

THE MINERAL MATTER IN
SOME SOUTH AFRICAN
COALS

by

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Submitted in partial fulfilment of the
requirements for the

DEGREE OF MASTER OF SCIENCE

in the Faculty of Science
University of Pretoria
PRETORIA

May 1980

SAMEVATTING

Die voorkoms en verspreiding van mineraalbestanddele in 35 steenkool-produkmonsters is met behulp van radio-frekwensie verassing en X-straaldiffraksiemetodes ondersoek.

Die voorkoms van illiet in hoërangse steenkool, in teenstelling met dié van kaoliniet in laerangse steenkool word verklaar deur nuutvorming („neoformation”) tydens laat-diagenese gelyktydig met die indringing van doleriete. Die verspreiding van nie-kristallyne bestanddele in die steenkoolprodukte kan moontlik ook deur metamorfose verklaar word.

Die verarming aan SiO_2 , MgO , Na_2O en K_2O in steenkoolas en die verryking aan Al_2O_3 en TiO_2 relatief tot die aardkors word verklaar deur loging in 'n suur omgewing en die aktiwiteit van plante.

Die berekende kleinorm vanaf die asanalises wyk af van die eksperimenteelbepaalde mineraalsamestelling maar kan dien om die totale mineraalinhoud van steenkool vas te stel.

Die paar spoorelementbepalings dui op 'n sterk verryking van wolfram in steenkoolas en beklemtoon die behoefte aan verdere spoorelementbepalings.

ABSTRACT

The occurrence and distribution of mineral matter in 35 coal product samples was determined by means of radio-frequency ashing and X-ray diffraction.

The association of illite with high rank coals in contrast with that of kaolinite with low rank coals is thought to be due to neoformation during late diagenesis coincident with the intrusion of dolerites. The distribution of non-crystalline material in the coal products may perhaps also be due to metamorphism.

The impoverishment of SiO_2 , MgO , Na_2O and K_2O in coal ash, and the enrichment of Al_2O_3 and TiO_2 relative to the earth's crust is thought to be due to acid leaching and the activities of plants.

The calculated argillaceous norm from the ash analysis differs from the determined mineral composition but can serve as an estimate of the total mineral matter content of the coal.

The few trace element determinations show a strong enrichment of tungsten in coal ash and underline the need for further trace element determinations.

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I. INTRODUCTION

The mineral matter may be defined as that part of coal resulting in a residue after burning. It is important in the mining, beneficiation and utilization of coal and may give indications of the conditions under which a particular coal seam was formed, or of the post-depositional changes to which a coal basin has been subjected.

Francis (1954, p.483) divided the inorganic constituents of coal into two classes. The first class consists of inorganic constituents present in the coal-forming plants ("inherent mineral matter"), and the second comprises the inorganic constituents added to the coal-forming deposit after the death of the plants ("adventitious mineral matter"). The "adventitious mineral matter" can be either syngenetic or epigenetic in origin.

Other definitions have been given (e.g. Watt, 1968, p.2) in which the "inherent mineral matter" is distinguished from the "adventitious mineral matter" on the basis of the ease with which they can be removed from coal by ordinary washing procedures. The inherent mineral matter is still present in cleaned coal.

Mackowsky (1968a) defined the mineral matter as being syngenetic or epigenetic in origin, but with the exception of typical clastic minerals such as zircon, rutile and ilmenite, it cannot be stated whether a particular mineral is syngenetic or epigenetic, except on the basis of a microscope investigation. Mackowsky (ibid.) stressed the technological importance of the distinction between syngenetic and epigenetic minerals.

In the present work, quantitative X-ray diffraction and radio-frequency ashing point to the existence of a crystalline class and a non-crystalline or amorphous class of mineral matter. Syngenetic and epigenetic minerals could not be distinguished from each other.

II. PRACTICAL IMPORTANCE OF MINERAL MATTER IN COAL

According to Mackowsky (1968a), the mineral matter intergrown with coal is of great practical importance because it may give an indication of the conditions under which the coal macerals formed. Characteristic mineral bands may make it possible to identify and correlate coal seams, or portions of a seam, if coal has to be mined for specific purposes. The nature of the clay minerals affects the properties of the roof and the floor in coal mining and contributes to sliming during coal transportation and beneficiation. The mineral matter of less than 5 μm diameter in coal and the country rock constitutes a health hazard since it can cause pneumoconiosis. The beneficiation of coal depends not only on the total mineral matter content, but also on the way in which the mineral matter is combined with the coal. The suitability of coal as a boiler fuel is affected by the mineral components in the coal, as they influence slag fusion point, corrosion and erosion of heating surfaces, air pollution and may be responsible for the formation of boiler deposits.

Nelson (1953) pointed out that the nature and distribution of inorganic matter in coal are of particular importance as some minerals may have a catalytic influence on the carbonization and spontaneous combustion of coal and its grindability and breakage characteristics.

Mineral matter in coal may also have economic importance. O'Gorman and Walker (1971) found enrichment ratios of copper and tin relative to the earth's crust, of 40 and 100 respectively, in Wyoming and Pennsylvanian coals.

Snyman (1978) pointed out that although fly-ash in South Africa has a high potential in the building industry, and could possibly be used as a raw material for the production of alumina, its minor element content is largely unknown, and ought to be researched. Pyrite and uranium minerals could probably also be extracted from some coals.

III. PREVIOUS WORK

In their pioneering work on mineral matter in coal, Nagelschmidt and Hicks (1944) combined X-ray diffraction methods with chemical analyses to give a quantitative estimate of the amount of illite, kaolinite, quartz and carbonates in some British coals. The average composition of the sinks at a specific gravity of 1,6 of 19 samples was as follows: illite 13 per cent, kaolinite 22 per cent, quartz 2 per cent and carbonates 42 per cent.

Mitra (1950, 1954) identified kaolinite, beidellite, aragonite, metahalloysite, quartz, pyrite, dolomite and anatase from the Jharia field, India and on the basis of X-ray methods determined proportions of the following minerals in coal from the Rangiganj field: quartz 10,09 per cent; kaolinite 12,99 per cent; apatite 1,48 per cent; pyrite 2,78 per cent and anatase 0,69 per cent (coal basis).

In addition to the more common minerals, Bardossy (1961) identified marcasite, gypsum, chamosite, chlorite, thuringite and rozenite in Hungarian coals.

Dixon et al. (1964), using chemical analyses of commercial grade coal from the East Midlands, showed quartz to be a significant component together with white mica, "degraded mica", "kaolin-type material" and kaolinite. Microscopically chlorite, siderite, apatite, rutile and tourmaline were also identified.

Kemezys and Taylor (1964) microscopically identified plagioclase and orthoclase in a few Australian coal seams. These minerals appeared fresh and unweathered, and were thought to be tuffaceous in origin. The authors also stated that dolomite was unknown from Australian coals, that siderite was abundant only in the seams having fresh water sedimentary rocks rather than marine sedimentary rocks overlying them and that ankerite occurred more commonly than calcite. Of the sulphides pyrite, marcasite, sphalerite, galena, chalcopyrite and millerite were noted. Barite was identified from a seam in Queensland, and fluorapatite, zircon, goethite and limonite were also observed as accessory minerals.

Warne (1965) described a DTA method for the semi-quantitative determination of mineral matter in coal. Small amounts of marcasite and pyrite could not be distinguished from each other and detection limits for the commonly occurring minerals are poorer than with X-ray diffraction methods (see Section IV of the present work) at 0,5 per cent for pyrite, 1 per cent for marcasite, 1 - 2 per cent for calcite, 3 - 5 per cent for siderite and kaolinite, 15 - 20 per cent for montmorillonite and quartz and 30 - 35 per cent for illite.

In their study on the effects of mineral matter in NSW (Australia) coke-making coals Brown et al. (1965) found pyrophyllite, chlorite, vermiculite, feldspar, siderite and apatite in addition to mixed-layer montmorillonite-illite, kaolinite and quartz. The montmorillonite in the mixed-layer clays varied from 5 to 90 per cent, with an average of about 30 per cent, and was responsible for sliming in some coal washing plants, although in some cases it was beneficial in improving the strength of coke.

Using single particles of coal of 60 - 100 mesh (250 - 150 μm) directly in a Debye-Scherrer powder camera Rekus and Haberkorn (1966) identified eighteen minerals including epidote, diaspore, barite, mullite, chrysotile, anhydrite, lepidocrocite, goethite, hematite and magnetite. The study was carried out on the Lower Kittanning seam, Pennsylvania.

Using chemical and microscope methods Kunstmann and Kerkovius (1968) identified detrital quartz (average diameter 100 μm) and secondary quartz with an average diameter of 5 μm in South African coal products. Quartz was considered to be a major constituent in South African coals - values as high as 7 per cent (coal basis) were determined for OFS and Soutpansberg coals, and the Witbank No. 5 Seam was found to have a higher free quartz content in the coal ash of 23 - 34 per cent, than other Witbank product samples.

Estep et al. (1968) used infra-red spectrometry to do quantitative analysis of kaolinite, quartz, calcite, gypsum and pyrite occurring in coal. Due to strong absorption from the coal itself, it was necessary to remove carbon from the samples by radio-frequency ashing. Difficulties were experienced in determining pyrite in the presence of kaolinite because their important absorption bands overlap.

Kunstmann and Van Rensburg (1968) showed that manganese was not enriched in South African coal ash relative to its concentration in the earth's crust. Cold acetic acid extraction on a series of floats at different specific gravities showed manganese, in most instances, to be combined with carbonate, probably in ankerite, $\text{Ca (Mg, Fe, Mn) (CO}_3)_2$.

Dixon et al. (1970a) using chemical, X-ray diffraction and infra-red methods, showed that although the Al in the kaolinite component was unsubstituted, substitution of Al by Fe, Mg, Ti and possibly Ca in mica and hydro-mica did take place. Methods were given whereby the amount of clay minerals could be calculated from the chemical analysis of the coal ash.

Using chemical analyses and thin section microscopy on cleat material separated at different specific gravities from East Midlands coal Dixon et al. (1970b) found the cleat material to consist mainly of calcite and ankerite (54 per cent CaCO_3 , 24 per cent MgCO_3 , 20 per cent FeCO_3 and 2 per cent MnCO_3). No magnesite, siderite or dolomite was present, although barite occurred in some samples.

O'Gorman and Walker (1971) used radio-frequency oxidation in order to concentrate mineral matter from coal for study by X-ray diffraction, infra-red absorption and chemical methods. Semi-quantitative data showed kaolinite to vary from 1 to more than 70 per cent, whereas illite, montmorillonite and mixed-layer

clays amounted to less than 40 per cent in 12 bituminous coal and anthracite samples. Aragonite was detected in only one sample. Trace element analysis showed an anthracite sample from Pennsylvania to contain over 4 000 ppm, on an ash basis, of tin which occurred as cassiterite. A bituminous coal sample from Wyoming contained enough copper at 2 500 ppm, (coal ash), to qualify as a low grade copper ore.

Rao and Gluskoter (1973) determined regional variations in the content of clay minerals, quartz, pyrite and calcite for the Herrin (No. 6) coal member of the Illinois basin, using X-ray diffraction and chemical methods on the radio-frequency ash. The distribution of the minerals was considered to result from palaeobasin conditions. Mean values for the Illinois basin are as follows: total clays 52 per cent, pyrite 23 per cent, quartz 15 per cent and carbonates 9 per cent.

Mukherjee and Chowdhury (1976) studied the effect of mineral constituents as catalysts in the hydrogenation of coal and came to the conclusion that both iron and titanium had a catalytic effect, increasing oil yields from the coal.

Mitchell and Gluskoter (1976) heated samples of mineral matter residue which had been prepared by radio-frequency ashing, from 400 to 1 400°C at 100°C intervals and found that some high temperature phases were formed in limited temperature ranges and could thus be used as mineralogical thermometers. High temperature minerals were the following: anhydrite, anorthite, calcium iron oxide (CaO.FeO), clinopyroxene, corundum, cristobalite, ferric sulphate, gehlenite, hematite, lime, magnetite, meta-kaolinite and mullite.

Ward (1977) carried out a study on the Springfield-Harrisburg (No. 5) coal member in the Illinois basin, and found kaolinite more dominant in the basin-ward, sediment-starved regions of the basin. The kaolinite was thought to have formed from dissolved silica and alumina in the peat swamp, catalysed by organic acids.

A study of the mineral matter in Australian coals (Ward, 1978) showed that illite was a very minor constituent of the coal, although it was common in roof and floor rocks. The formation of authigenic kaolinite was thought to be responsible for the relatively low proportion of illite in the coal.

IV. SAMPLES STUDIED

Thirty-five samples of commercial grade coals (coal products or production samples) taken during 1975 and 1976 from most of the coal-producing areas or seams in the Republic, were used for the present study. Standard sampling procedures were followed and the samples represent the typical production of a particular size-grade of coal in the year of sampling. Eleven samples originated from the Witbank area, three from the Breyten-Ermelo area, five from the South Rand and OFS, and the remaining sixteen samples were distributed between the Klip river, Utrecht and Paulpietersburg-Vryheid areas of Natal.

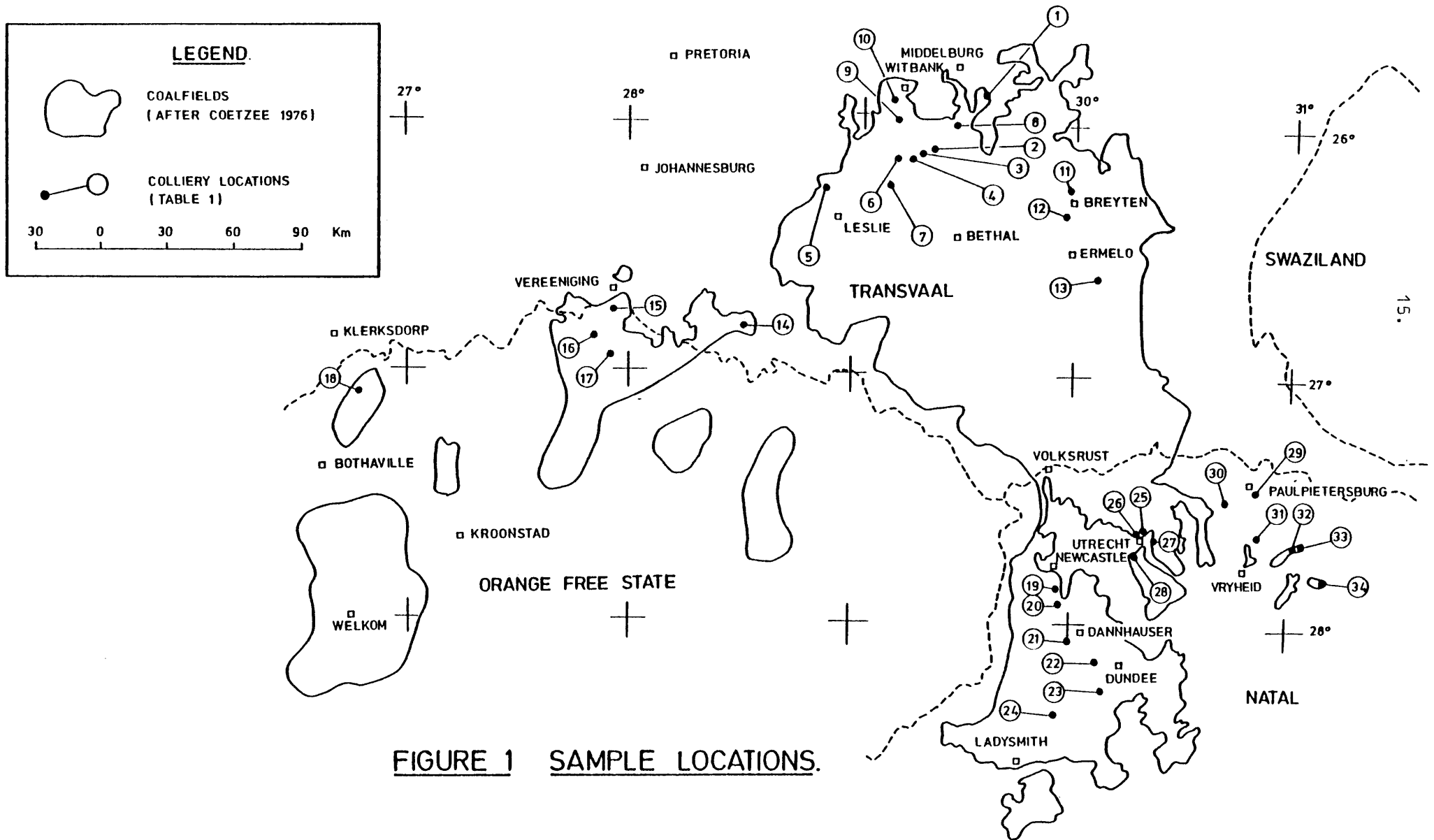
The products include coking and blend-coking coals for the metallurgical industry, bituminous coals and anthracites prepared for the domestic market as well as low quality coal used for the generation of electricity. Mainly the smaller size-grade was sampled varying from nuts to mixed duff and except for the power station coals, almost all the product samples had been beneficiated by washing and screening prior to sampling and presumably extraneous material originating from the roof or floor, or thick partings in the coal seams, were absent from the samples.

