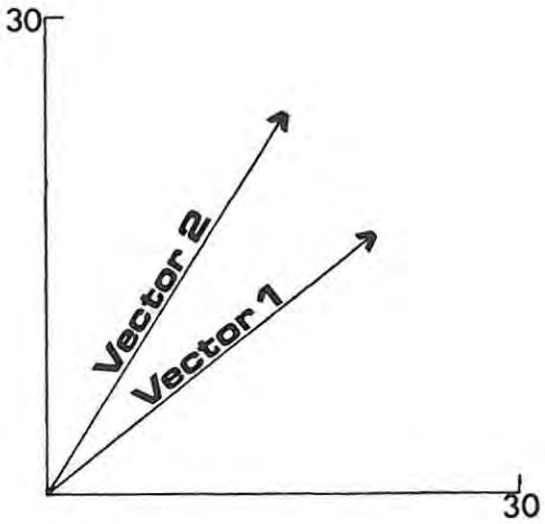


Figure 16(c) : Representation of variances and covariances as vectors.

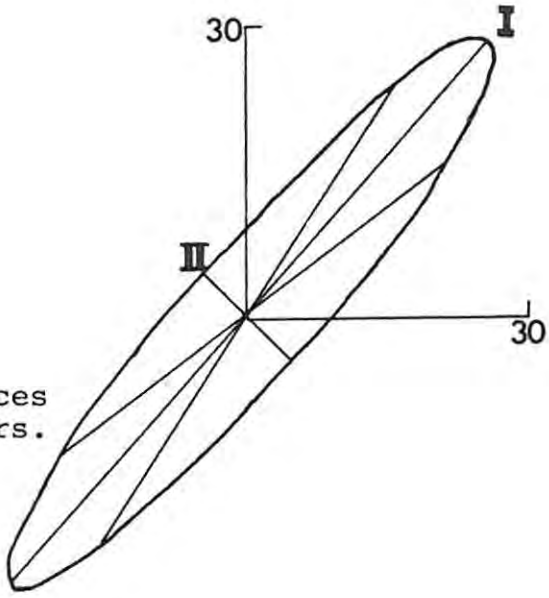


Figure 16(d) : Ellipse defined by variances and covariances of data.

upwards it runs 0,66 units along X_1. For the second principal axis the eigenvector $_{II} = \begin{bmatrix} 0,75 \\ -0,66 \end{bmatrix}$ which can be recognised as being at right angles to I. The associated eigenvalue is 6,5. The two principal axes of the ellipse which define the variance-covariance in the data are plotted in Figure 16(d). The total variance in the data is equal to the sum of the individual variances, i.e. 20,3 + 24,1 = 44,4. Since the individual variances are located along the diagonals of the variance-covariance matrix, calculating the total variance is equivalent to finding the trace of the matrix, or in other words the sum of the eigenvalues of the matrix. The principal axes also represent the total variance of the data set, and each accounts for an amount of the total variance equal to the eigenvalue divided by the trace. Thus the first principal axis accounts for $37,9/44,4$ or 86% of the total variance, whereas the second principal axis accounts for 14%. The process of extracting eigenvalues in the examples examined is very simple; when larger matrices are involved, the procedure becomes extremely complex. Eigenvalues for large matrices are normally found by a process of matrix manipulation involving a series of successive approximations or iterations. The use of a high speed computer is generally required.

The next step is the conversion of the eigenvectors to initial factors. It is necessary first that the data be standardized and the eigenvectors normalized. Standardization of the data by use of a correlation matrix has already been discussed. Eigenvectors are extracted from the correlation matrix rather than the original data matrix. Normalized eigenvectors, i.e. vectors defining a unit length are then calculated by multiplication of each element in the vector by a constant β such that :

$$\beta = \frac{1}{\sqrt{E_{j=1}^{m} b^2_{jk}}}$$

Further explanation of this formula may be obtained from Davis (1973, p 505).

The normalized vectors are then converted to a form where the vector length represents the magnitude of the eigenvalue by multiplying each element in the eigenvector by the square root of the corresponding eigenvalue. The result of this is a factor, a vector which is weighted proportionally to the amount of total variance it represents. Since the lengths of the factors are a function of the eigenvalues the factors must also represent the variance in the data. Each of the factor loadings on the variables is thus weighted proportionally to the square root of the amount of variance contributed by that variable to the factor. Factor loadings may then be rearranged into an initial factor matrix. If the elements in the factor matrix are squared and summed within each variable, the totals express the amount of variance of each variable retained in the factor. These totals are known as communalities. If m factors are extracted from an mXm matrix, then the communalities are equal to the original variances. Since standardized variables are being dealt with, these communalities will be 1,00. However if less than m factors are extracted then the communalities will be less than the original variances; the magnitude of the communalities are thus dependent on the number of factors extracted. This brings us to the problem of how many factors should be extracted. One pragmatic approach to the problem is to only extract two or three factors, which is the maximum conveniently displayed on diagrams. Another approach is to extract as many factors as required to explain an arbitrary amount of variance, for example 5 factors might have to be extracted to explain 90% of the total variance. Alternatively all the factors with an eigenvalue of above a certain figure could be extracted. Davis (1973) suggests that all factors with eigenvalues greater than 1,0 be extracted. In this way only those factors which explain more variance than the original standardized variables are extracted. In most cases no more than a few factors should be necessary to explain the variance in the data set; if this is not so then the factor model is probably not applicable to the problem in any case.

(iii) Factor rotation

Even though factor analysis has the effect of reducing problems to a manageable size, the meaning of the different factors may still be difficult to deduce. To facilitate the interpretation, the principal factor axes may be rotated. If the rotation is performed so that the axes correspond to the dominant clusters of variables, then the interpretive problem has been simplified. Various techniques are available for axis rotation (vanimax, quartimax, equimax) of which Kaiser's vanimax scheme is probably the most commonly used. This scheme involves maximization of the variance of the loadings on the factors and is achieved by moving each factor axis in turn to positions so that the projections from each variable onto the factor axes are either near the extremities or near the origin. Figure 17 illustrates the effect of rotation.

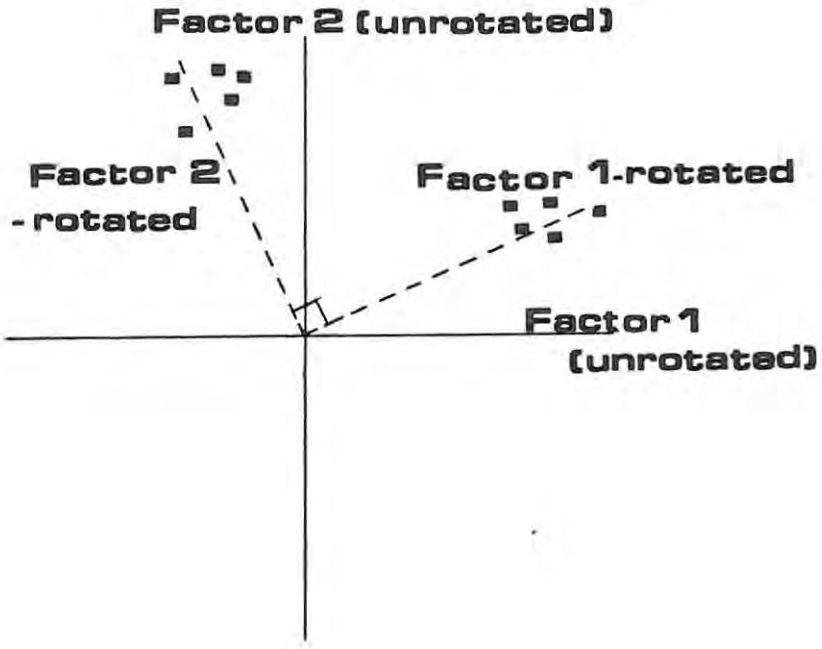


Figure 17 : Effect of rotation on factor axes.