As far as possible, the samples originated from a specific seam, but except for the Witbank area, the samples represent mixtures of two or more seams and the relative proportion of coal from a particular seam included in the product sample is unknown.

A list of the samples appears in Table 1 and their localities are indicated in Figure 1.

TABLE I
SAMPLE DESIGNATION AND LOCALITY

Colliery	Sample No.	Product	Designation	Locality in Fig. 1
Eikeboom	75/208D	Pea	Witbank No. 2 Seam	1
Springbok	75/424A	Nut	Witbank No. 2 Seam	2
New Clydesdale	75/414A	Nut	Witbank No. 2 Seam	3
Albion	75/576B	Pea	Witbank No. 2 Seam	4
Delmas	75/38D	Mixed small	Witbank No. 2 Seam	5
South Witbank	75/572D	Pea	Witbank No. 4 Seam	6
Anglo Power (Kriel)	75/553A	Crushed	Witbank No. 4 Seam	7
Blesbok	76/965A	Blend coking	Witbank No. 5 Seam	8
Springbok	76/246C	Blend coking	Witbank No. 5 Seam	2
Greenside	75/408D	Blend coking	Witbank No. 5 Seam	9
Navigation	75/569B	Blend coking	Witbank No. 5 Seam	10
Union	75/124B	Pea	Breyten-Ermelo	11
Spitzkop	75/586B	Pea	Breyten-Ermelo	12
Usutu (S & E)	76/234A	Crushed	Breyten-Ermelo	13
Grootvlei	75/562A	Crushed	South Rand & OFS	14
Cornelia Bertha I	75/393A	Pea	South Rand & OFS	15
Sigma	75/557B	13 x 0 mm	South Rand & OFS	16
Coalbrook No. 2	75/45A	Mixed small	South Rand & OFS	17
Vierfontein	75/202A	Mixed small	South Rand & OFS	18
Kilbarchan	75/55A	Mixed small	Klip River, Natal	19
Ballengeich	75/303B	Pea	Klip River, Natal	20
Durban Navigation	76/680A	Coking	Klip River, Natal	21
Natal Navigation	76/684A	Coking	Klip River, Natal	22
Indumeni	76/683A	Coking	Klip River, Natal	23
Newcastle-Platberg	75/304B	Pea	Klip River, Natal	24
Balgray	76/40B	Mixed small	Utrecht	25
Utrecht	75/310B	Pea	Utrecht	26
Umgala	76/933A	Small	Utrecht	27
Zirbutu	76/934C	Pea	Utrecht	28
Dumbe	76/223A	Coking	Paulpietersburg-Vryheid	29
Brockwell Anthracite	76/44D	Mixed small	Paulpietersburg-Vryheid	30
Tendega	76/955A	Coking	Paulpietersburg-Vryheid	31
Hlobane	76/691A	Coking	Paulpietersburg-Vryheid	32
Vryheid Coronation	76/946A	Coking	Paulpietersburg-Vryheid	33
Aloe Anthracite	8434	Mixed duff	Paulpietersburg-Vryheid	34



V. THE DETERMINATION OF THE AMOUNT OF MINERAL MATTER

An ash determination underestimates the amount of "inorganic" material in coal because at the temperature at which it is carried out (815°C) many of the minerals are altered or destroyed. The clay minerals lose water of constitution and the sulphides and carbonates are decomposed.

Indirect methods have been used to determine the amount of mineral matter in coal. From various formulae the ash yield can be recalculated to the mineral matter content, but certain variables have to be known. Parr's formula (quoted by Brown et al., 1952) requires a total sulphur determination, and that of King, Maries and Crossley (KMC-formula) requires determinations of pyritic sulphur, carbonate and chlorine, and also of sulphate in coal and in ash (Brown, op.cit.).

A serious limitation of the accuracy of these indirect methods is the variable moisture loss of the clay minerals which cannot be corrected for by a universal factor, viz. 1,08 for the Parr-formula and 1,07 to 1,13 for the KMC-formula. At various times modifications to the constants in the formulae were suggested, viz. Brown (op. cit.), Pringle and Bradburn (1958), Brown et al. (1959), and Millot (1958).

A more direct method of determining the mineral matter content is by acid digestion of the mineral constituents (Bishop and Ward, 1958). However, values determined by this method seemed low for South African coals, compared with the indirect methods (Savage, 1968b).

The combustion of coal at 370°C (Brown et al., 1959) has also been used, but corrections have to be carried out for pyrite and siderite decomposed in the ashing process.

However, developments in plasma technology in the sixties made it possible to ash coal at an even lower temperature (150 to 170°C), at which the principal minerals appear to be unaffected.

According to Gleit (1963) and Gleit and Holland (1962) the oxygen passed at reduced pressure through a field generated by a radio-frequency oscillator (13,56 M Hz) is activated into ionic and vibrationally excited states. This excited oxygen can react with organic compounds at relatively low temperatures.

Gluskoter (1965) and Frazer and Belcher (1973) used the radio-frequency ashing method on coal samples and found that no irreversible changes had occurred in the mineral matter, when the radio-frequency power was less than 300 Watt. At higher powers pyrite tended to be oxidized and at lower power some organic sulphur tended to be fixed as $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (bassanite). Gypsum was also dehydrated to bassanite. The ashing temperature appeared to lie between 150 and 200°C. These findings were largely confirmed by Miller *et al.* (1979) who stressed that the ashing conditions had to be rigorously controlled for reproducible results.

A. Experimental method

The radio-frequency ashing was carried out in a commercially available radio-frequency asher: Model LTA 505 of the LFE Corporation. Fifty ml of oxygen per minute at 200 Watt power was used and infra-red radiation measurements indicated that ashing occurred in the temperature range 130 - 160°C.

One gram coal samples were used and the ash-residue was weighed at 24 hour intervals. When loss in mass was less than 1 per cent, the ashing was terminated. The period of time required for the ashing varied from 3 to 8 days, depending on the ash yield and rank of the coal. The high ash, low rank OFS coals required the longer periods of time.

B. Results and discussion

Table II gives ash yield at 815°C (Savage *et al.*, 1977), mineral matter content determined by radio-frequency ashing (this study), and the ratio of mineral matter to ash (i.e. the mineral matter factor) for the 35 coal samples.

TABLE II
ASH YIELD*, MINERAL MATTER CONTENT AND MINERAL MATTER
TO ASH RATIO OF COAL PRODUCT SAMPLES

Colliery	Mass % (air-dry)		Ratio: $\frac{M.M.}{Ash}$
	Ash* at 815°C	Mineral matter 130 - 160°C	
<u>Witbank No. 2 Seam</u>			
Eikeboom	9,6	11,4	1,18
Springbok	13,7	16,3	1,19
New Clydesdale	15,4	19,1	1,24
Albion	16,8	20,5	1,22
Delmas	19,0	23,4	1,23
<u>Witbank No. 4 Seam</u>			
South Witbank	20,2	24,3	1,20
Anglo Power (Kriel)	20,4	25,3	1,24
<u>Witbank No. 5 Seam</u>			
Blesbok	13,5	15,2	1,13
Springbok	11,4	12,9	1,13
Greenside	11,5	13,7	1,19
Navigation	11,9	13,5	1,13
<u>Breyten-Ermelo</u>			
Union	13,0	16,0	1,23
Spitzkop	13,2	16,1	1,22
Usutu (S & E)	16,7	20,5	1,23
<u>South Rand and OFS</u>			
Grootvlei	26,8	32,1	1,20
Cornelia Bertha I	26,2	31,5	1,20
Sigma	30,2	34,9	1,15
Coalbrook No. 2	24,6	30,6	1,24
Vierfontein	30,1	35,2	1,17
<u>Klip River, Natal</u>			
Kilbarchan	24,7	29,3	1,19
Ballengeich	16,1	18,9	1,17
Durban Navigation	11,0	13,2	1,20
Natal Navigation	13,6	15,9	1,17
Indumeni	10,4	12,7	1,22
Newcastle-Platberg	23,2	26,5	1,14
<u>Utrecht</u>			
Balgray	15,2	18,2	1,20
Utrecht	13,5	16,7	1,23
Umgala	13,4	16,7	1,25
Zimbutu	12,7	15,8	1,24
<u>Paulpietersburg-Vryheid</u>			
Dumbe	10,7	12,6	1,18
Brockwell Anthracite	13,6	15,5	1,14
Tendega	12,1	13,9	1,15
Hlobane	12,9	14,7	1,14
Vryheid Coronation	12,5	14,2	1,14
Aloe Anthracite	11,8	12,7	1,08

*Savage et al., 1977

Mineral matter factors are shown to be rather variable and both maximum (1,25 Umgala product) and minimum (1,08 Aloe Anthracite product) values were obtained on coals originating from Natal. The high factor of most of the Utrecht coal products is probably due to their generally high content of carbonates (Table VII), whereas the mineral matter in the sample from Aloe Anthracite consisted almost entirely of illite and quartz, with a little pyrite. This factor of 1,08 agrees with the water of constitution of the clays in Parr's formula (quoted in Brown et al., 1952) which is not surprising as the mineral matter consists of about 86 per cent clay (Table VII).

In Figure 2 frequency histograms and cumulative frequency distributions are given for the ash, mineral matter and mineral matter factors. The amount of mineral matter in the coal samples is seen to vary over a wider range (11 to 36 per cent) than the ash yields (9 to 31 per cent). The histogram for the mineral matter factors shows a polymodal distribution with maxima centered about 1,14; 1,19 and 1,23. No particular significance can be attached to this due to the ubiquitous presence of calcite in the samples (Table VII) which loses 44 per cent of its mass on ashing. Where carbonates and pyrite are absent from a sample, a high mineral matter factor indicates that kaolinite is a predominant mineral as it loses 12,2 per cent of its mass on ignition (Grim, 1962, p.88) in contrast with illite which has a loss on ignition of only 7,1 per cent (Grim, op. cit., p.90).

In the present series of samples the median coal product yielded 13,4 per cent of ash; 16,0 per cent of mineral matter and had a mineral matter factor of 1,19.

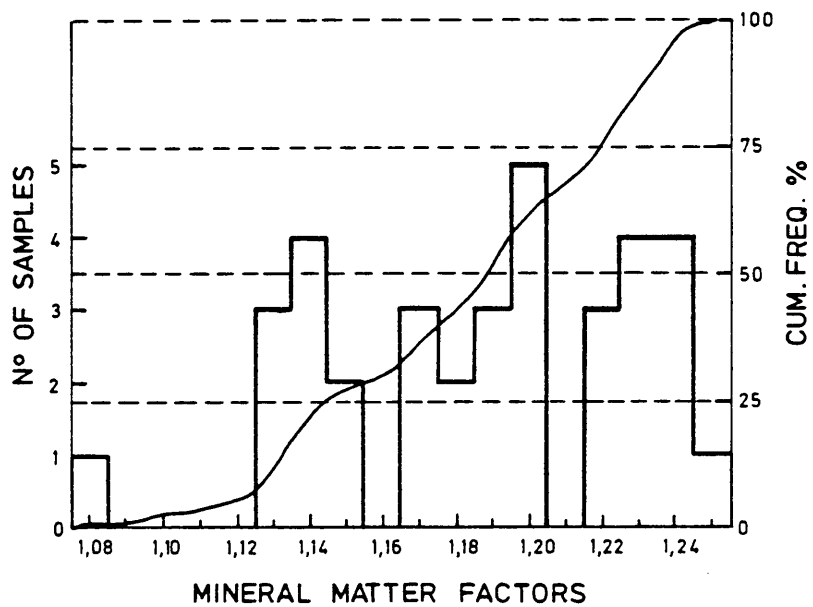
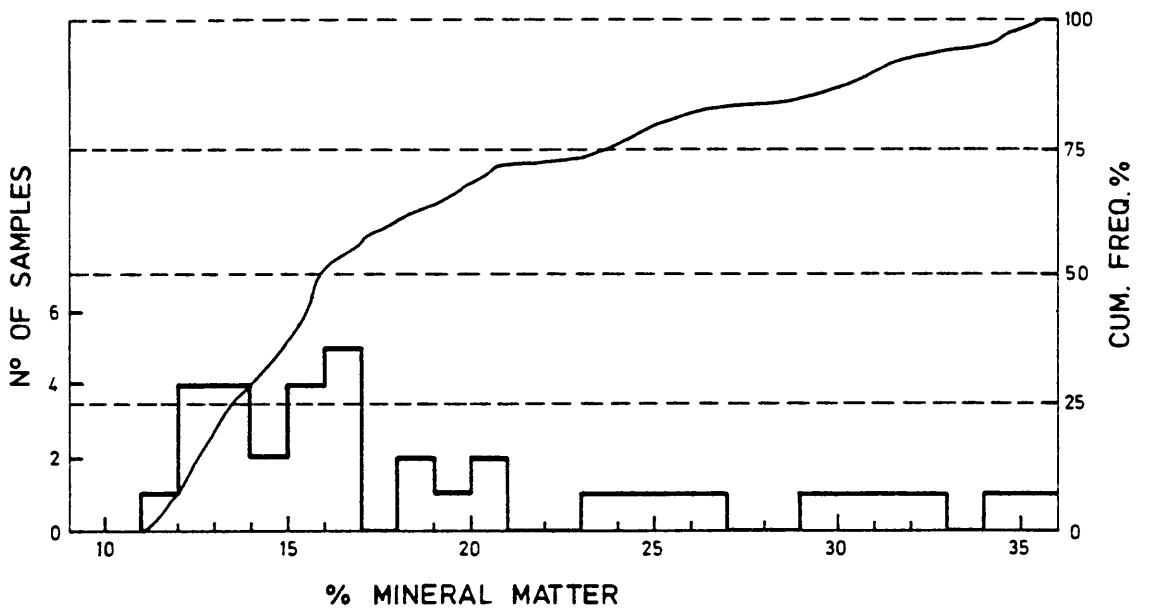
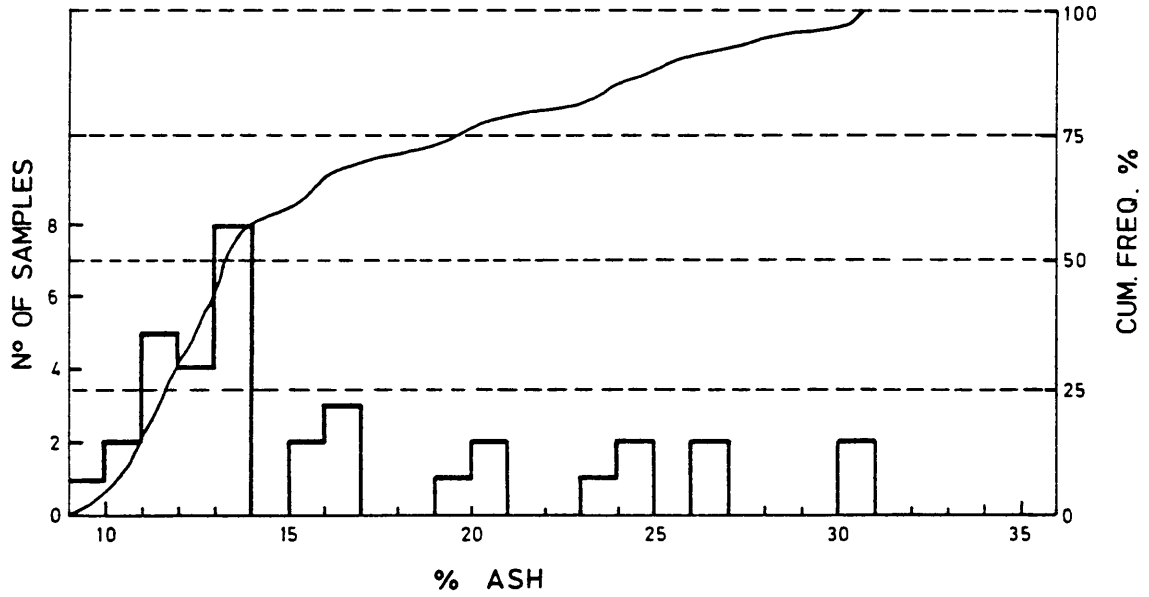


FIGURE 2 FREQUENCY DISTRIBUTIONS OF ASH, MINERAL MATTER & MINERAL MATTER FACTORS.