If the rotated axes remain at right angles to each other then the rotation is orthogonal. A choice may be made at

this point to relax the restriction of orthogonality. Since the factors influencing geochemical data are not likely to be uncorrelated, oblique rotation (i.e. non-orthogonal rotation) may in fact be more empirically realistic (Spencer et al., 1968; Cosgrove, 1973; Herbosch, 1975). The resulting oblique factors may be more easily interpreted because extreme loadings may be obtained on the factors. However, as Davis (1973) points out, the original factor analytical model assumed that the observed matrix of variance-covariance resulted from correlations between m variables and p mutually uncorrelated factors. A relaxation of the constraint of orthogonality would seem to invalidate the original model and while Davis (1973) does not totally reject oblique rational methods, he does, however, consider that resolution of a factor problem should be possible by orthogonal rotation. If this is not so then the problem is probably not amenable to solution by the factor model in any case.

c. Factor analysis of the Molteno Formation

Statistical analyses in this study were performed with FACTOR, a programme in "Statistical Package for Social Sciences" (Nie et al., 1975), and run on the Rhodes University ICL 1903S computer. All element concentrations were subjected to log transformation so as to approximate as closely as possible a normal distribution of data. R-mode factor analysis was applied and the rotation of the factor axes was orthogonal and executed by the varimax criterion. Only factors with eigenvalues greater than 1,0 were extracted. The anomalously high yttrium value of AJR61 was omitted from the data in order to avoid "nonsense correlations" which can be produced by anomalously high element concentrations. This procedure has also been adopted by Mackin and Owen (1979).

The eigenvalues of the matrix are given in Table 9(a), the initial factor matrix in Table 9(b), and the rotated factor matrix in Table 9(c). The rotated orthogonal factors are graphically presented in Figure 18.

Interpretation

A convenient view of factor scores is that they represent the influence of the factors on the samples. Where an element is confined to a single factor it is likely that its occurrence within the sediments can be explained by a single process. Where a complex factor pattern is observed several independent or partially independent processes have been involved. There is no adequate test of the significance of factor loadings (Spencer, 1966); a rough estimate may be obtained from Harman's (1967, p435) table of standard error loadings. According to this table it is probable that loadings greater that 0,28 are significant for the present data.

As can be seen in Table 9(a), the first 3 factors have eigenvalues of greater than 1,0; together they explain 82,4% of the total variance in the data. The communalities, which give the fraction of the variance of each element that is explained by the factors extracted, vary over a fairly large range (0,55625 to 0,95319). In most cases (9 out of 14), over 75% of the variance is explained by the 3 factors extracted (Table 9(b). The factor pattern demonstrated in Table 9(b) is essentially simple. No element is significantly loaded on all 3 factors; Zr, Y, Zn, Mn, Ba and Co are only loaded on one factor while the rest of the elements are loaded on 2 of the 3 factors.

Factor 1 : The high loadings for Zr, Y, Cr and V coupled with lesser loadings on Nb, Rb, Cu, Ni, Co and Ti suggest that this factor should be designated a "heavy mineral factor". The residence of Rb is somewhat doubtful since it does not substitute into any common detrital heavy minerals. It could possibly imply the presence of K-feldspar associated with the heavy mineral suite. This "heavy mineral factor" may be considered to be a response to various physical sorting processes.

Factor 2 : This factor is characterized by very high loadings on Mn and Ba, lesser loadings on Zn, Cu and Ni and a low,

TABLE 9(a) : EIGENVALUES OF MATRIX

Factor	Eigenvalue	Pct of var	Cum pct
1	6.94077	49.6	49.6
2	3.00997	21.5	71.1
3	1.59101	11.4	82.4
4	0.71008	5.1	87.5
5	0.48319	3.5	91.0
6	0.37939	2.7	93.7
7	0.28561	2.0	95.7
8	0.23541	1.7	97.4
9	0.17489	1.2	98.6
10	0.08987	0.6	99.3
11	0.04498	0.3	99.6
12	0.03411	0.2	99.9
13	0.01751	0.1	100.0
14	0.00320	0.0	100.0

TABLE 9(b) : INITIAL FACTOR MATRIX

	Factor 1	Factor 2	Factor 3	Est Communality
Nb	-0.66763	0.23173	0.52002	0.88388
Zr	-0.68801	0.32505	-0.17558	0.74270
Y	-0.64199	0.52096	-0.28374	0.82358
Sr	-0.57243	-0.11775	0.55764	0.72635
Rb	-0.79134	0.22421	0.51265	0.88388
Zn	-0.75414	-0.54633	-0.04842	0.84864
Mn	-0.57326	-0.76672	-0.10373	0.95151
Ba	-0.52176	-0.82309	0.05892	0.95151
Cu	-0.63488	-0.34920	-0.26403	0.73153
Ni	-0.71996	-0.44759	-0.25970	0.77084
Co	-0.72252	0.18193	-0.03340	0.72959
Cr	-0.65838	0.47231	-0.47421	0.81909
V	-0.89539	0.34296	-0.12259	0.82358
Ti	-0.76988	0.32815	0.12577	0.80677

TABLE 9(c) : ROTATED FACTOR MATRIX

	Factor 1	Factor 2	Factor 3
Nb	0.31297	0.07049	0.81666
Zr	0.72336	0.15086	0.25265
Y	0.85854	-0.01051	0.16387
Sr	0.03237	0.29340	0.75192
Rb	0.39339	0.14599	0.87363
Zn	0.20616	0.86624	0.27689
Mn	-0.01093	0.95695	0.10663
Ba	-0.15727	0.94049	0.20960
Cu	0.34714	0.68605	0.05957
Ni	0.34456	0.81151	0.09412
Co	0.59397	0.25610	0.37130
Cr	0.93562	0.07752	0.00505
V	0.84333	0.23912	0.40742
Ti	0.62987	0.13056	0.54993

just significant loading on Sr. The pattern of loadings especially those for Mn and Ba suggest that Factor 2 represents the occurrence of Fe-Mn oxide/hydroxide phases. The formation of such a phase can be related to a 'pH' or 'Eh' factor.

Factor 3 : High loadings displayed by Nb, Sr and Rb allied with moderate loadings on Co, V and Ti designate this a "clay mineral" factor.

The graphical representation of these factors and the element loadings on each (Figure 18 (a), (b) and (c)), give an indication of the extent of interrelation between the factors. In analysing the graphs, three features are important :

a) The relative distance of a variable from the two axes.

b) The direction of a variable relative to the axes (both positive and negative loadings may be displayed).

c) The clustering of the variables.

If variables do form clusters and lines drawn from the origin through the clusters are less than 90^{o} apart, then the factors do show a degree of correlation.

The plot of Factor 1 vs Factor 2 (Figure 18 (a)) indicates a slight clustering of variables. Cr, Y, V and Zr constitute a cluster on Factor 1 while Mn, Ba, Zn, Ni and Cu show a diffuse grouping on Factor 2. A slight degree of correlation between the two factors is possible.

Factor 1 vs Factor 3 (Figure 18 (b)) shows no appreciable groupings with most of the variables being moderately loaded on both factors.

In Figure 18(c) the clustering of Zn, Mn, Ba, Cu and Ni is evident on Factor 2, and that of Nb, Sr, Rb on Factor 3. A slight degree of correlation between the 2 factors is also visible.

Figure 18(a) :

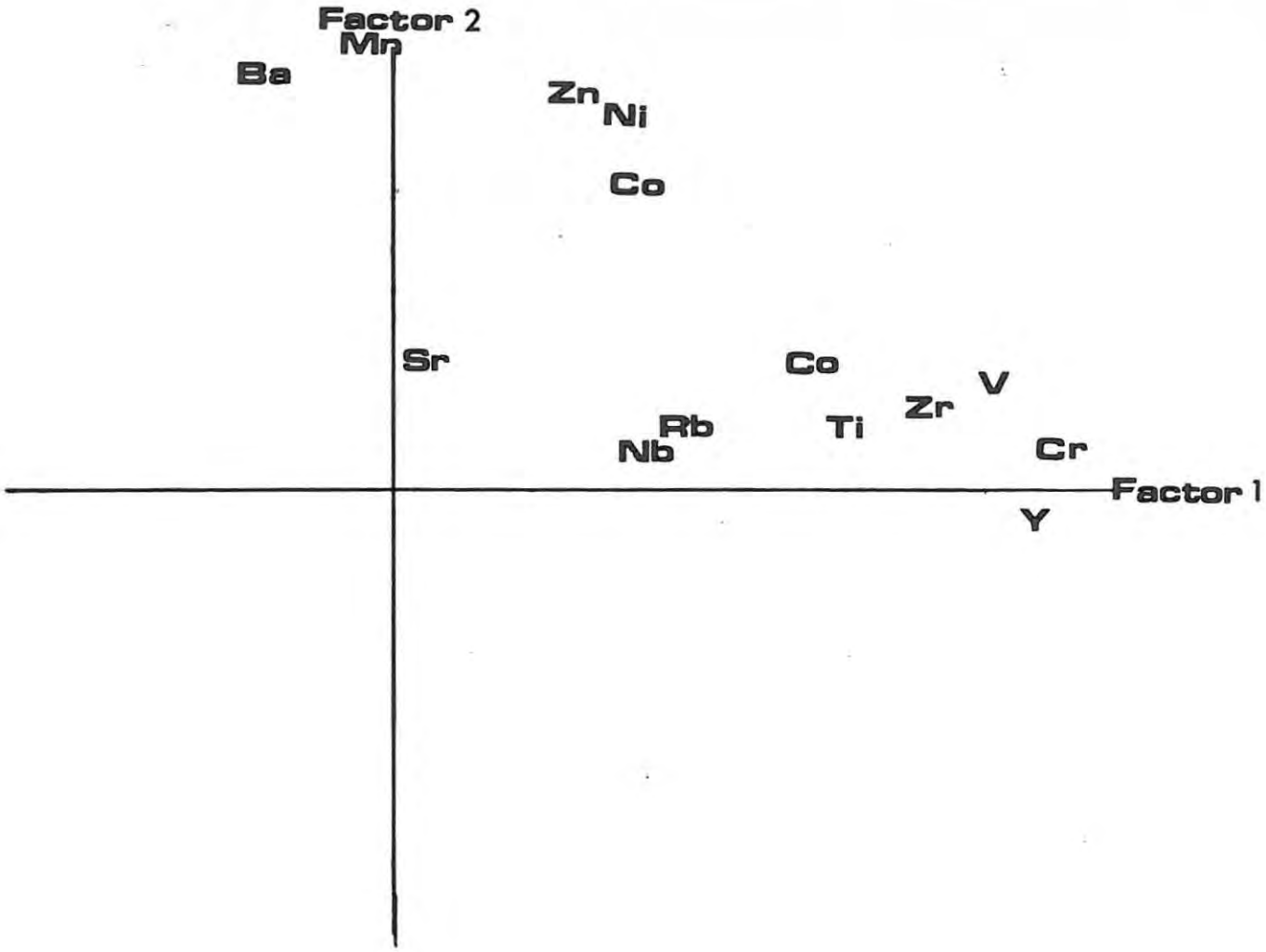


Figure 18 : Rotated factor axes.

Figure 18(b) :

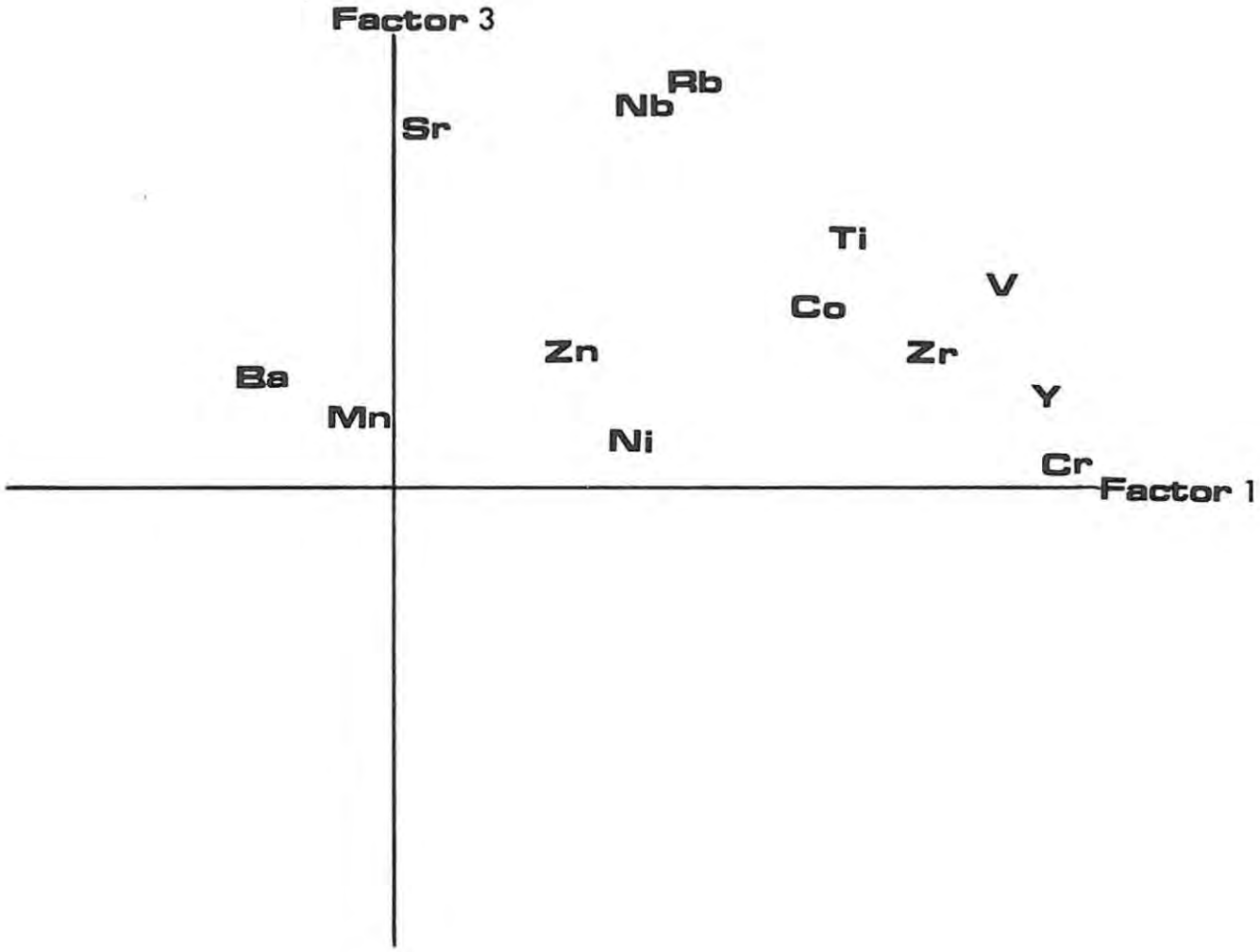
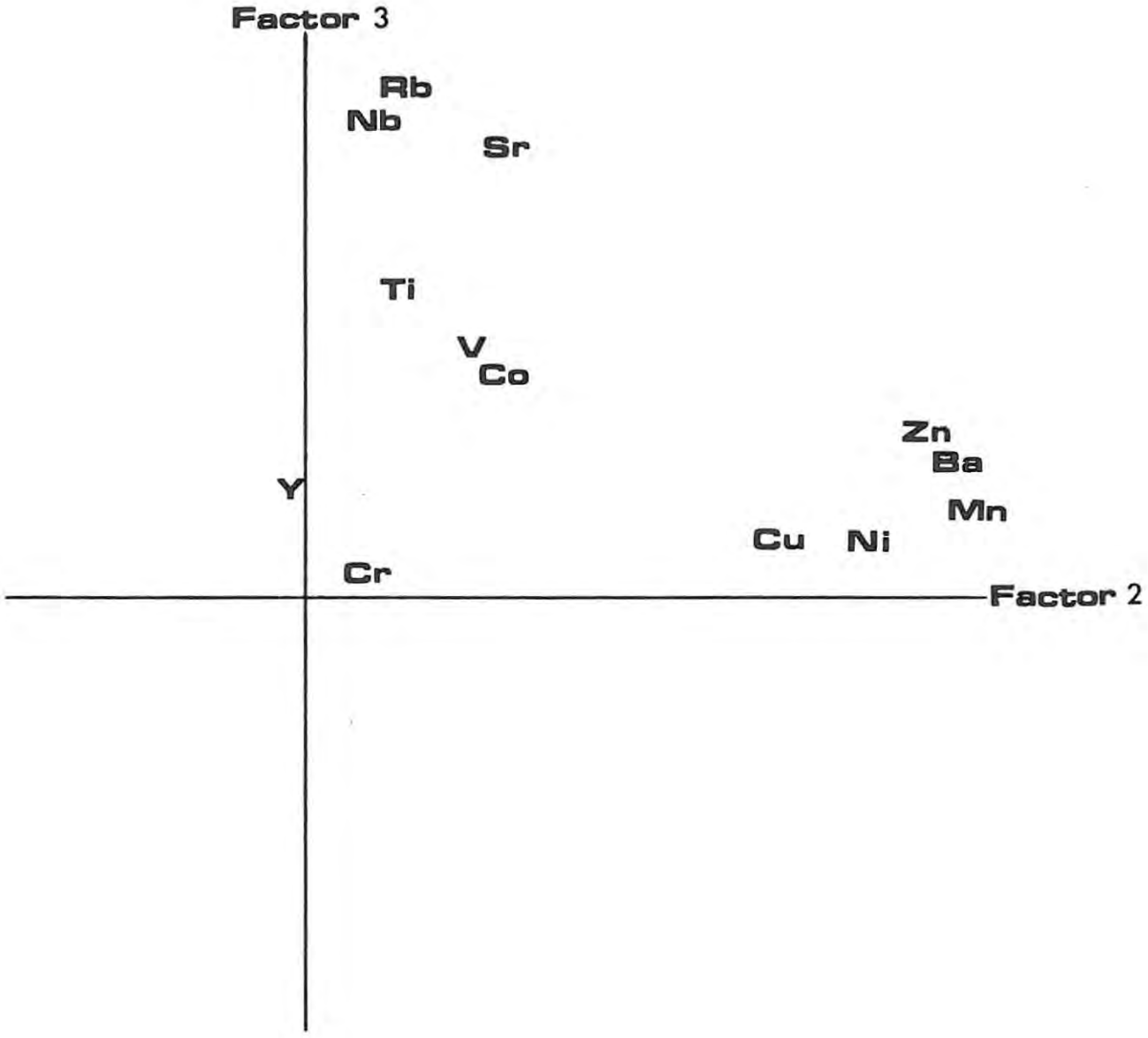