VI. THEORETICAL AND PRACTICAL CONSIDERATIONS OF QUANTITATIVE X-RAY
DIFFRACTION METHODS USED

Klug and Alexander (1974, p.535) have shown that for a mixture containing a weak and a strong absorber, the intensity of the diffraction peaks for the strong absorber appear to be stronger and that of the weak absorber weaker, than would be expected from a linear relationship between composition and diffraction peak intensity - the so-called "matrix effect". In the general case where the mass absorption coefficient of the material sought is different from the mass absorption coefficient of the mixture, which is also unknown, indirect methods of analysis have to be used.

One such method of excluding the matrix effect is by the use of an internal standard. Calibration mixtures are made up using the material sought and a suitable internal standard, for example fluorite in quartz analyses and when the internal standard is added in constant proportion, the ratio of the diffraction peak intensities of the material sought to the internal standard becomes a linear function of the mass proportion of the material sought (Klug and Alexander, op. cit., p.537). Thus a known amount of the internal standard is added to the mixture to be analysed, the diffraction peak intensity ratios are determined and mass proportions are read from calibration lines.

Chung (1974) simplified quantitative X-ray diffraction procedures further by introducing his "matrix-flushing" concept. He showed that for any component in a multicomponent system:

$$X_i = \left\{ \begin{array}{ccc} k_i & n & I_i \\ \frac{I_i}{I_i} & \Sigma & \\ I_i & i=1 & k_i \end{array} \right\}^{-1}$$

where X_i = mass proportion of i

k_i = a constant specific to i

I_i = diffraction peak intensity of i .

Thus the mass proportion of any component is expressed in terms of ratios like I_i/I_j and k_i/k_j ($i, j = 1, 2 \dots n$) and the matrix effect is excluded by the use of the k-ratio.

Further, for any pair of components in a multi-component system:

$$\text{since } I_i = k_i X_i$$

$$\frac{I_i}{I_j} = \frac{k_i \cdot X_i}{k_j \cdot X_j}$$

(which is the equation for a straight line of the form $y = bx$).

In other words, a plot of the intensity ratio (I_i/I_j) to the mass ratio (X_i/X_j) is a straight line passing through the origin with a slope equal to (k_i/k_j). (See Figures 4 and 16 in the present work).

When the components i and j are present in the mixture in equal mass proportions:

$$\frac{X_i}{X_j} = 1, \text{ then } \frac{I_i}{I_j} = \frac{k_i}{k_j} = \text{constant}$$

As the component j , any suitable reference material can be chosen, for example corundum, in which case $k_j = k_c = 1$. Therefore the reference intensity of the component i is given as:

$$k_i = \left\{ \frac{I_i}{I_c} \right\}_{50/50}$$

where the subscript c denotes corundum.

In the present work corundum could not be used as a reference material because its 3,48 Å peak overlaps with the strong second order basal reflection of kaolinite at 3,57 Å. Therefore fluorite was used as reference material, or internal standard, although its mass absorption coefficient was rather unfavourable for copper K α -radiation in a predominantly coal and clay matrix and corrections had to be carried out for a minor pyrite peak overlapping with the fluorite peak at 3,15 Å.

Although Chung (op. cit.) showed that the reference intensity could be determined from a single mixture, it was preferred to make up at least five mixtures and to use the value of the slope of the calibration line for the reference intensity value.

As a working equation, the following relationship from Chung (op. cit.) was used:

$$X_i = \frac{X_f \cdot I_i}{k_i \cdot I_f}$$

where X_f and I_f are mass proportion and diffraction peak intensity of the internal standard fluorite, and I_i and k_i are diffraction peak intensity and reference intensity of the substance sought.

Because the height of a diffraction peak is also dependent on the crystallinity of the substance being analysed (Klug and Alexander, 1974, p.545), the area under a peak on a chart recording, or the integrated counts over the peak give a better measure of its intensity. All peak intensities in the present work were obtained by stepscanning (Klug and Alexander, op. cit., p.406) and represent integrated counts. X-ray diffraction measurement conditions are discussed in the relevant Sections: VII for orientated aggregates and VIII for unorientated samples.

Due to the strong influence of particle size on primary extinction, particle absorption and preferred orientation (Klug and Alexander, 1974, pp.541 - 4) which affect quantitative X-ray diffraction results, sample preparation had to be standardised. Because the minerals occurring in coal vary in grindability it was not possible to reduce them all to the optimum 5 μm particle diameter (Klug and Alexander, loc. cit.) simultaneously. When the quartz and pyrite components were milled to 5 μm , diffractograms of the coal samples showed that the softer minerals like fluorite (used as internal standard), calcite and kaolinite had undergone appreciable peak broadening due to the excessive milling.

Thus, as standard practice, the samples were milled for a fixed period of time resulting in 100 per cent minus 25 μm particles (seen microscopically) in which only negligible peak broadening of the softer minerals was observed. The diffractometer specimen holder was also rotated in order to reduce intensity fluctuations and allow larger crystallites to be used (Klug and Alexander, op. cit., p.368).

Counting statistics (Klug and Alexander, 1974, p.540) were optimized as far as possible in relation to the time required - about 40 minutes for the measurement of eight diffraction peaks in a quantitative determination at a moderate X-ray tube setting of 40 kV and 30 mA. For the internal standard fluorite, at 10 per cent concentration, more than 100 thousand counts were integrated (net intensity) with a theoretical standard error of intensity which was probably far less than 1 per cent. Since specific minerals in the coal products were rarely present in such high concentration and the coal itself resulted in high background counts, theoretical counting statistics on the minerals were less favourable. However, duplicate determinations on the coal samples, in which new diffractometer sample mounts were made up for the duplicates, indicate a standard error of $\pm 0,28$ mass per cent for kaolinite in the concentration range of 1 to 12 per cent and for quartz varying from 0,3 to 8 per cent in concentration, the standard error was slightly more favourable at $\pm 0,22$ mass per cent (Table VI).

Detection limits under the X-ray diffraction conditions used appear to be about 0,02 mass per cent for the strongly diffracting quartz, pyrite and carbonates, while kaolinite at a concentration of 0,2 mass per cent in coal could probably still be detected. Although the detection limit for weakly diffracting illite in unorientated diffractometer mounts probably varies from 0,2 to 1 per cent concentration and is possibly even poorer, depending on its degree of crystallinity, the quantitative X-ray diffraction method is clearly superior to the DTA method where detection limits of 0,5 - 1 per cent (pyrite); 1 - 2 per cent (calcite and

dolomite); 2,5 - 5 per cent (siderite and kaolinite); 15 - 20 per cent (quartz) and 30 per cent for illite (Warne, 1965) were established. Detection limits are strongly matrix dependent for the infra-red method (Estep et al., 1968) and pyrite, even at a concentration as high as 20 per cent cannot be detected in the presence of 30 per cent of kaolinite in mineral matter samples prepared from coal by radio-frequency ashing.

VII. THE CLAY MINERAL COMPOSITION OF COAL, USING ORIENTATED
AGGREGATES

Since the clay minerals form a high percentage of the inorganic material in coal and have specific properties related to their grain size, crystal structure and chemical activity, they are of great technological importance in the mining, beneficiation and utilization of coal. The clay minerals may also act as geological markers indicating paleobasin conditions and may be useful in correlating coal seams.

In the mining of coal, "roof" rocks containing expandable clays will tend to be unstable, thus increasing mining costs and strongly influencing safety conditions underground. Coals containing expandable clays may tend to undergo fretting or "slacking" during storage and shipment as they swell in the presence of moisture. According to Grim (1962, p.248), kaolinite swells 5 - 60 per cent, illite 15 - 120 per cent, calcium-montmorillonite 45 - 145 per cent and sodium-montmorillonite 1400 - 1600 per cent by volume.

In the upgrading of coal by various beneficiation procedures the clay minerals, due to their small grain-size, are the last to be liberated by milling. Their relative proportions and mode of dispersion may set the limit to which coal can be washed economically. According to Grim (1962, p.12) kaolinite crystallites vary from 0,3 to 4 μm in diameter and from 0,05 to 2 μm in thickness, and montmorillonite crystallites vary from 0,015 to 0,15 μm in diameter and may be 0,0015 μm thick when dispersed. The crystallite size of illite depends on its degree of crystallinity and varies within the ranges given above.

Sliming problems in dense medium separators may be caused by the dispersion of clay aggregates into particles of crystallite size when they come into contact with water. The swelling clays are particularly bad in this respect, since they may break down into particles of nanometer dimensions.

The dispersability of clay may also be a useful attribute. The stability index of Newcastle coke (NSW, Australia) was improved by the addition of half a per cent of bentonite (Brown et al., 1965) which had the same effect as inorganic additives such as iron oxide.

The thermal behaviour of the clays influences the pyrolysis of coal, for example in gasification plants and in coal-fired boilers. Pure kaolinite is extremely refractory with a fusion temperature of 1650 - 1775^oC (Grim, 1962, p.121) whereas the other clays melt between 1000 - 1500^oC depending on their chemical composition and thus influence the formation of clinker in combustion appliances.

In oil-from-coal processes by direct hydrogenation, the clay minerals may influence the results by acting as catalysts. Grim (1962, p.30) gives the chemical activity of the clay minerals as measured by their ion-exchange capacity, as follows: kaolinite 3 - 15, illite 10 - 40 and montmorillonite 80 - 150 milli-equivalents per 100 g.

A. Sample preparation and layer thickness

Five gram charges of minus 60 mesh (250 μ m) coal were ashed at 350^oC in a muffle furnace following the procedure of Brown et al. (1959). By regulating the circulation of air through the furnace, visible ignition of the coal samples was prevented. The ashing required about a week per sample.

Due to their poor crystallinity, orientated aggregates which enhance the intensity of the 00 ℓ diffraction peaks of the clays are usually used for X-ray diffractometer work. However, in any sedimentation procedure sample segregation is likely to occur (Gibbs, 1971). Some preliminary tests were thus carried out using an artificial 1:1 mixture by mass of kaolinite and illite in order to determine optimum aggregate thickness.

Figure 3 shows the results of varying the amount of material sedimented and the calculated layer thickness using a density of 2,58 g per ml for the mixture. The total number of counts on adding the net integrated intensities of illite and kaolinite increases as the number of crystallites on the slides increase (top curve), to a layer thickness of about 16 μm (400 mg sedimented). However, at a layer thickness of about 32 μm the total number of counts is reduced, probably as a result of the X-ray diffractometer focussing geometry being brought out of alignment since spacers between the glass slides and the diffractometer sample clamp were not used.

The ratio of the intensity of illite to kaolinite diffraction peaks also varies according to the thickness of the sedimented layer (Figure 3, bottom curve). It reaches a maximum between 4 and 8 μm layer thickness and then the intensity ratio diminishes as the layer becomes thicker, probably due to sample segregation which results in the more dense illite crystallites being progressively "buried" beneath kaolinite crystallites out of reach of the direct X-ray beam.

On the basis of these results it was decided to use 200 mg for the sedimentations (corresponding to a calculated layer thickness of about 8 μm) which results in a layer thickness well within the 12 μm X-ray penetration depth at $12^\circ 2\theta$ given by Gibbs (1971) for copper $K\alpha$ -radiation.

B. X-ray diffraction and analytical procedure

Copper $K\alpha$ -radiation was used at 40 kV and 30 mA with 1° slits and a graphite monochromator in the diffracted beam to eliminate $K\beta$ and suppress fluorescence radiation. Peak intensities were integrated from stepscans (0,04 $^\circ 2\theta$ interval for kaolinite and 0,1 $^\circ 2\theta$ for illite and expandable clays). Background corrections were carried out by averaging counts on the small and large angle sides of the peaks.