Figure 18(c) :



It would perhaps be unrealistic to suppose that all of the influences of the trace element geochemistry of the Molteno Formation have been delineated. Independent effects may easily be confounded when small numbers of samples are studied. Only 3 factors were extracted; it is possible that by extraction of factors with eigenvalues less than 1,0, further significant factors might be identified. However it was felt that the somewhat conservative approach adopted was preferable, in order to avoid possible spurious factors resulting from error or lack of sensitivity in the analytical techniques. Another possible weakness was that only 14 elements were determined. Further factors might have been identifiable through analysis for other elements. Nevertheless it was felt that the elements analyzed did in fact cover just about all the possibilities. For example, while the samples were not analyzed for Ca, a high loading on which would indicate the possible presence of a carbonate phase, the samples were analyzed for Sr which fulfils the same role in identifying a carbonate phase.

Returning to the viewpoint held by Spencer et al. (1968), that source area composition and climate are the only two independent factors influencing trace element distributions in sediments, we can see that this is, in fact, the case for the Molteno Formation. The first factor, a heavy mineral factor, is directly dependent on the composition of the source rocks while the second factor, an Fe-Mn oxide/hydroxide phase which is related to a "pH" or "Eh" factor is largely dependent on the climate (hot, dry conditions leading to high Eh; cool, wet conditions leading to low Eh). Both the composition of the source rocks and the prevailing climate would interact to control the "clay mineral" factor, whether or not Hofmeyr (1971), is correct in concluding that the clay minerals have principally formed in the source area rather than as a result of post-depositional diagenetic processes.

d. Comparison of the Molteno Formation with the Elliot Formation

The Elliot Formation consists of alternating layers of mudstone, siltstone and sandstone. The sedimentary process from the Molteno Formation through to the Elliot Formation was continuous but the character of the sedimentation changed markedly (Botha, 1968). The main lithological differences are the finer grain sizes exhibited by the Elliot Formation and the predominantly red colouration. Deposition would have taken place in shallow water conditions typical of alluvial flats in a continental environment. In effect conditions returned to those prevalent in Upper Beaufort times.

7 samples have been analyzed from the Elliot Formation; 6 were taken from cuttings in the Barkly Pass area and one from the Matatiele area. The stratigraphic positions of the Barkly Pass samples are shown in Figure 19. Trace element concentrations and summary statistics are presented in Tables 10(a) and (b). Concentrations of trace elements versus stratigraphic height have been plotted for the 6 samples from the Barkly Pass. There is a significant increase in Rb (at the 95% confidence level) with increase in height. This relationship is illustrated in Figure 20 Other relationships are not significant.

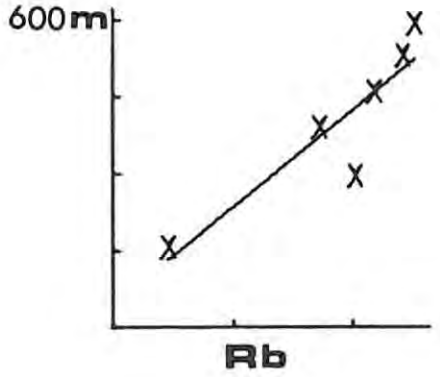


Figure 20 : Trace element variation with height - Elliot Formation.

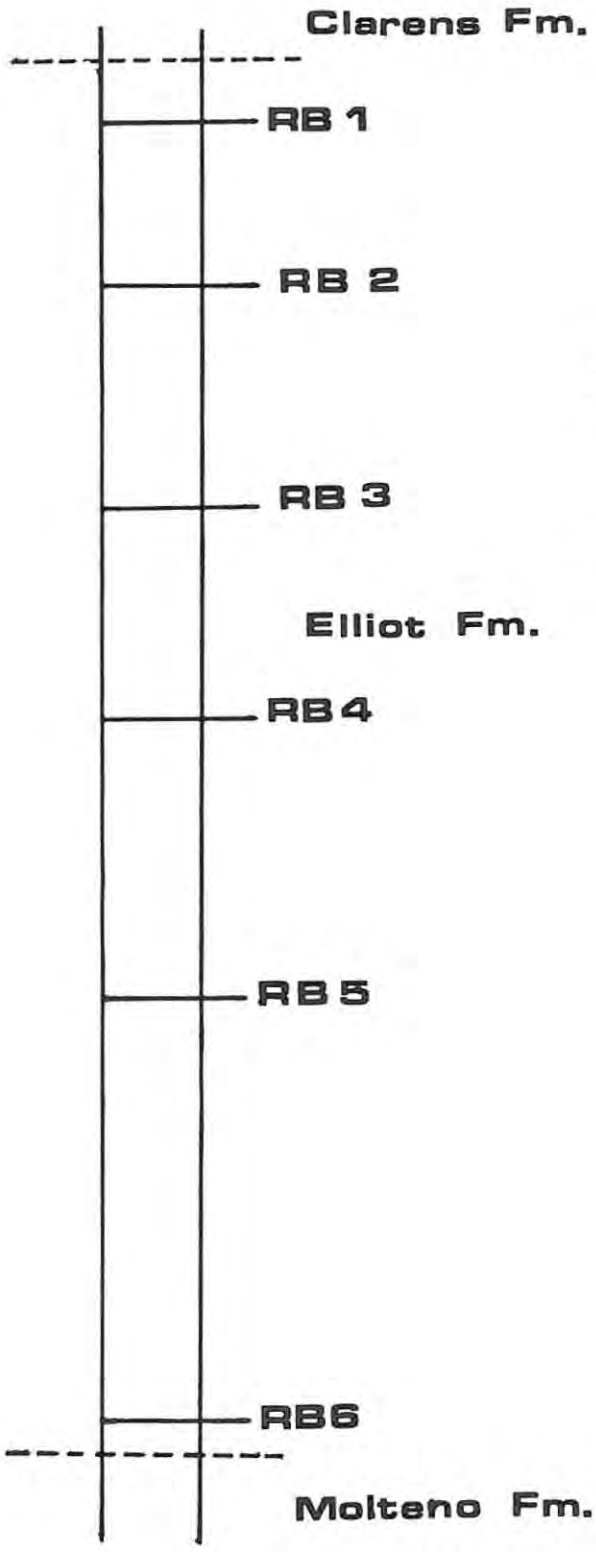


Figure 19

Sample positions –
Elliot Fm, Barkly Pass

Vertical Scale –
1cm :55m

TABLE10(a):TRACE ELEMENT ANALYSES - ELLIOT FORMATION

	Nb	Zr	Y	Sr	Rb	Zn	Mn	Ba	Cu	Ni	Co	Cr	V	Ti
RB1	15	321	26	132	126	42	300	900	8	7	6	7	37	4600
RB2	14	314	41	127	121	50	250	900	7	6	8	11	18	3800
RB3	11	344	26	522	109	34	250	1500	10	10	7	8	26	4300
RB4	10	462	25	275	86	37	700	1000	17	13	7	22	136	5400
RB5	11	271	24	81	101	37	350	1500	9	8	10	24	50	6300
RB6	12	92	17	130	23	35	500	250	6	4	5	3	14	2000
RB7	9	277	25	58	78	21	200	1000	3	6	6	14	72	5200

TABLE10(b): SUMMARY STATISTICS FOR ELEMENTS ANALYSED - ELLIOT FORMATION

Element	N	Mean	Standard Deviation	Range
Nb	7	12	2,1	9-15
Zr	7	318	119,4	92-462
Y	7	25	8,4	17-41
Sr	7	198	155,1	81-522
Rb	7	90	36,3	23-126
Zn	7	34	14,0	21-50
Mn	7	364	177,3	200-700
Ba	7	1007	424,7	250-1500
Cu	7	7	2,3	3-17
Ni	7	8	2,9	4-13
Co	7	7	1,6	5-10
Cr	7	13	7,8	3-24
V	7	50	42,7	14-136
Ti	7	4660	1338,8	2000-6300

Factor analysis was then applied to the Elliot Formation samples. The sample population is probably too small for a valid analysis (n = 7), but nevertheless it was thought that an indication of the factors operative in the Elliot sedimentation process could be obtained. Comparison with the factors obtained for the Molteno Formation might prove useful.

Table 11(a) lists the eigenvalues for the matrix, of which 5 eigenvalues have values greater than 1,0; together they explain 97,4% of the total variance. Tables 11(b) and (c) list the initial and rotated factor matrices.

Factor 1 : High loadings on Nb, Y, Rb, Mn and Cu indicate this factor probably represents Fe-Mn oxide/hydroxide phases, in other words a "pH" or "Eh" factor.

Factor 2 : Co, Cr and V are highly loaded on this factor which probably represents some type of opaque heavy mineral factor.

Factor 3 : Sr is highly and uniquely loaded on this factor; lesser loadings occur for Mn and Ba. This probably indicates the presence of a carbonate phase.

Factor 4 : High loadings for Zr and Ti indicate this is probably a heavy mineral factor.

Factor 5 : Loadings on Ba, Ni, V and Ti indicate this might possibly be a "clay mineral" factor.

It is evident that the factors operative in the Elliot Formation are more complex than those in the Molteno Formation. It appears possible that there are two types of heavy mineral factor but this is questionable. More important than that is the presence of a carbonate factor in the Elliot Formation, similar to the 1st factor. This is also controlled by an underlying "pH" factor. The development of the "carbonate" factor is confirmed by petro-

TABLE 11(a) : EIGENVALUES OF MATRIX

Factor	Eigenvalue	Pct of var	Cum pct
1	4.35355	33.5	33.5
2	3.70835	28.5	62.0
3	2.04943	15.8	77.8
4	1.53417	11.8	89.6
5	1.00466	7.7	97.3
6	0.34984	2.7	100.0
7	0.00000	0.0	100.0
8	0.00000	0.0	100.0
9	0.00000	0.0	100.0
10	-0.00000	-0.0	100.0
11	-0.00000	-0.0	100.0
12	-0.00000	-0.0	100.0
13	-0.00000	-0.0	100.0

TABLE 11(b) : INITIAL FACTOR MATRIX

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Nb	0.82742	-0.34265	-0.18355	-0.22683	-0.20506
Zr	-0.03527	0.26753	0.16847	0.96518	-0.00634
Y	0.82312	0.11778	0.05285	0.10235	-0.10654
Sr	-0.04434	-0.16446	0.89302	0.18090	-0.00789
Rb	0.75685	0.31640	0.26226	0.37006	-0.30620
Mn	0.56684	0.22118	0.68894	-0.28053	0.07955
Ba	0.08988	0.27535	0.61654	0.54423	0.50608
Cu	0.92889	-0.06508	0.10520	-0.27532	0.28256
Ni	-0.05073	-0.13708	0.02247	0.02337	0.98775
Co	0.08686	0.73612	0.57874	0.23665	-0.24476
Cr	0.03862	0.95433	-0.07321	0.11465	-0.17919
V	-0.05568	0.86008	-0.05965	0.32599	0.42016
Ti	-0.27192	0.24639	-0.00211	0.68244	0.61610

TABLE 11(c) : ROTATED FACTOR MATRIX

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Nb	0.47398	-0.76414	-0.08887	0.22467	-0.24957
Zr	-0.81565	0.13653	0.07921	-0.07294	-0.58078
Y	-0.14169	-0.77300	-0.01957	0.23592	-0.20587
Sr	-0.36177	-0.18124	-0.32740	-0.76646	0.03037
Rb	-0.46942	-0.79171	0.18458	0.03365	0.30010
Mn	-0.28156	-0.75422	-0.25604	-0.21855	0.41042
Ba	-0.87223	-0.04774	-0.47901	-0.15097	-0.03176
Cu	0.09046	-0.83709	-0.45130	0.33663	0.08886
Ni	-0.16080	0.31194	-0.86187	0.32302	0.16653
Co	-0.80194	-0.31494	0.36414	-0.26287	0.23725
Cr	-0.62108	-0.09856	0.61607	0.32792	0.28340
V	-0.82808	0.18373	0.09671	0.49374	0.23790
Ti	-0.70575	0.51424	-0.33898	0.23246	-0.22018

graphic examination of the Elliot Formation.

Overall it can be said that the factors influencing the geochemistry of the Elliot Formation are more numerous and also more complex than those operative in the Molteno Formation.

CONCLUSIONS

The Molteno Formation is a clastic sedimentary sequence dominated by cyclical sedimentation. Coarse to medium grain sandstone is the most common rock type; finer grain sandstones, siltstones, shales and coals are also present.

Detritus entered the basin from 2 directions and was derived from two compositionally different source areas. Various techniques were applied to further define the composition of the source rocks and the relative influence of each provenance.

The presence of rounded quartz overgrowths has been noted using orthodox petrographic methods. Further examination using scanning electron microscopy has shown the large amount of authigenic quartz overgrowth. Etching of quartz and garnet as well as the abundant overgrowths clearly indicates the considerable diagenetic activity since deposition. Intrastratal solution of garnets was probably an important diagenetic process in the Molteno Formation.

Varietal analysis of certain of the heavy minerals present has been carried out using X-ray diffraction and the electron microprobe. Rutile, as well as the 2 authigenic polymorphs of rutile, anatase and brookite have been identified using the Gandolfi method. Tourmaline (variety dravite) and a pyrope garnet have also been identified using this method. X-ray diffraction affords a simple, quick method of mineral identification; unfortunately if the mineral is part of a solid solution series, it cannot be used to determine the exact chemical composition. For this reason further examination of garnets was carried out using the electron microprobe.

The important indicators to provenance composition are summarized in Figure 20.