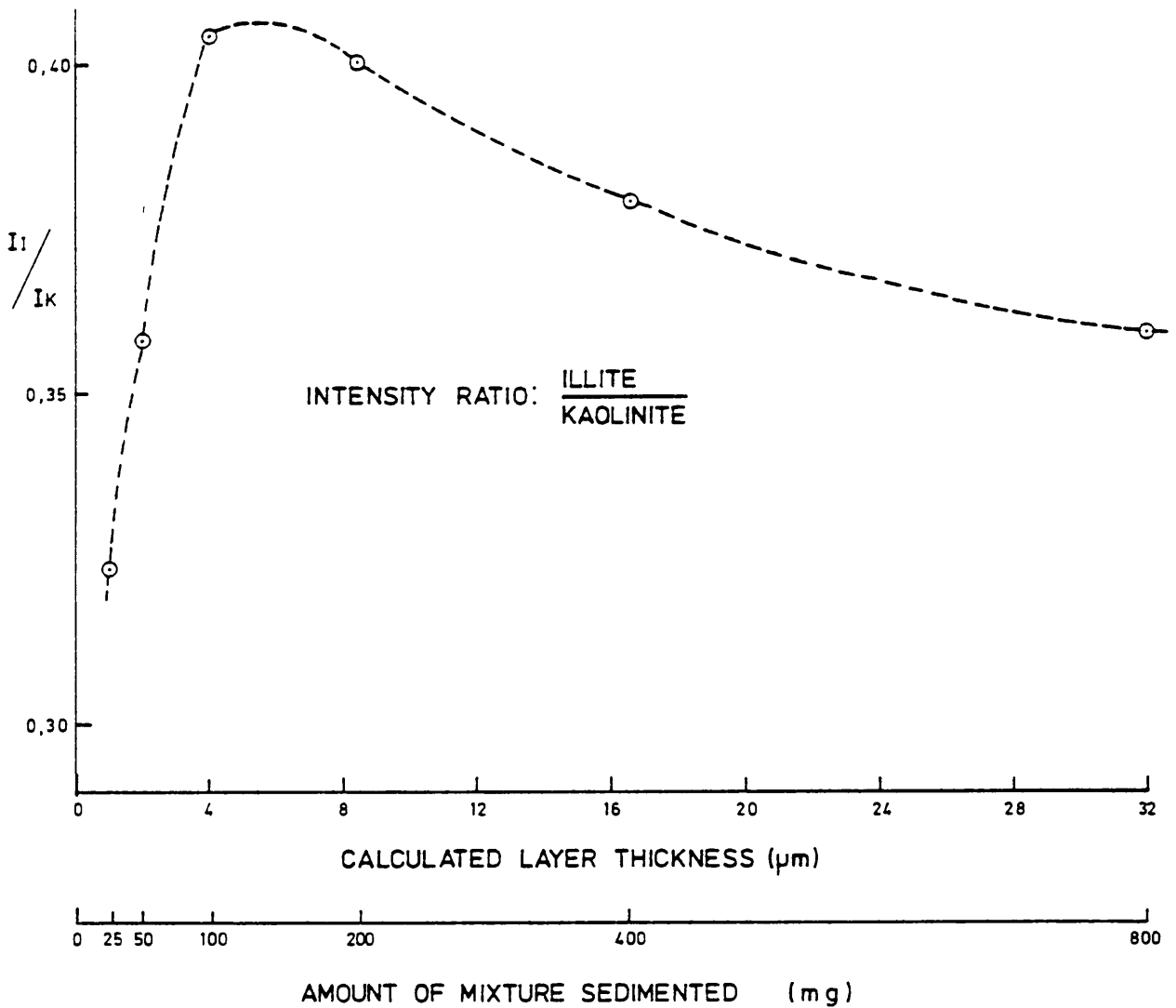
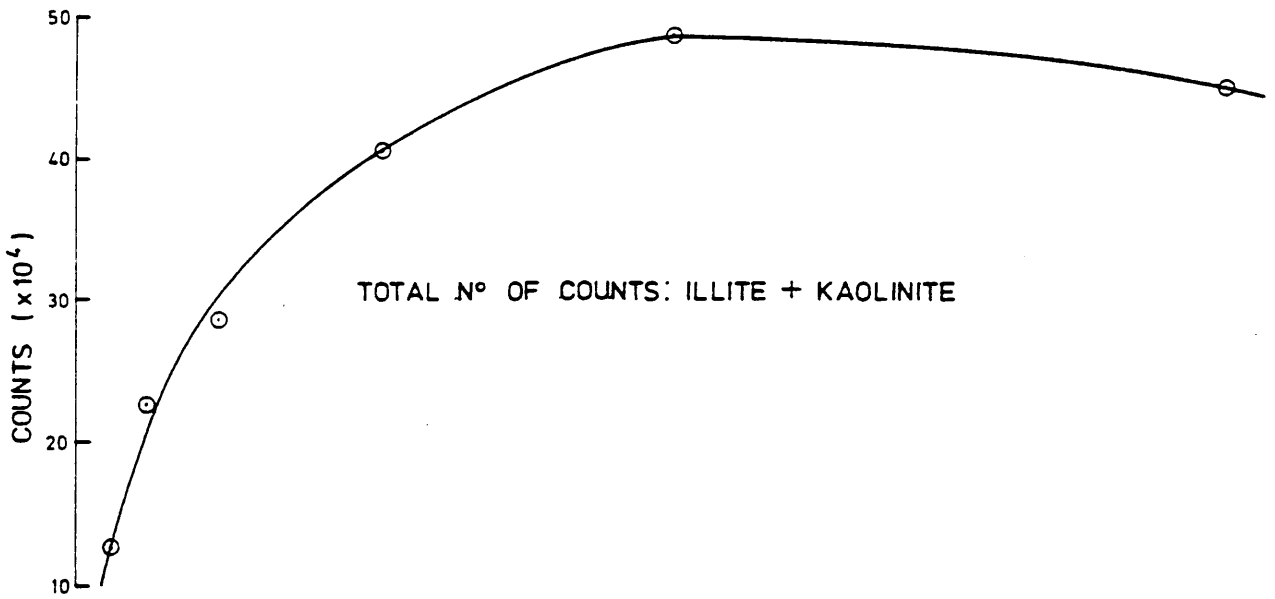


FIGURE 3 EFFECT OF THICKNESS OF THE SEDIMENTED LAYER OF A MIXTURE OF ILLITE & KAOLINITE (MASS RATIO 1:1) ON THE TOTAL NUMBER OF COUNTS AND THE INTENSITY RATIO ILLITE: KAOLINITE

The analytical procedure was as follows:

1. 200 mg of low temperature (350°C) ash was dispersed in 40 ml of distilled water by milling for 10 minutes in a McCrone mill.
2. The resulting slurry was poured over a 50 by 50 mm glass slide on the bottom of a petri-dish of 50 ml capacity.
3. The water was evaporated in a drying oven (105°C) and following Gluskoter (1967), the orientated aggregate was then heated at 350°C for 1 hour and allowed to cool to room temperature in a desiccator.
4. X-ray diffractometer scans were carried out from 2 to 14 °2θ and the intensities of the 10 Å and 7 Å peaks were obtained.
5. The orientated aggregate was then placed in a desiccator containing ethylene glycol and left overnight, and the X-ray diffractometer work was repeated with only the intensities of the 10 Å and 7 Å peaks being measured on the glycolated slides.

Due to the heating, interlayer water had been expelled from the expandable clays and a diffraction peak at 10 - 12 Å represented illite plus expandable clays and any chlorite would be visible at the 14 Å position. The glycolation caused the expandable clays to alter their basal spacings to values of 17 Å (montmorillonite), 11 to 16 Å (mixed-layer illite-montmorillonite) or 27 and 13,6 Å (first and second order basal reflections of regularly interstratified illite-montmorillonite). Illite by definition has no expanding properties and any diffraction peak at 10 Å was taken to represent this mineral. Where mixed-layer illite-montmorillonite was present overlapping on the illite peak, the rather arbitrary, but reproducible procedure was followed of integrating intensities from 7,5 to 9,5 °2θ for the illite component, background measurements being carried out at half degree intervals to either side of the peak.

For the quantitative work a modification of the method of Griffin (1971) was used, where the constants in his equations were determined experimentally on Lewistown kaolinite (API No. 17), Fithian illite from Illinois (API No. 35) and a Wyoming bentonite (API No. 26).

Reference intensities (Section VI and Chung, 1974) were determined relative to Lewistown kaolinite and the calibrations used are given in Figure 4. The data points for illite determined both on heated and glycolated slides, approximate to a straight line, but the points for montmorillonite (heated slides) are more scattered. The reason for this is unknown but it may perhaps be ascribed to the spontaneous rehydration of montmorillonite in the sample during the X-ray determination.

An example of the calculations, with intensity measurements in arbitrary units and where I = illite, Ex = expandable clays and K = kaolinite, is as follows:

Dumbe coking product

Heated slide:

Intensity of 10 - 12 Å peak = 321,1 = I + Ex

Intensity of 7 Å peak = 761,4 = K

Intensity of I + Ex relative to K = $\frac{321,1}{761,4} = 0,4217$

Glycolated slide:

Intensity of 10 Å peak = 145,6 = I

Intensity of 7 Å peak = 753,4 = K

Intensity of I relative to K = $\frac{145,6}{753,4} = 0,1933$

Intensity of Ex relative to K = $0,4217 - 0,1933 = 0,2284$

∴ Intensity ratio K : I : Ex = 1 : 0,1933 : 0,2284

Converting intensity ratios to mass ratios, the intensity ratios are divided by the reference intensities: $I/K = 0,357$ and $Ex/K = 0,628$.

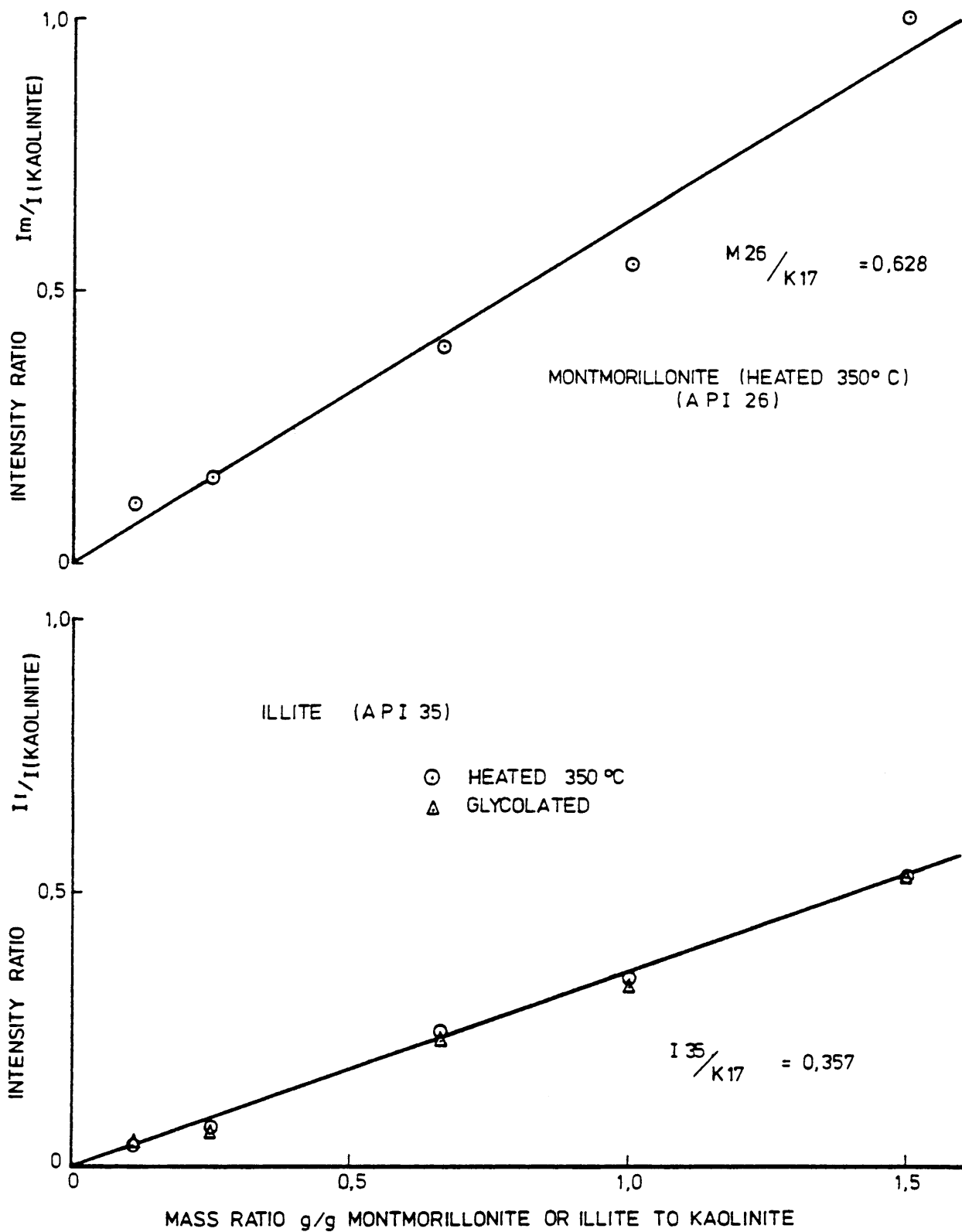


FIGURE 4 CALIBRATION LINES FOR ILLITE AND EXPANDABLE CLAYS RELATIVE TO KAOLINITE (A P I 17).

∴ Mass ratio K : I : Ex = 1 : 0,542 : 0,364

Recalculating to 100%: K = 52,5

I = 28,4

Ex = 19,1

C. Results of clay determinations

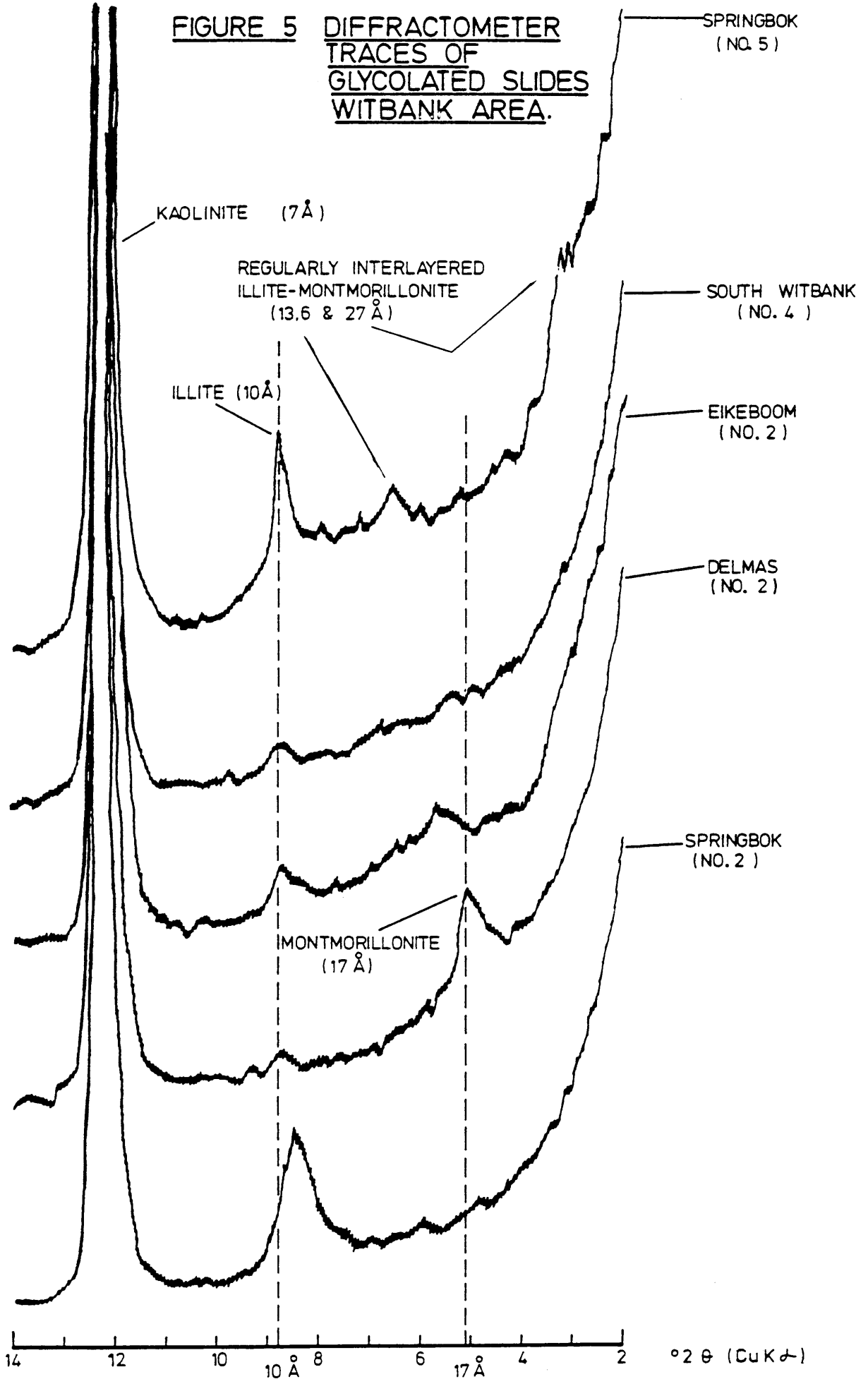
(a) Diffractograms

Figures 5 to 9 are diffractometer traces of glycolated slides of the low temperature (350°C) ash of some of the coal products. Perhaps not unexpectedly, the clay mineral suite is characteristic of a particular coal seam in a particular area.

In Figure 5 a diffractometer trace for a Witbank No. 2 Seam product (Springbok No. 2) is given: the rather broad peak at $8,5^{\circ}2\theta$ ($10,4 \text{ \AA}$) represents illite since the proportion of montmorillonite in the mixed-layers is too low to cause an appreciable peak shift, i.e. at least to $7^{\circ}2\theta$ (12 \AA) on glycolation (Bradley and Grim, 1961, p.225). This diffractogram is characteristic for the other collieries in this area (Albion and New Clydesdale), but to the western and eastern extremities of the coalfield the clay minerals change, as is shown by the Delmas product containing clear 17 \AA montmorillonite with hardly any illite, and the Eikeboom product containing possibly mixed-layer illite-montmorillonite at about 16 \AA also given in Figure 5.

The Witbank No. 4 Seam is represented by two products: Anglo Power (Kriel) and South Witbank. Their diffractograms are very similar and rather different from the Witbank No. 2 Seam. The South Witbank product is shown in Figure 5: the sample is highly kaolinitic with only traces of illite and expandable clays.

The Witbank No. 5 Seam products represent blend coking coals. Well crystallized 10 \AA material occurs together with regular interstratified illite-montmorillonite,



with first order and second order basal reflections at 27 Å and 13,6 Å in the four samples studied. The diffractogram for the Springbok No. 5 Seam product is shown in Figure 5.

Some Ermelo products resemble the Witbank No. 5 Seam containing illite and regular interstratified illite-montmorillonite, for example the Spitzkop product (Figure 6), but clay from the slightly lower rank coal (Usutu sample) contained few expandable clays.

The clay assemblage from the South Rand and OFS products was very similar representing the highest kaolinite compositions noted of coals in the survey. The Sigma product (Figure 6) contained a little illite and poorly defined expandables, but the product from Vierfontein Colliery situated between Klerksdorp and Bothaville to the west, contained a clear montmorillonite peak at about 17 Å (Figure 6).

A feature of the Natal coals is the large variation in rank over short distances which is caused by the many dolerite intrusions. This is also reflected by their clay minerals in which the high volatile coals tend to contain kaolinite as the principal clay mineral, whereas the anthracites are highly illitic.

Diffractograms of glycolated orientated aggregates of products from the Klip River coalfield are shown in Figure 7. The products from Kilbarchan Colliery and Newcastle-Platberg, which are medium volatile coals contained a relatively low proportion of kaolinite and rather high proportion of illite and mixed-layer clays. The Durban Navigation sample, a coking coal product, contained regular interlayered illite-montmorillonite which is also always present in the Witbank No. 5 Seam coking products.

FIGURE 6 DIFFRACTOMETER TRACES OF
GLYCOLATED SLIDES
ERMELO AND O.F.S.

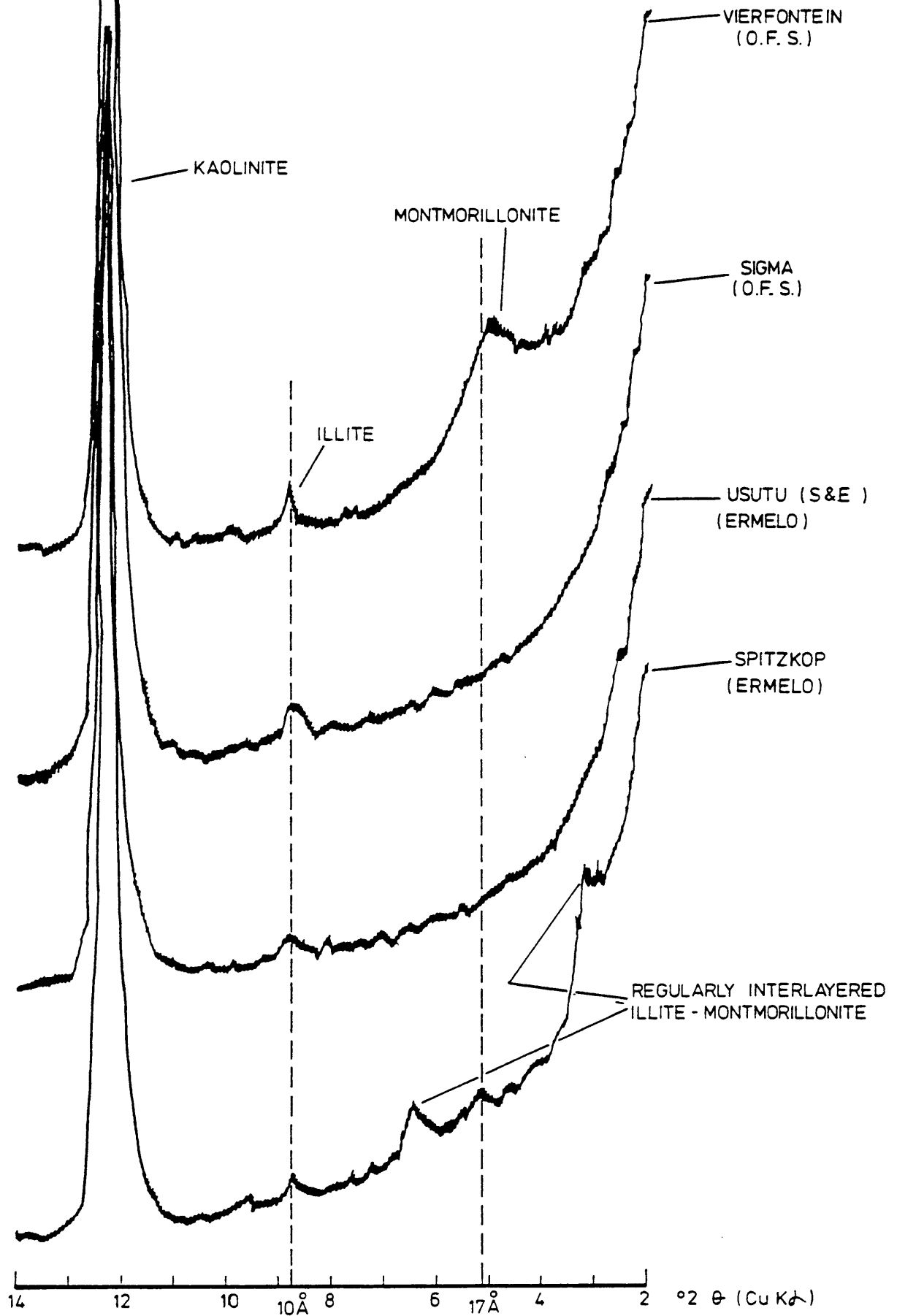
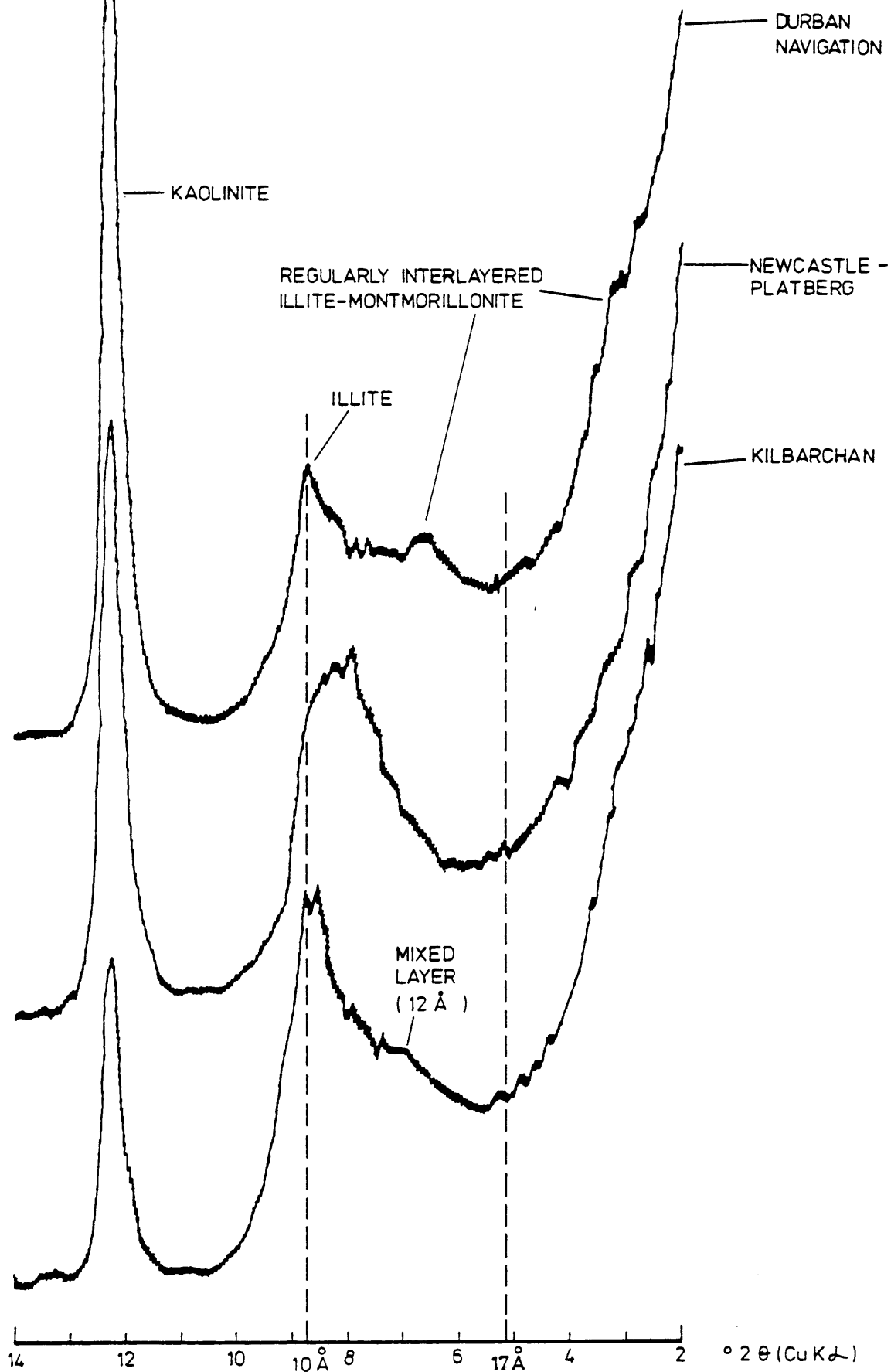


FIGURE 7 DIFFRACTOMETER TRACES OF
GLYCOLATED SLIDES
KLIP RIVER AREA.



In the Utrecht coalfield (Figure 8) the high volatile Zimbutu product contained montmorillonite and regularly interlayered illite-montmorillonite, in addition to traces of illite, but in the low volatile Balgray coal the proportion of kaolinite was low, relatively more illite was present, and a diffraction peak at 14 \AA represented chlorite. This was confirmed by heating the slide at 550°C : kaolinite was destroyed and the second order basal reflection of chlorite, also at 7 \AA became visible.

In the Paulpietersburg-Vryheid coalfield the association of relatively high contents of kaolinite and expandable clays with high volatile coal and high contents of illite with anthracites is well shown. Figure 9 shows the coking coal product from Dumbe (high volatile coal) and the clay assemblage from Brockwell Anthracite Colliery, consisting mainly of illite.

(b) Quantitative clay determinations

Results of quantitative clay determinations using the X-ray diffraction and sample preparation methods discussed in Subsections A and B are given in Table III, together with the estimated moisture and dry ash-free volatile matter content of the coal samples. The data given for average moisture and dry ash-free volatile matter are of similar products, sampled during the same year (FRI: 1976, 1977).

Dry ash-free carbon contents (from the ultimate analysis) which were determined on similar products sampled during 1967 are also given (Savage, 1968a). Where no such product was sampled or where a large difference in volatile matter content shows that coal of different character is being mined at present, the dry ash-free carbon content was estimated from a Seyler-chart modified by M.C. van Vuuren (Moodie, 1975, facing p.17).

FIGURE 8 DIFFRACTOMETER TRACES OF
GLYCOLATED SLIDES
UTRECHT AREA.

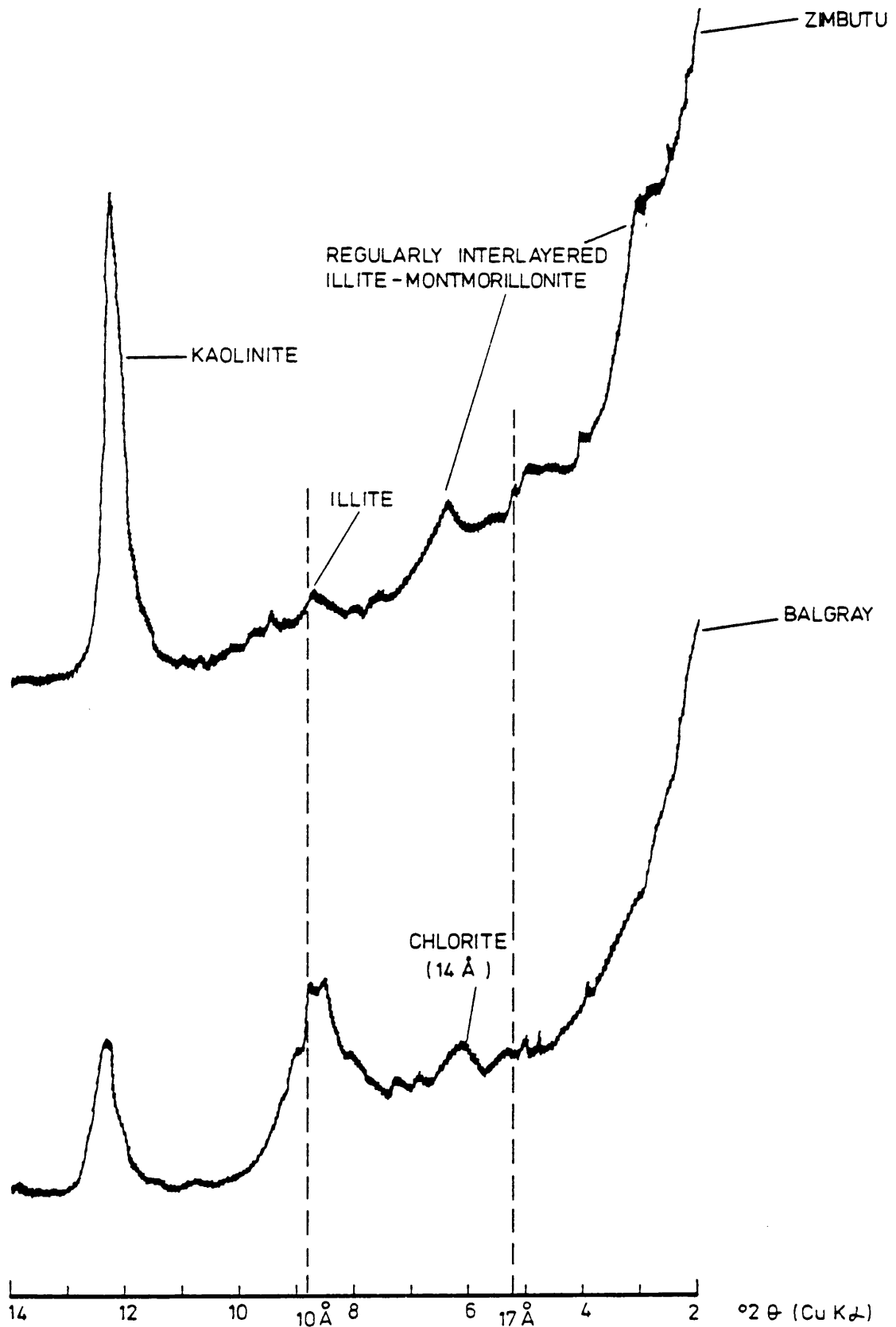


FIGURE 9 DIFFRACTOMETER TRACES OF
GLYCOLATED SLIDES
PAULPIETERSBURG AREA.