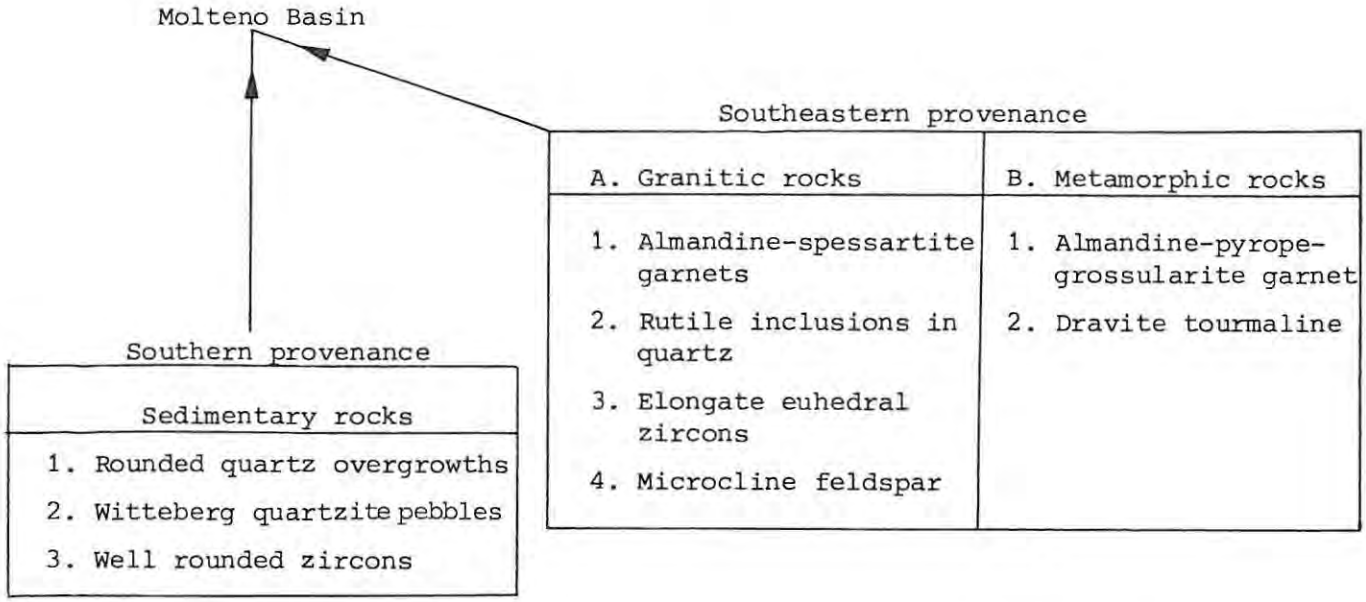


FIGURE 20 : Provenance diagram for the Molteno Formation showing the important indicators of provenance composition.

Abundances of Nb, Zr, Y, Sr, Rb, Zn, Mn, Ba, Cu, Co, Cr, V and Ti have been determined for the Molteno Formation, and while the absolute amounts of these trace elements is low, significant variations do, nevertheless, occur.

Examination of the trace element variations with stratigraphic height has shown a depletion in certain elements (Zr, Y, Sr, Mn, Cr and Co) in the Indwe Sandstone Member relative to the lithologies above and below. With the exception of this there are no other potentially useful stratigraphical variations in geochemistry. A problem with any such attempt at geochemical stratigraphic correlation is that with slight changes in lateral position the vertical succession may change markedly. In this way, changes due to vertical variation can be confused with those due to horizontal variation.

The geographic variation in trace element content has also been examined. Zr, Co, Ni and Mn show marked variation with lateral position, reflecting the presence of source areas of different composition. More detailed sampling

would be required here in order to establish these relationships more rigorously.

Using the technique of factor analysis it has proved possible to identify the underlying factors which influence the geochemistry of the Molteno Formation. Three factors have been isolated, a "heavy mineral" factor, an "Fe-Mn oxide/hydroxide" factor and a "clay mineral" factor. The "heavy mineral" factor is a reflection of the source rock composition while the "Fe-Mn oxide/hydroxide" factor is a reflection of the prevailing Eh-pH conditions which are largely dependent on the climate. The "clay mineral" factor is controlled by both the source rock composition and the climate.

Comparison with the overlying Elliot Formation reveals a more complex factor pattern in the Elliot Formation and serves to confirm that while the process of sedimentation was continuous the actual character of the sedimentation changed. One of the most significant differences is the development of a "carbonate" factor in the Elliot Formation, reflecting change to more alkaline conditions.

A conclusion as to the specific location of the south-easterly source area is not possible, but it does seem likely that the granitic and metamorphic rocks of the Falkland Island plateau could have been the ultimate source of detritus. The sedimentary source to the south would have comprised rocks of the Cape Supergroup, with perhaps a small contribution from the Karroo Supergroup.

To sum up in the words of Blatt (1967), "more detailed investigations of the mineralogy of sandstones are required and the complexity of sedimentary petrogenic problems requires that we use all available techniques".

REFERENCES

Anderson, H.M. (1975). A review of the genus Dicroidium from the Molteno Formation, South Africa. Unpub. Ph.D thesis, Univ. of Witwatersrand, Johannesburg.

Bence, A.E. and Albee, A.L. (1968). Empirical correction factors for the electron micro-analysis of silicates and oxides. Jour. Geol., 76, 382-403.

Blatt, H. (1967). Provenance determination and the recycling of sediments. J. Sedim. Petrol., 37, 1031-1044.

Blatt, H. and Sutherland, B. (1969). Intrastratal solution and non-opaque heavy minerals in shales. J. Sedim. Petrol., 39, 591-600.

Botha, B.J.V. (1968). The stratigraphy of the Red Beds Stage, Karroo System at Elliot. Trans. Geol. Soc. S. Afr., 71, 101-118.

Bramlette, M.N. (1929). Natural etching of detrital garnet. Am. Miner., 14, 336-337.

Carroll, D. (1957). A statistical study of heavy minerals in sands of the South River, Agusta Country, Virginia. J. Sedim. Petrol., 27, 387-404.

Carver, R.E. (1971). Procedures in Sedimentary Petrography. Wiley, New York.

Cattell, R.B. (1965). Factor analysis : an introduction to essentials, I. Biometrics, 21, 190-215.

Chayes, F. (1954). The lognormal distribution of the elements - a discussion. Geochim. Cosmochim Acta, 6, 119-120.

Cosgrove, M.E. (1973). The geochemistry and mineralogy of the Permian red beds of south west England. Chem. Geol., 11, 31-47.

Davies, D.K. and Moore, W.R. (1970). Dispersal of Mississippi sediment in the Gulf of Mexico. J. Sedim. Petrol., 37, 1031-1044.

Davis, J.C. (1973). Statistics and data analysis in geology. John Wiley and Sons Inc., New York.

Degenhaardt, H. (1957). Untersuchungen zur geochemischen Verteilungs der Zirconiums in der lithosphäre. Geochim. Cosmochim. Acta, 11, 273-309.

Degens, E.T. (1965). Geochemistry of sediments, a brief survey. Prentice-Hall, New Jersey.

Du Toit, A.L. (1903). Geological Survey of Elliot, Xalanga, and Tembuland. Annu. Rep. G.C., C.G.H., 169-205.

Du Toit, A.L. (1906). The Stormberg Formation in Cape Colony. Rep. and Papers, S.A.A.A. Sc., 2, 47p.

Du Toit, A.L. (1910). Report on the Geological Survey of Maclear and portions of Encobo, Mt. Fletcher, Qumbu and Mt. Frere. Annu. Rep. G.C., C.G.H., 69-110.

Du Toit, A.L. (1911). Report on the Geological Survey of parts of the Stormberger. Annu. Rep. G.C., C.G.H.

Du Toit, A.L. (1926). Geology of South Africa. Oliver and Boyd. London.

Du Toit, A.L. (1954). Geology of South Africa. Oliver and Boyd. London.

Ellenberger, F., Ellenberger, P. and Ginsburg, L. (1967). The appearance and evolution of dinosaurs in the Trias and Lias : a comparison between South African upper Karroo and Western Europe based on vertebrate footprints. 1st I.U.G.S. Symposium on Gondwana stratigraphy, Unesco, Paris.

Ellenberger, P. (1970). Les niveaux palaeontologiques de premier apparition des mammiferes prëmordiaux en Afrique du Sud et ichnologie. Establissement de zones stratigraphiques detailees dans le Stormberg du Lesotho (Afrique du Sud) (Trias superieure à jurassique). In Haughton, S.H. (ed), Proc. 2nd I.U.G.S. symposium on Gondwana stratigraphy and palaeontology. C.S.I.R., Pretoria, 343-370.

Erlank, A.J., Smith, H.S., Marchant, J.W., Cardoso, M.P. and Ahrens, L.H. (1978). Zirconium. In Wedephol, K.H. (ed) Handbook of Geochemistry, Springer-Verlag, Berlin.

Friedman, G.M. and Saunders, J.E. (1978). Principles of Sedimentology. Wiley, New York.

Gilbert, C.M. (1955). Sedimentary Rocks. In Williams, H., Turner, F.J. and Gilbert, C.M.,. Petrology, Friedman, San Francisco.

Gravenor, C.P. (1979). The nature of the Late Palaeozoic glaciation in Gondwana as determined from an analysis of garnets and other heavy minerals. Can. J. Earth Sci., 16, 1137-1153.

Green, A.H. (1883). Report on coals of the Cape Colony. Parliamentary Report, Cape Town, 1-33.

Haughton, S.H. (1924). Fauna and stratigraphy of the Stormberg Series. Ann. S. Afr. Mus., 12.

Haughton, S.H. (1969). Geological History of South Africa. Geol. Soc. S.Afr., Cape Town.

Harman, H.H. (1967). Modern Factor analysis. Univ. of Chicago Press, Chicago.

Heinrich, E.W. (1965). Microscopic identification of minerals. McGraw-Hill, New York.

Herbosch, A. (1974). Facteurs controllent La distribution des elements dans les shales uraniferes du bassin permien de Lodeve (Herault, France). In Formation of Uranium deposits, I.A.E.A., Vienna.

Hirst, D.M. and Kaye, M.J. (1971). Factors controlling the mineralogy and chemistry of an Upper Visean Sequence from Rockhope, Country Durham. Chem. Geol., 8, 37-59.

Hofmeyr, P.K. (1971). The abundances and distribution of some trace elements in some South African shales. Unpub. Ph.D. thesis, Univ. of Cape Town.

Hubert, J.F. (1962). A zircon-tourmaline-rutile maturity index and the interdependence of the composition of heavy mineral assemblages with the gross composition and texture of sandstones. J. Sedim. Petrol., 32, 440-450.

Imbrie, J. and van Andel, T.H.V. (1964). Vector analysis of heavy mineral data. Bull. Geol. Soc. Am., 75, 1131-1156.

Johnson, M.R. (1967). The stratigraphy of the Cape and Karoo Systems in the Eastern Cape Province. Unpub. M.Sc. thesis, Rhodes Univ.

Joyce, A.S. (1976). Exploration Geochemistry. Techsearch Inc. and Australian Mineral Foundation.

Koen, G.M. (1955). Heavy minerals as an aid to the correlation of sediments of the Karroo System in the northern part of the Union of South Africa. Trans. Geol. Soc. S. Afr., 58, 281-366.

Krinsley, R.H. and Doornkamp, J.C. (1973). Atlas of quartz sand surface textures. Comb. Univ. Press, Cambridge.

Landergren, S. (1969). Vanadium. In Wedepohl, K.H. (ed) Handbook of Geochemistry, Springer-Verlag, Berlin.

Mackin, J.E. and Owen, R.M. (1979). The geochemistry of sediments from Little Traverse Bay, Lake Michigan : influence of physical processes. Can. J. Earth. Sci., 16, 532-539.

Marchant, J.W. and Moore, A.E. (1978). Geochemistry of the Table Mountain Group, II : Analysis of 2 suites of Western Graafwater Rocks. Trans. Geol. Soc. S. Afr., 81, 353-357.

Marshall, B. (1966). The present status of zircon. Sedimentology, 9, 119-136.

Milner, H.B. (1962). Sedimentary Petrology, Vol. II, MacMillan, New York.

Nesbitt, R.W., Mastins, H., Scholz, G.W. and Bruce, D.R. (1976). Matrix corrections in trace element analysis by X-ray fluorescence : an extension of the Compton scattering peak to long wavelengths. Chem. Geol., 18, 203-213.

Nicholls, G.D. and Loring, D.H. (1962). The geochemistry of some British Carboniferous sediments. Geochim. Cosmochim. Acta, 26, 181-123.

Nicol, I., Garret, R. and Webb, J.S. (1969). The role of some statistical and mathematical models in the interpretation of regional geochemical data. Econ. Geol., 64, 204-220.

Nie, N.H., Hull, H.C., Jenkin, J.G., Steinbrenner, K. and Brent, D.H. (1975). Statistical package for the Social Sciences. McGraw-Hill, New York.

Norrish, K. and Hutton, J.T. (1969). An accurate X-ray spectrographic method for the analysis of a wide range of geologic samples. Geochim. Cosmochim. Acta, 33, 431-453.

Pearson, E.S. and Hartley, N.D. (1972). Biometrika tables for statisticians. Camb. Univ. Press, Cambridge.

Pettijohn, E.J. (1975). Sedimentary Rocks. 3rd ed. Harper and Row, New York.

Poldervaart, A. (1950). Statistical studies of zircon as a criterion in granitization. Nature, 165, 574-575.

Potter, P.E. (1968). The distribution of garnet in compacted sediments. J. Sedim. Petrol., 38, 1340-1344.

Puckelt, H. (1972). Barium. In Wedepohl, K.H. (ed), Handbook of Geochemistry, Springer-Verlag, Berlin.

Rahmani, R.A. (1973). Grain surface features of some heavy minerals. J. Sedim. Petrol., 43, 882-888.

Rankama, K. and Sahama, T.G. (1952). Geochemistry. Univ. of Chicago Press, Chicago.

Reynolds, R.C. (1963). Matrix corrections in trace element analysis by Compton scattering. Am. Miner., 48, 1133-1143.

Robinson, D.N., Beer, H.M., Nutsch, F.M. and Trumpelmen, F. (1969). The geology and oil potential of the Stormberg Group. Unpub. report, Soekor, Johannesburg.

Rust, I.C. (1959). On the sedimentation of the Molteno Sandstones in the vicinity of Molteno, C.P. Ann. Univ. Stellenbosch, 37, 165-240.

Ryan, P.J. (1963). Petrology, origin and deposition of the Molteno Stage in the Indwe area of the north-east Cape Province. Unpub. M.Sc. thesis, Univ. of Witwatersrand.

Saager, R. and Esselaar, P.A. (1969). Factor analysis of geochemical data from the Basal Reef, Orange Free State Goldfield, South Africa. Econ. Geol., 64, 445-451.

Saager, R. and Sinclair, A.J. (1974). Factor analysis of stream sediment geochemical data from the Mount Nansen area, Yukon territory, Canada. Mineralium Deposita, 9, 243-252.

Schwarz, E.H.L. (1916). Diamonds from the Molteno Beds. Trans. Geol. Soc. S. Afr., 14, 33-35.

Selley, R.C. (1976). An introduction to sedimentology. Academic Press, London.

Simpson, G.S. (1976). Evidence of overgrowths on, and solution of, detrital garnets. J. Sedim. Petrol., 46, 689-693.

South African Committee for Stratigraphy, (1971). Trans. Geol. Soc. S. Afr., 74, 111-131.

Spencer, D. (1966). Factors affecting element distributions in a Silurian graptolite band. Chem. Geol., 1, 221-249.

Spencer, D., Degens, E.T. and Kulbicki, G. (1968). Factors affecting element distributions in sediments. In Ahrens, L.H. (ed). Origin and distribution of the elements. Pergamon, London.

Spotts, J.H. (1962). Zircon and other accessory minerals, Coastal Range Batholith, California. Bull. Geol. Soc. Am., 73, 1221-1240.

Stavrakis, N. (1979). Sedimentology of the Katberg Sandstone. Unpub. M.Sc. thesis, Rhodes University.

Stephens, W.E., Watson, S.W., Philip, P.R. and Wein, J.A. (1975). Element associations and distributions through a lower Palaeozoic graptolite sequence in the Southern Uplands of Scotland. Chem. Geol., 16, 269-294.

Stockley, G.M. (1947). Report on the geology of Basutoland. Maseru Government Report.

Suttner, L.J. (1974). Sedimentary petrographic provinces : An evaluation. In Ross, C.A. (ed). Palaeogeographic provinces and provinciality. Soc. of Econ. Palaeont. and Mineral., Special Publ. No. 21.

Theron, J.C. (1970). Some geological aspects of the Beaufort Series in the Orange Free State. Unpubl. D.Sc. thesis, Univ. of Orange Free State.

Theron, J.N. (1962). An analysis of the Cape Folding in the district of Willowmore, C.P. Ann. Univ. Stellenbosch, 37, 349-407.

Theron, J.N. (1972). The stratigraphy and sedimentation of the Bokkeveld Group. Unpub. D.Sc. thesis, Univ. of Stellenbosch.