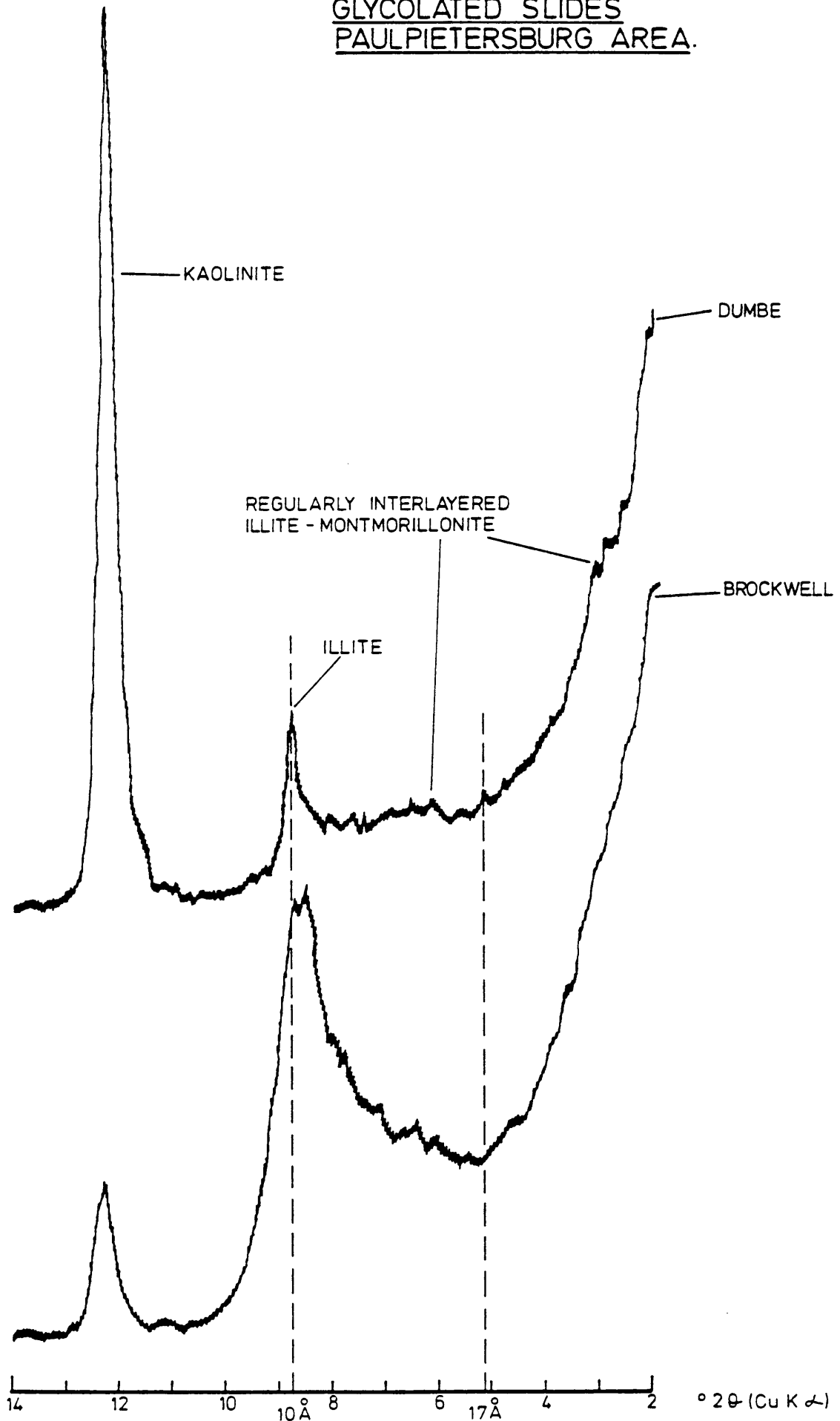


TABLE III
RELATIONSHIP BETWEEN CLAY MINERAL COMPOSITION AND ESTIMATED RANK
OF THE COAL EVALUATED FROM THE DATA OF EQUIVALENT PRODUCTION SAMPLES

Colliery	Seam or Area	H ₂ O ⁽¹⁾ in coal %	% in coal (dry ash-free)		Composition of clay % ⁽³⁾			Nature of ⁽⁴⁾ exp. clays			Chlorite 14 Å
			Volatile Matter ⁽²⁾	Carbon ⁽²⁾	Kaolinite	Illite	Expandable clays	17 Å	27 & 13,6 Å	12 - 16 Å	
Eikeboom	Witbank No. 2	3,7	33,0	81,9	87,9	3,6	8,5	-	-	P	-
Springbok	Witbank No. 2	2,4	31,6	84,4	63,3	35,8	0,9	-	-	-	-
New Clydesdale	Witbank No. 2	2,5	32,1	83,6	64,2	29,1	6,7	-	-	P	-
Albion	Witbank No. 2	2,7	31,2	84,0	55,4	43,6	1,0	-	-	-	-
Delmas	Witbank No. 2	4,2	32,9	81,6	88,5	0,7	10,8	P	-	-	-
South Witbank	Witbank No. 4	3,4	34,2	82,3	90,6	5,1	4,3	-	-	?	-
Anglo Power (Kriel)	Witbank No. 4	4,7	31,6	80,6	92,5	2,7	4,8	-	-	?	-
Blesbok	Witbank No. 5	3,2	36,8	83,0	52,4	22,4	25,2	-	P	-	-
Springbok	Witbank No. 5	2,6	38,2	82,9	55,4	14,7	29,9	-	P	-	-
Greenside	Witbank No. 5	2,7	36,9	82,1	76,6	9,7	13,7	-	P	-	-
Navigation	Witbank No. 5	2,4	36,4	82,9	65,0	15,3	19,7	-	P	-	-
Union	Breyten-Ermelo	2,7	35,5	81,7	78,9	3,5	17,6	-	P	-	-
Sptizkop	Breyten-Ermelo	3,1	37,2	81,1	80,5	3,3	16,2	P	P	-	-
Usutu (S & E)	Breyten-Ermelo	5,0	32,9	80,1	93,2	6,7	0,1	-	-	-	-
Grootvlei	South Rand & OFS	5,6	30,5	79,8	93,7	5,7	0,6	-	-	-	-
Cornelia Bertha I	South Rand & OFS	7,0	33,0	77,8	98,2	1,8	0,0	-	-	-	-
Sigma	South Rand & OFS	6,0	32,9	77,9	90,2	5,1	4,7	-	-	?	-
Coalbrook No. 2	South Rand & OFS	6,0	31,8	78,9	98,9	0,4	0,7	-	-	-	-
Vierfontein	South Rand & OFS	6,7	34,1	78,5	86,6	8,8	4,6	P	-	-	-
Kilbarchan	Klip River, Natal	1,9	24,2	86,2	9,5	56,1	34,4	-	-	P	-
Ballengeich	Klip River, Natal	2,1	28,4	85,4	28,2	38,5	33,3	-	P	-	-
Durban Navigation	Klip River, Natal	1,5	34,6	86,3	28,0	37,4	34,6	-	P	-	-
Natal Navigation	Klip River, Natal	1,2	24,7	88,0	23,3	44,8	31,9	-	-	P	-
Indumeni	Klip River, Natal	1,2	27,3	88,0	13,5	59,1	27,4	-	P	P	-
Newcastle-Platberg	Klip River, Natal	1,4	22,7	87,8	20,6	53,6	25,8	-	-	?	-
Balgray	Utrecht	2,0	7,5	89,7	12,5	74,6	12,9	P	-	-	P
Utrecht	Utrecht	1,7	12,4	88,9	13,5	58,2	28,3	P	P	-	P
Umgala	Utrecht	2,3	27,0	85,3	21,7	20,1	58,2	P	P	-	-
Zimbutu	Utrecht	2,8	31,9	83,0	44,9	10,8	44,3	P	P	-	-
Dumbe	Paulpietersburg-Vryh.	2,1	38,9	84,5	52,5	28,4	19,1	-	P	-	-
Brockwell Anthracite	Paulpietersburg-Vryh.	2,6	9,5	90,4	3,9	96,1	0,0	-	-	-	-
Tendega	Paulpietersburg-Vryh.	1,5	32,3	85,6	50,6	24,9	24,5	-	-	P	-
Hlobane	Paulpietersburg-Vryh.	1,4	25,6	88,6	32,8	35,6	31,6	-	-	P	-
Vryheid Coronation	Paulpietersburg-Vryh.	1,2	25,1	88,5	24,6	67,5	7,9	-	-	?	-
Aloe Anthracite	Paulpietersburg-Vryh.	1,9	7,0	91,3	2,2	97,8	0,0	-	-	-	P

NOTES: (1) Average moisture and dry ash-free volatile matter for equivalent product (FRI: 1976, 1977).

(2) Dry ash-free carbon content of equivalent product (Savage, 1968a).

(3) Relative to Lewistown kaolinite (API 17), Fithian illite (API 35) and Wyoming bentonite (API 26).

(4) Refers to basal spacing after glycolation: 17 Å = montmorillonite; 27 and 13,6 Å = regularly interlayered illite - montmorillonite; 12 - 16 Å mixed-layer clay; P = present.

(5) Estimated from Seyler chart (Moodie, 1975).

(6) Kubler index (width of 001 diffraction peak at half maximum height in mm where 10 mm = 1°2θ) of 8.

(7) Kubler index of 10.

In Figure 10 the clay mineral data of Table III are plotted together with the average data (Table IV). The fields occupied by coals from the Illinois basin (Rao and Gluskoter, 1973) and by Permian Australian coals (Ward, 1978) are also indicated.

D. Discussion of results

(a) Relationship between clay mineral composition and coal rank

From Tables III and IV there appears to be a relationship between the relative proportions of kaolinite, illite and expandable clays in the coal and its geographical location, as well as its probable rank. On average the clay mineral composition of Transvaal coals falls close to the composition field for Australian coals (Ward, 1978) but contains somewhat less expandable clays, whereas the average for Natal coals falls within the composition field for Illinois coals (Rao and Gluskoter, 1973). The overall average, marked 12 in Figure 10 falls outside both these composition fields.

The low rank OFS coals contain the highest average proportion of kaolinite (94 per cent). Coal products from the Ermelo area and the Witbank No. 4 Seam also contain high proportions of kaolinite (84 and 92 per cent, respectively).

In the Witbank No. 2 Seam where coal products from the extremities of the coalfield (Eikeboom and Delmas collieries) are of slightly lower rank (with an average of 4 per cent of moisture), they also contain a higher kaolinite content at 88 per cent compared with the 61 per cent kaolinite from the central part of the coalfield.

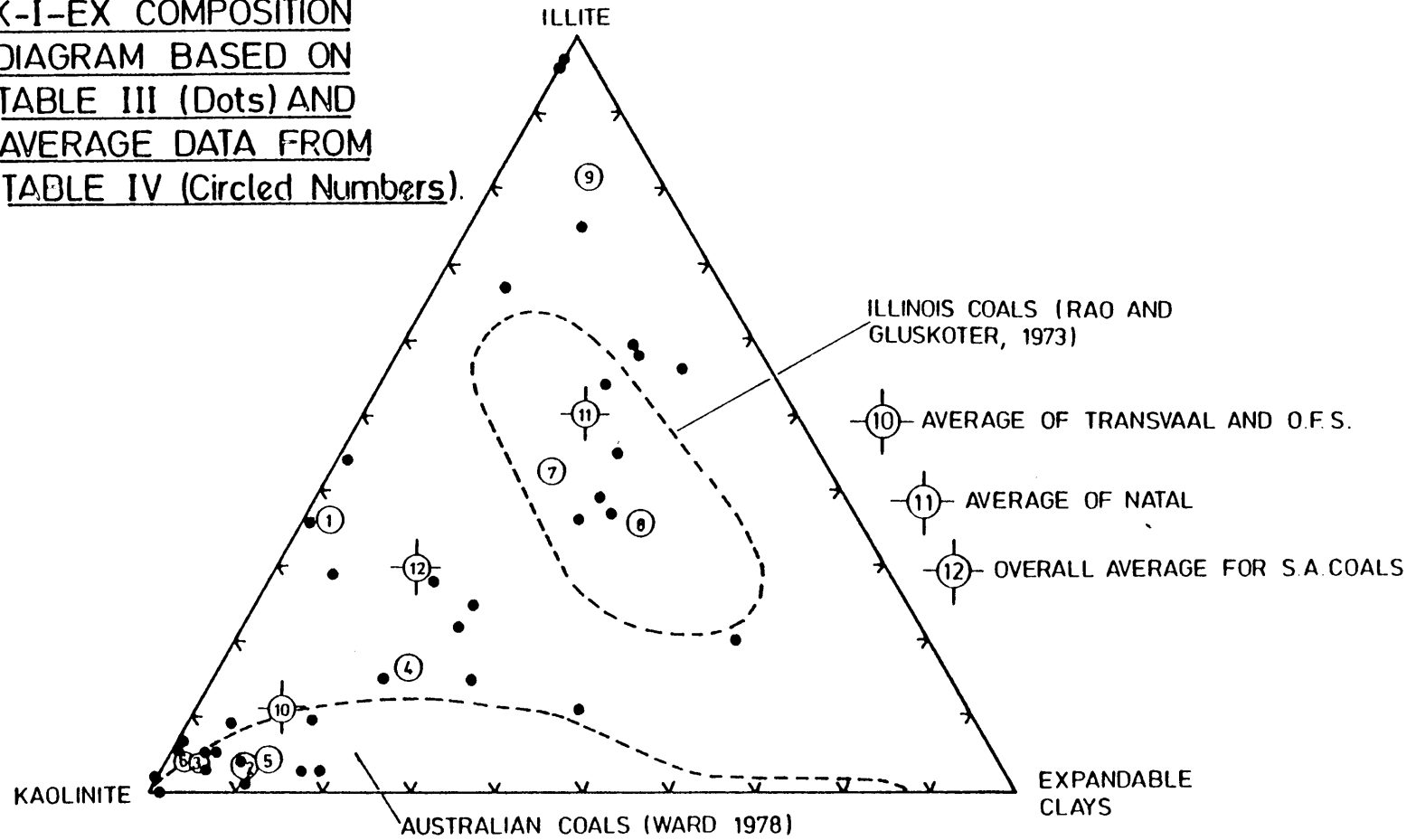
The association of relatively higher kaolinite contents with lower rank coal (and higher illite content with higher rank coal) is well demonstrated by the Natal coals,

TABLE IV

AVERAGE DATA FOR CLAY MINERAL COMPOSITION AND ESTIMATED COAL RANK (FROM TABLE III)

No. in Figure 10	Seam or Area	No. of products	H ₂ O %	Dry ash-free		% of clay		
				VM %	C %	Kaolinite	Illite	Exp. clays
1	Witbank No. 2 (Central)	3	2,5	31,6	84,0	61,0	36,2	2,8
2	Witbank No. 2 (East and West)	2	4,0	33,0	81,8	88,2	2,2	9,6
3	Witbank No. 4	2	4,0	32,9	81,4	91,6	3,9	4,5
4	Witbank No. 5 (Transvaal coking products)	4	2,7	37,1	82,7	62,4	15,5	22,1
5	Breyten-Ermelo	3	3,6	35,2	81,0	84,2	4,5	11,3
6	South Rand and OFS	5	6,3	32,5	78,6	93,5	4,4	2,1
7	Natal coking products	7	1,4	29,8	87,1	32,2	42,5	25,3
8	Natal bituminous (excluding coking)	5	2,1	26,8	85,5	25,0	35,8	39,2
9	Natal low volatile	4	2,0	9,1	90,1	8,0	81,7	10,3
10	Transvaal and OFS coals	19	4,0	33,8	81,3	79,5	11,5	9,0
11	Natal coals	16	1,8	23,7	87,4	23,9	50,2	25,9
12	Overall average for S.A. coal products	35	3,0	29,2	84,1	54,1	29,2	16,7

FIGURE 10 K-I-EX COMPOSITION
DIAGRAM BASED ON
TABLE III (Dots) AND
AVERAGE DATA FROM
TABLE IV (Circled Numbers).



where rank variations occur over short distances. Natal bituminous coals contain an average of 25 per cent of kaolinite, compared with an average of 8 per cent for the anthracitic and lean coals.

A feature of the Paulpietersburg-Vryheid anthracites (Brockwell and Aloe products) is that the clay mineral suite consists almost entirely of illite. The crystallinity of the illite as measured by their Kubler indexes (width of the 001 diffraction peak measured at half maximum height in mm where $1^{\circ}2\theta = 10$ mm) of 8 and 10 shows that the "anchimetamorphic zone" (Dunoyer de Segonzac, 1970; Kisch, 1974) has not yet been reached (Kubler index less than 7,5) and that the South African anthracites represent lean coals in the late diagenetic zone of metamorphism (zeolite facies). The crystallinity results do not differ significantly from the findings of Soekor (Rowsell and De Swart, 1976).

The proportion of expandable clays in the coal product samples do not show clear-cut relationships, except that they tend to be absent from some high rank coals (dry ash-free carbon content greater than 91 per cent). There was an uncertainty due to the analytical procedure, in which the different species of expandable clays (montmorillonite, regularly interlayered illite-montmorillonite and mixed-layer illite-montmorillonite) were not differentiated, but determined relative to Wyoming bentonite. However, the coking coals always contain a relatively high percentage of expandable clays: average of 22 per cent for Transvaal (Witbank No. 5 Seam products) and 25 per cent for the Natal coking coals.

Some authors (Gluskoter, 1967; Rao and Gluskoter, 1973; and Ward, 1977) preferred to exclude kaolinite from their clay ratios and used parameters such as illite divided by the sum of illite and expandable clays, because much of the kaolinite seen on scanning electron photomicro-

graphs was relatively coarse grained, well crystallized and present in cleats, and was therefore obviously late epigenetic in origin. However, in the present study it was decided to consider kaolinite as an integral part of the clay mineral suite. Also, the practice of sedimenting a minus 2 μm fraction was discarded, because it was felt that the total clay composition might be more meaningful than the composition of a minus 2 μm fraction, which would be dependent on the disaggregation of clay aggregates.

In Figure 11 the mass proportions of kaolinite in the clay are plotted against the estimated dry ash-free carbon content as a parameter of coal rank. There is a good negative correlation between the kaolinite content and the estimated coal rank with a regression coefficient of -8,08 and correlation coefficient $r = 0,94$. A graph (not shown) of per cent illite plotted against the estimated coal rank showed the inverse trend with the proportion of illite increasing as the estimated coal rank increased (regression coefficient 6,7; $r = 0,91$). No clear correlation was apparent when the percentage of expandable clays or other ratios using expandables as a parameter, were plotted against coal rank.

In Figure 12 generalized iso-rank lines are shown, based on the estimated dry ash-free carbon values and the clay mineral compositions of the thirty-five coal products (Table III). Obviously when more data become available, the iso-rank lines may have to be amended. However, for ordinary production samples or coal products Figure 12 can be used to estimate the probable range in clay mineral composition, when the rank of the coal - expressed as percentage dry ash-free carbon - is known.

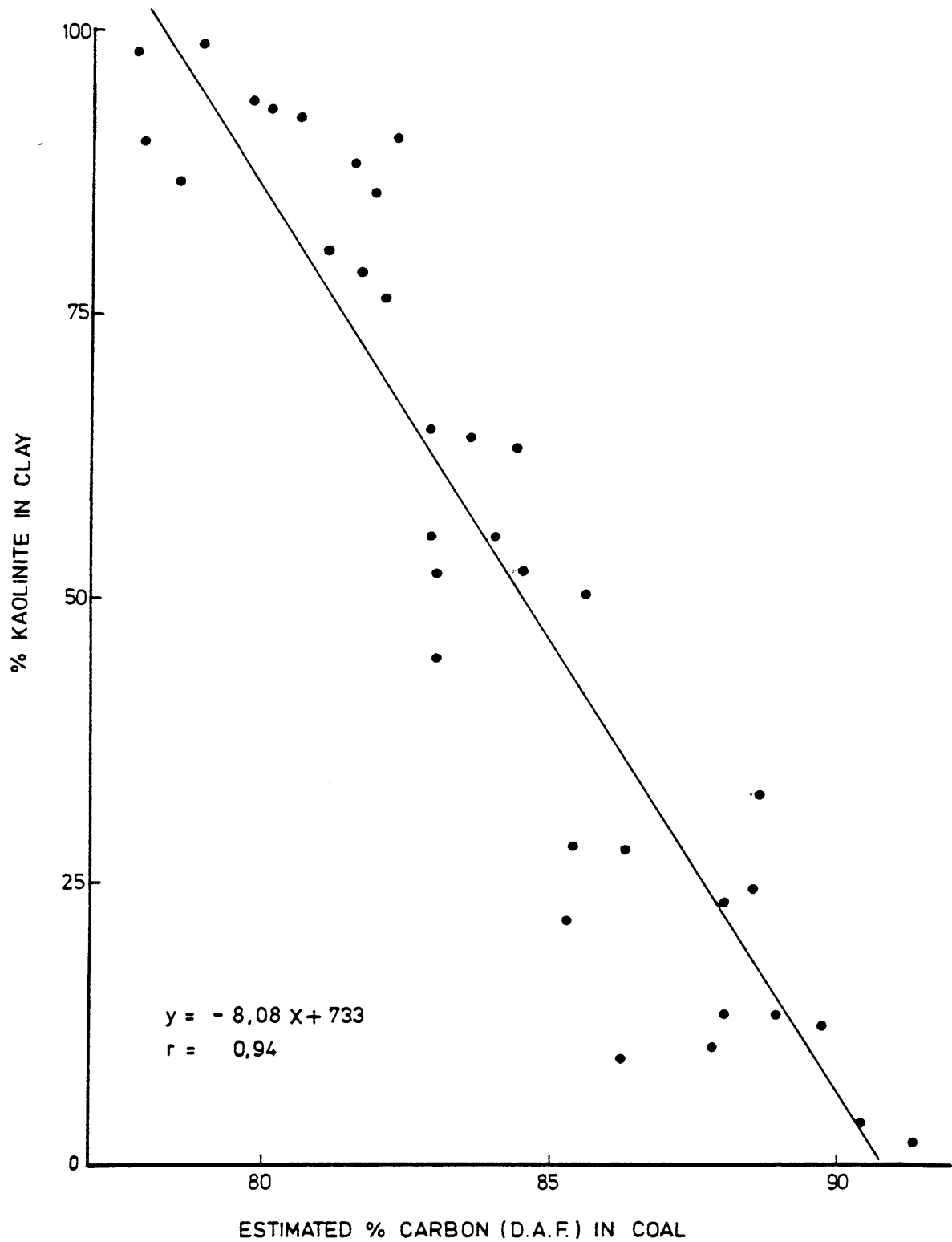
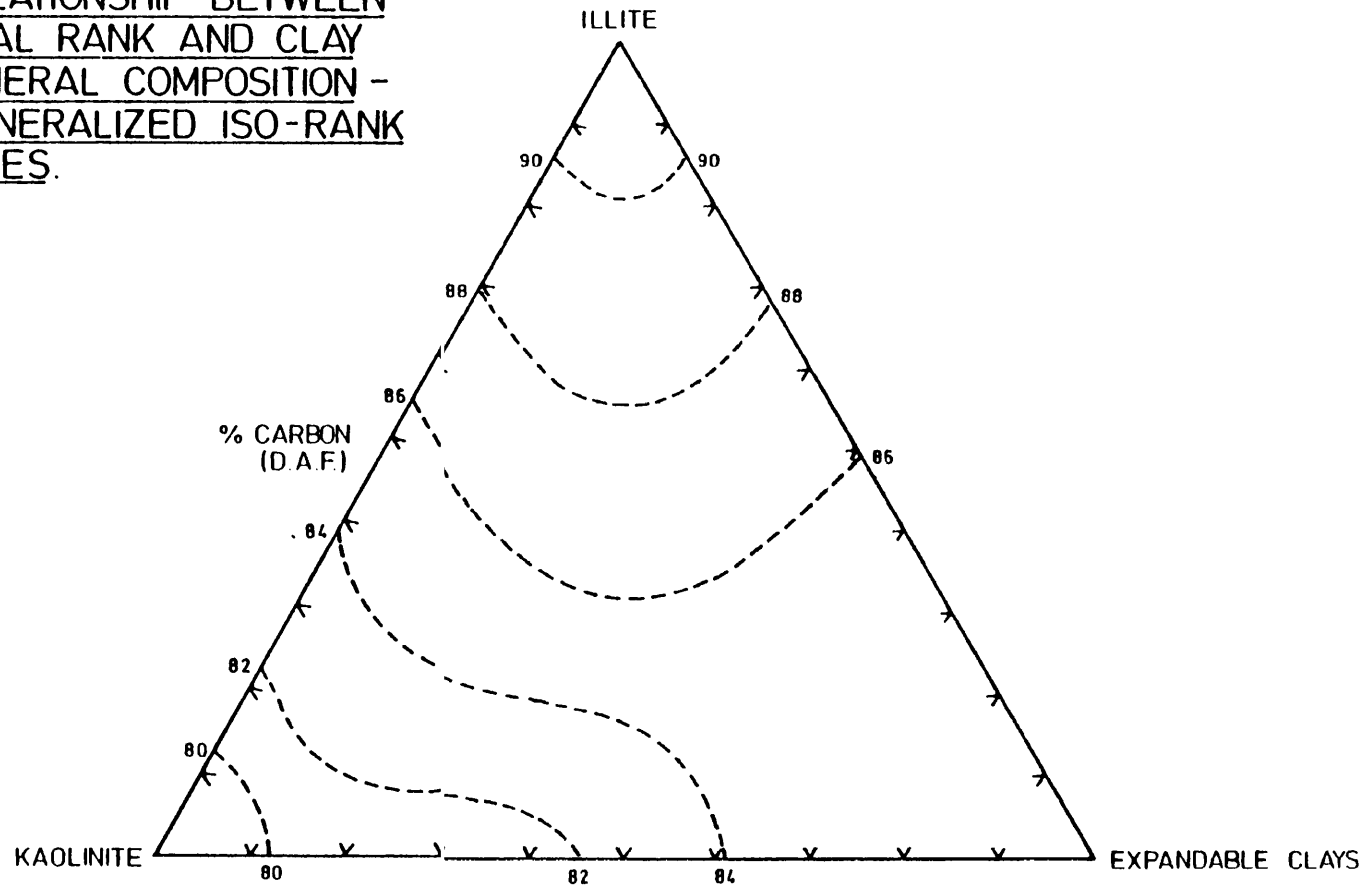


FIGURE 11 RELATIONSHIP BETWEEN PROPORTION OF KAOLINITE IN CLAY AND PROBABLE RANK OF COAL SAMPLES.

FIGURE 12 RELATIONSHIP BETWEEN COAL RANK AND CLAY MINERAL COMPOSITION - GENERALIZED ISO-RANK LINES.



(b) Relationship between clay mineral composition and coal type and quality

On account of the different physical, morphometric and grain-size characteristics of the clays - for example the diameter of kaolinite crystallites varies from 0,3 to 4 μm which is ten times more coarse-grained than illite and a hundred times more coarse-grained than smectite crystallites (Grim, 1968, pp.171 - 7) - it is to be expected that coal type and quality will also influence the relative proportions of kaolinite, illite and expandable clays associated with the coal.

In Table V correlation coefficients and regression constants are given for the plot of clay mineral composition and total clay in coal determined by X-ray diffraction versus the percentage of coal macerals and reflectance of vitrinite determined microscopically, from unpublished data on file of 16 coal samples (Gray, 1979). Witbank No. 5 and No. 2 Seams, OFS, Natal and Waterberg fields are included and consequently the coals have a wide range in petrographic character as well as in rank with vitrinite varying 23 to 83 per cent, inertinite 6 to 65 per cent and maximum reflectance in oil of vitrinite varying 0,6 to 2,0.

The total clay content in the coal samples shows a negative regression when plotted against vitrinite and positive regressions against inertinite and visible mineral matter (correlation coefficient r of about 0,5 in all cases) which is as expected since the association of the clay minerals with inertinite has been reported from microscope investigations (Mackowsky, 1968b, p.338; Snyman, 1976). The amount of kaolinite in the clay shows similar trends when plotted against the microscope data with correlation coefficients of about the same order, except that the correlation with the visible mineral matter is poor ($r = 0,28$) and a fair correlation occurs

TABLE V

RELATIONSHIP BETWEEN CLAY MINERAL COMPOSITION AND COAL TYPE - CORRELATION COEFFICIENTS AND REGRESSION CONSTANTS FOR COAL MACERALS AND REFLECTANCE OF VITRINITE (DEPENDENT VARIABLE y) VERSUS CLAY MINERAL COMPOSITION AND TOTAL CLAYS IN COAL (INDEPENDENT VARIABLE x) FOR 16 COALS⁽¹⁾

Clay mineral composition and total clays in coal (x)	Range ⁺ (vol. or mass %) Minimum Maximum	Coal macerals and reflectance (y)				
		Vitrinite 22,8 ⁺ 83,2 ⁺	Exinite 1,0 ⁺ 8,0 ⁺	Inertinite 5,7 ⁺ 64,6 ⁺	Visible m.m. 1,0 ⁺ 12,7 ⁺	Ro (max.) 0,569 ⁺ 2,015 ⁺
Kaolinite	r ⁽³⁾	0,51	0,07	0,47	0,28	0,57
	b ⁽³⁾	-0,399	-0,005	0,370	0,035	-0,008
	a ⁽³⁾	70,1	4,6	21,5	3,7	1,244
Illite	r	0,24	0,11	0,20	0,18	0,74
	b	0,277	-0,013	-0,232	-0,034	0,015
	a	40,9	4,6	48,0	6,5	0,458
Expandable clays	r	0,61	0,24	0,58	0,27	0,12
	b	0,827	0,035	-0,802	-0,060	0,003
	a	30,6	3,6	58,8	6,9	0,737
Total clays in coal	r	0,51	0,10	0,43	0,55	0,00
	b	-1,79	-0,038	1,52	0,312	0,000
	a	69,0	4,8	24,2	1,9	0,794

NOTES: (1) From unpublished data on file (Gray, 1979).

(2) Determined by X-ray diffraction.

(3) r = correlation coefficient; b = regression coefficient; a = intercept on y-axis, i.e. $y = bx + a$.

with the reflectance data ($r = 0,57$). The amount of illite in the clay correlates rather poorly with the coal macerals (r less than $0,25$) but, significantly, a positive regression with a clear correlation ($r = 0,74$) occurs when illite is plotted against reflectance. The expandable clays tend to be associated with vitrinite (positive regression, $r = 0,61$).

The correlations found between the proportions of kaolinite and illite in the clay and the reflectance data, and hence coal rank (Teichmüller and Teichmüller, 1968; Snyman, 1976) prompted a further test to be carried out. In Figure 13 the data of inertinite versus clay composition from Table V are plotted for the relatively low and higher rank coals separately, using the reflectance value of $0,700$ to separate the two classes. Without exception the amount of inertinite (and vitrinite in inverse proportion since the samples are low in exinite) in the lower rank coals correlates well with the clay mineral composition (r varies from $0,80$ to $0,97$) whereas poor or almost no correlation occurs for the higher rank coals (r varies from $0,01$ to $0,30$). Thus in the lower rank coals the petrographic composition (coal type) may have an important bearing on the clay mineral composition, but for the higher rank coals this does not appear to be the case and the correlation found between coal rank and clay mineral composition (Figures 11 and 12) is not disproved by the further series of samples.