Todd, T.W. (1968). Palaeoclimatology and the related stability of feldspar minerals under atmospheric conditions. J. Sedim. Petrol., 38, 832-844.

Turner, B.R. (1969(a)). Stratigraphy and sedimentary history of the Molteno Stage in part of the N.E. Cape Province. Unpub. M.Sc. thesis, Univ. of the Witwatersrand.

Turner, B.R. (1969(b)). The use of the Indwe Sandstone as a stratigraphic marker in the Molteno Stage of the Karroo system. Palaeont. Afr., 12, 203-204.

Turner, B.R. (1970). Facies analysis of the Molteno sedimentary cycle. In Haughton, S.H. (ed). Proc. 2nd I.U.G.S. Symposium on Gondwana stratigraphy and palæontology. C.S.I.R. Pretoria.

Turner, B.R. (1971). The geology and coal reserves of the N.E. Cape Province. Bull. Geol. Survey S. Afr., 52.

Turner, B.R. (1972(a)). Revision of the stratigraphic position of cynodonts from the upper part of the Karroo (Gondwana) system in Lesotho. Geol. Mag., 109, 349-360.

Turner, B.R. (1972(b)). Silica diagenesis in the Molteno. Trans. Geol. Soc. S. Afr., 75, 55-60.

Turner, B.R. (1975(a)). The stratigraphy and sedimentary history of the Molteno Formation in the Main Karroo Basin of South Africa and Lesotho. Unpub. Ph.D. thesis, Univ. of Witwatersrand.

Turner, B.R. (1975(b)). Statistical appraisal of Triassic Molteno sedimentary cycles from the upper part of the Karroo (Gondwana) system in South Africa. J. Sedim. Petrol., 45, 95-104.

Turner, B.R. (1977). Fluviatile cross-bedding patterns in the Upper Triassic Molteno Formation of the Karroo (Gondwana) Supergroup in South Africa and Lesotho. Trans. Geol. Soc. S. Afr., 80, 241-254.

Turner, B.R. (1978). Palaeohydraulics of clast transport during deposition of the Upper Triassic Molteno Formation in the main Karroo Basin of South Africa. S. Afr. J. Sci., 74, 171-174.

Van Eeden, O.R. (1937). The geology of the country around Bethlehem and Kestell. Mem. Geol. Surv. Un. S. Afr., 33, Pretoria.

Van de Kamp, P.D., Leake, B.E. and Senior, A (1976). The petrography and geochemistry of some Californian arkoses with application to identifying gneisses of sedimentary origin. J. Geol., 84, 195-212.

Whittaker, E.J.W. and Muntus, R. (1970). Ionic radii for use in geochemistry. Geochim. Cosmochim. Acta, 34, 945-956.

Wyatt, M. (1954). Zircons as provenance indicators. Am. Miner., 39, 983-990.

APPENDIX A : X-RAY FLUORESCENCE SPECTROMETRY

Major element analyses (5 samples) and trace element analyses (28 samples) were conducted in the Department of Geology, Rhodes University using a Phillips DW 1410 spectrometer, under the guidance of Dr. J.S. Marsh. Data was reduced by means of various programmes run on the Rhodes University ICL 1903S computer.

Samples were initially reduced to chip sizes using a jaw crusher. Further finer crushing to $\pm$ 120 mesh was achieved using a Herzog swing mill. In the case of major element analyses (except Na) fusion discs were prepared using the method of Norrish and Hutton (1969). H_2O^- was determined gravimetrically by heating the samples at 110° for 6 hours. LOI was determined by igniting at $950^{\circ}C$ overnight. Iron is expressed as Fe_2O_3. Corrections were made for dead-time, background and instrumental drift.

Trace element analysis (excluding Mn, Ba, Zn, Cu and Ni - analysed by Anglo American) was performed on pressed powder briquettes, using approximately 4g of sample which had been further ground in an agate mortar and pestle. Corrections for background, spectral line interference, dead time and instrumental drift were all applied. Since major element data were only available for 5 samples, mass absorption coefficients could not be calculated using the common technique of calculation from the whole rock data.

Instead estimation of mass absorption coefficients using the intensity of the Compton scatter peak was applied. Using the method described by Reynolds (1963) mass absorption coefficients were found for Nb, Zr, Y, Sr and Rb. For the elements with atomic number <28 (Co, Cr, V, Ti) the method described by Nesbitt et al. (1976) was applied.

Analytical conditions are given in Table 12; the lower limit of detection and error for the trace elements are given in Table 14.

TABLE 13: X-RAY FLUORESCENCE ANALYTICAL CONDITIONS : TRACE ELEMENTS

Element	Tube	kV	mA	Crystal	Time(secs)	Counter	Collimator	Specimen
Nb	W	55	40	Lif 220	100	Scint.	Fine	Power disc
Zr	W	55	40	Lif 220	100	Scint.	Fine	Power disc
Y	W	55	40	Lif 220	100	Scint.	Fine	Power disc
Sr	W	55	40	Lif 220	100	Scint.	Fine	Power disc
Rb	W	55	40	Lif 220	100	Scint.	Fine	Power disc
Co	W	55	40	Lif 220	200	Scint.	Fine	Power disc
Cr	W	55	40	Lif 220	200	Flow	Fine	Power disc
V	W	55	40	Lif 220	200	Flow	Fine	Power disc
Ti	W	55	40	Lif 200	40	Flow	Fine	Power disc

TABLE 12: MAJOR ELEMENT ANALYTICAL CONDITIONS

Element	Tube	kV	mA	Crystal	Time(s)	Counter	Specimen
Si	Cr	55	40	Ge Pet	40	Flow	Bead
Ti	Cr	55	40	Lif 200	10	Flow	Bead
Al	Cr	55	40	Ge Pet	40	Flow	Bead
Fe	Cr	55	40	Lif 200	20	Flow	Bead
Mn	Cr	55	40	Lif 200	40	Flow	Bead
Mg	Cr	55	40	Tlap	200	Flow	Bead
Ca	Cr	55	40	Lif 200	10	Flow	Bead
Na	Cr	55	40	Tlap	100	Flow	Power disc
K	Cr	55	40	Lif 200	10	Flow	Bead
P	Cr	55	40	Fe Pet	20	Flow	Bead

TABLE 14: LOWER LIMIT OF DETECTION AND ERROR FOR ANALYSES

	LLD	Error
Nb	0,33	0,11
Zr	0,30	0,18
Y	0,30	0,12
Sr	0,28	0,15
Rb	0,31	0,14
Co	0,18	0,04
Cr	0,19	0,05
V	0,25	0,06
Ti	3,6	11,1
Cu	2	10%
Ni	2	10%
Zn	2	10%
Mn	10	20%
Ba	50	20%

APPENDIX B : COMPARISON OF d-spacings (Å) OBTAINED BY THE GANDOLFI METHOD WITH THOSE GIVEN BY JCPDS CARDS

Observed	JCPDS	Observed	JCPDS	Observed	JCPDS
Rutile		Brookite		Anatase	
3,22	3,25	3,513	3,51	3,51	3,52
2,4734	2,487	-	3,47	-	2,431
2,2845	2,297	-	2,90	2,3723	2,578
2,1820	2,188	2,4846	2,476	-	2,332
2,0478	2,054	2,4085	2,409	1,8897	1,892
1,6832	1,6874	-	2,244	1,6950	1,6999
1,6206	1,6237	-	2,133	1,6624	1,6665
1,4512	1,4797	-	1,969	-	1,4930
-	1,4528	1,8897	1,893	1,4794	1,4808
1,3580	1,3598	-	1,851		
		1,6998	1,691		
		1,6693	1,662		
		1,4794	1,473		
Dravite		Pyrope			
6,3481	6,38	2,8714	2,98		
-	5,32	2,5782	2,58		
4,95	5,00	2,4514	2,46		
4,58	4,59	2,3422	2,35		
4,2155	4,22	2,2522	2,26		
3,961	3,98	2,0969	2,10		
3,4559	3,48	-	2,03		
-	3,38	1,8626	1,87		
-	3,01	-	1,82		
2,95	2,966	1,6602	1,66		
-	2,899	1,5934	1,60		
-	2,848	1,5412	1,54		
2,5721	2,573				
2,3373	2,337				
2,1610	2,1610				