In Figure 14 (from unpublished data on file (FRI, 1978)), results are shown of specific gravity separations of three coal samples. The sinks contain relatively less clay in the mineral matter, but more kaolinite in the clay, by a factor of nearly 2 compared with the floats. These results are explained by the relative difficulty of liberating the clay minerals from coal compared with minerals like quartz, calcite and pyrite since all the

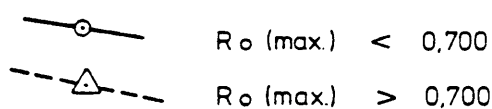
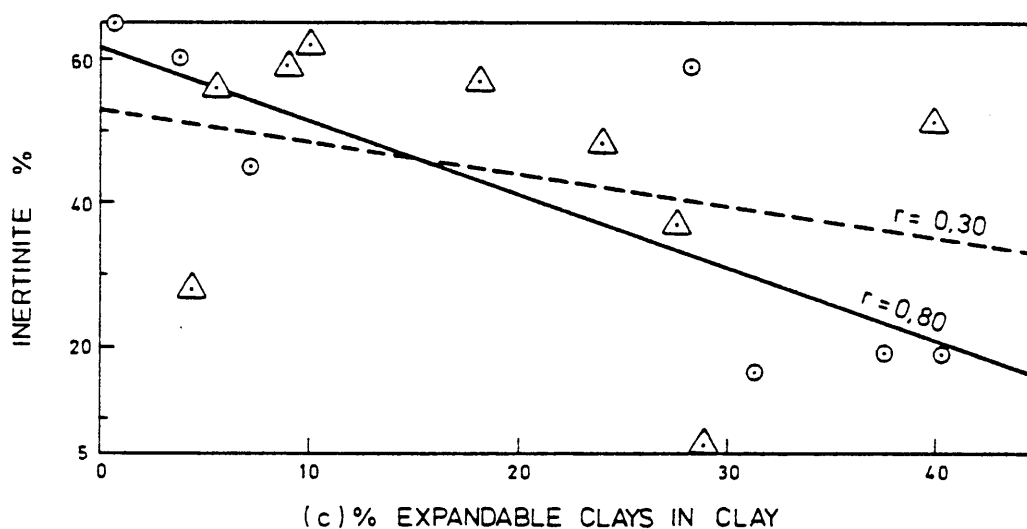
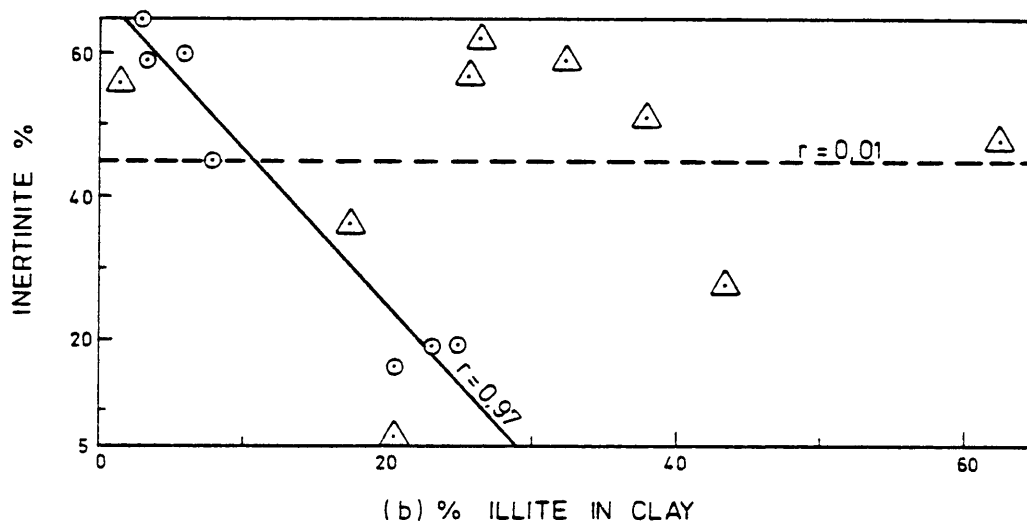
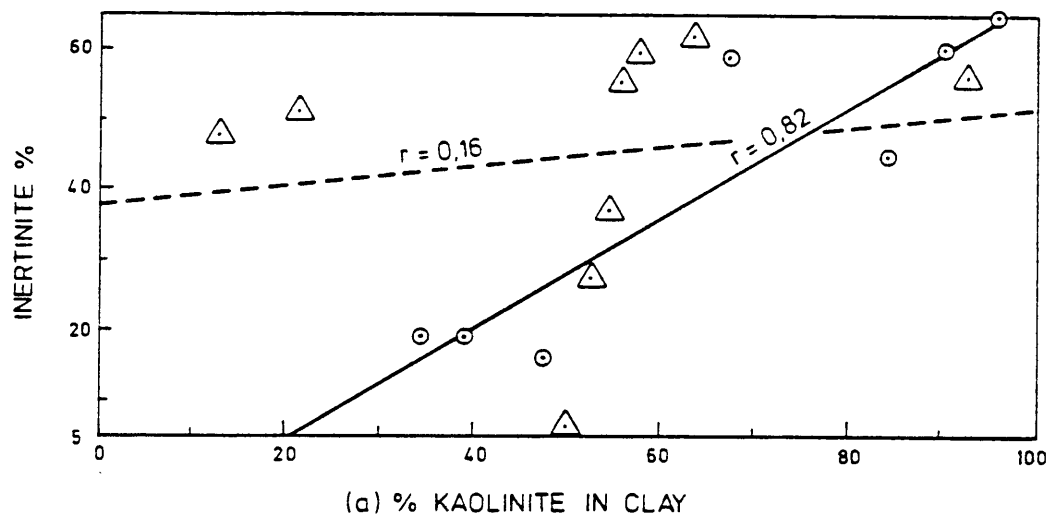


FIGURE 13 REGRESSION LINES AND CORRELATION COEFFICIENTS FOR CLAY MINERAL COMPOSITION VERSUS AMOUNT OF INERTINITE IN COALS OF DIFFERENT RANK.

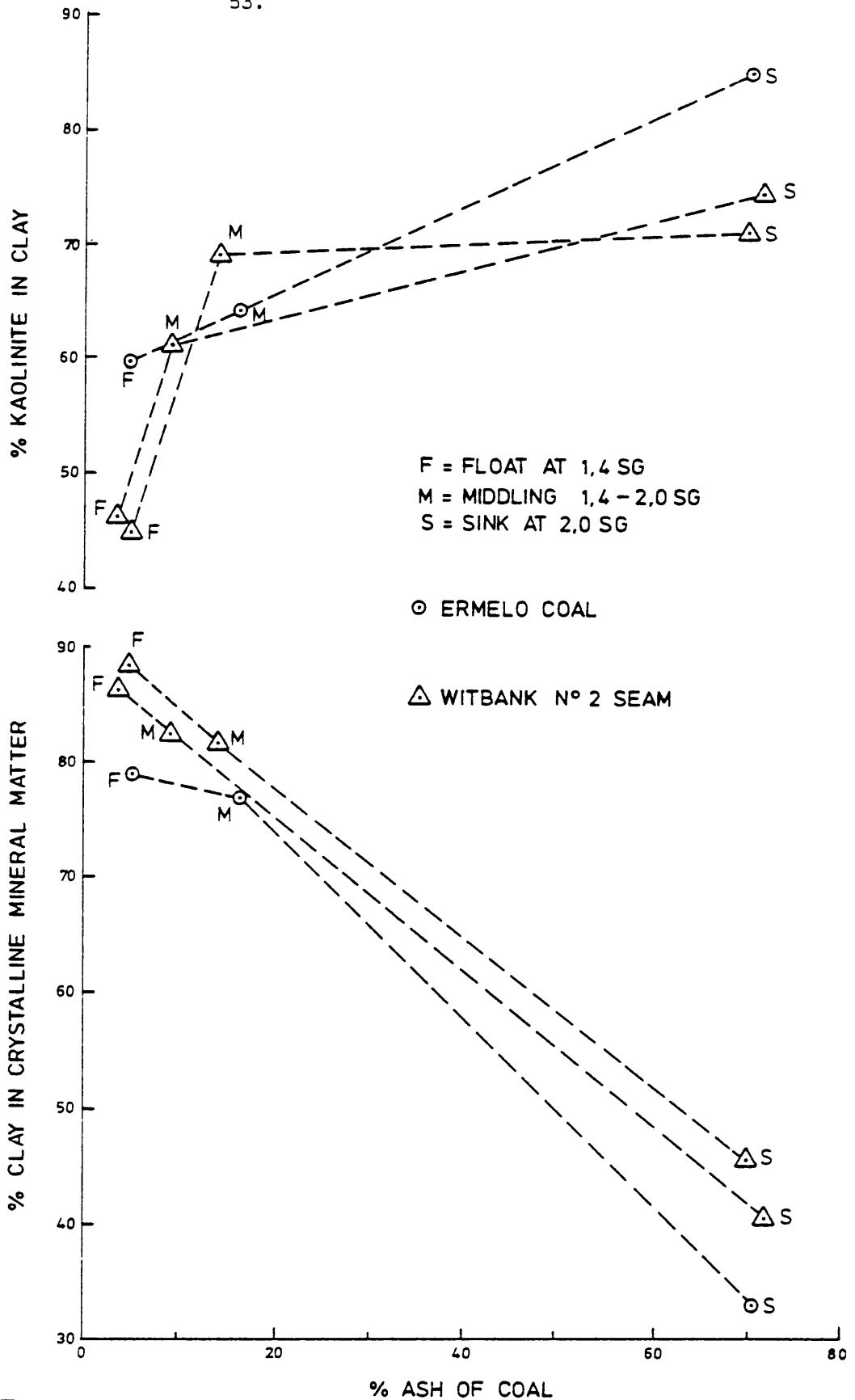


FIGURE 14
RELATIONSHIP BETWEEN COAL QUALITY AND AMOUNT
OF KAOLINITE IN CLAY AND AMOUNT OF CLAY IN
CRYSTALLINE MINERAL MATTER FOR WHOLE COALS
OF DIFFERENT RANK.

clay minerals should sink in a medium with a density of 2 g/cm^3 (Grim, 1968, p.466). Undoubtedly, the petrographic composition of the fractionated coal was changed relative to the whole coal by the gravity separations and the enrichment of kaolinite in the sinks is probably also due to their probable enrichment in inertinite. It is interesting that the slightly lower rank Ermelo coal with an estimated dry ash-free carbon content of 82 per cent (Savage, 1968a) also has the higher proportions of kaolinite in the sinks and floats compared with the Witbank No. 2 Seam coals (estimated carbon content 84 per cent), which is consistent with Figure 12.

E. Origin of the clays

Because it is relatively more coarse-grained than other clay minerals, detrital kaolinite is considered to be preferentially deposited along the margins of a basin or on the shoreward side of a lagoon. Conversely a high proportion of clastic illite in coal should indicate off-shore or midbasin conditions of coal deposition, as was found for underclays (Parham, 1964) and coals (Rao and Gluskoter, 1973) from the Illinois basin.

The neoformation of the clays (Millot, 1970) during and after diagenesis is a complex process, but acid leaching conditions should favour the formation of kaolinite (Grim, 1968, p.490) and any detrital illite is likely to be destroyed (Millot, op. cit., p.163). Ward (1978) pointed out that the assemblage of clay minerals in coal is quite different to that of the associated interseam strata for the Sydney basin and explained the relative absence of illite to be due to the interaction between detritus and organic acids in the peat swamps.

Dunnoyer de Segonzac (1970) distinguished three stages of clay mineral diagenesis lower than the anchimetamorphic phase, which could possibly be used to explain the distribution of clay minerals in South African coals.

During "early diagenesis" in the acid environment of a coal-forming bog, detrital illite is likely to be stripped of its potassium ions and to be degraded to form mixed-layer clays, expandable clays and ultimately to be hydrolised. Detrital kaolinite is stable and any detrital felspar is decomposed.

During "middle diagenesis" the sediments, though compacted through burial at moderate depths, are still permeable and circulating waters of various origins can pass through them. Acid leaching can take place and the neoformation of authigenic kaolinite can occur on a massive scale. These transformations are reversible and in alkaline environments rich in potassium, illite can form via mixed-layer intermediaries.

It is supposed that the intrusion of the Karroo dolerites must have started at the end of this stage, i.e. before the sediments had been strongly compacted and while the permeability was still high. The circulating waters now became alkaline and illite could form at the expense of kaolinite.

During "late diagenesis" brought on by deep burial, the sediments become compacted, water is expelled and the environment becomes confined i.e. the system becomes closed. The transformations of the clay minerals in a closed system are always aggradations leading to chlorite and illite. Kaolinite is unstable in this closed system and under acid conditions it recrystallizes to dickite and under basic conditions it is destroyed, providing ions for the neoformation of illite and chlorite.

Since coalification in South Africa is attributed to the influence of the dolerites (which are also expected to provide a basic environment) in contrast with the coalification of, for example, the coals in the Illinois basin, the abnormally high illite content of the South African anthracites can be explained. Although brackwater conditions in the original coal-forming swamps may have contributed alkalies for the

formation of illite (cf. the relatively high contents of K_2O and Na_2O in the Witbank No. 5 Seam and the Natal coals in Table IX) it is significant that the relatively higher alkali content, particularly Na_2O of the OFS coals compared with the Witbank No. 2 Seam, did not lead to any appreciable illite formation in the low rank OFS coals. The factor of metamorphism - manifesting itself in the rank of the coal - appears to be indispensable to the formation of illite in South African coals.

In the present work no dickite or pyrophyllite was noted in any of the product samples. The traces of chlorite occurring in some low volatile Natal coals (Table III) probably indicate an environment locally enriched in magnesium.

VIII. THE COMPOSITION OF MINERAL MATTER IN COAL, USING UNORIENTATED AGGREGATES

Figure 15 shows typical diffractograms ($6 - 16^{\circ}2\theta$ and $24 - 34^{\circ}2\theta$) of a Transvaal coal (South Witbank) and a Natal coal (Kilbarchan) prepared for quantitative X-ray diffraction determinations. Peak positions for illite, kaolinite 001 and 002, quartz, the internal standard fluorite, calcite, dolomite, siderite and pyrite are indicated. The minor peak at $14,6^{\circ}2\theta$ ($6,06 \text{ \AA}$) in Figure 15b may be due to bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) which results from heating gypsum at 105°C . Traces of gypsum occurring in some of the samples are thought to be due to weathering, as gypsum is not likely to be an original constituent in fresh coals, except in lignites, according to O'Gorman and Walker, (1971).

A. Sample preparation and X-ray diffraction procedure

Theoretical and practical considerations of the quantitative X-ray diffraction method used were discussed in Section VI. Following a standard procedure for the quantitative determinations 2 g samples of minus 60 mesh ($250 \mu\text{m}$) coal were mixed with 10 per cent of fluorite as internal standard and milled in 10 ml of ethanol for 30 minutes in a McCrone mill. The slurry and washings from the mill were dried in a drying oven at 105°C . Since sample segregation had probably occurred during the evaporation of the ethanol from the slurry, the milled sample was re-mixed by dry milling with a few 5 mm ball-bearings in an eccentric ball-mill for 1 hour.

Two X-ray diffraction sample mounts with a cavity of 25 mm diameter and 3 mm deep, loaded from the back following the procedure of McCreery (quoted in Klug and Alexander, 1974, p.373) in order to counter effects due to preferred orientation of platy minerals such as kaolinite, were prepared for each sample. Since the determinations were done on coal without prior concentration of the mineral matter, the dilution of the clay minerals by the coal should also serve to reduce preferred orientation.

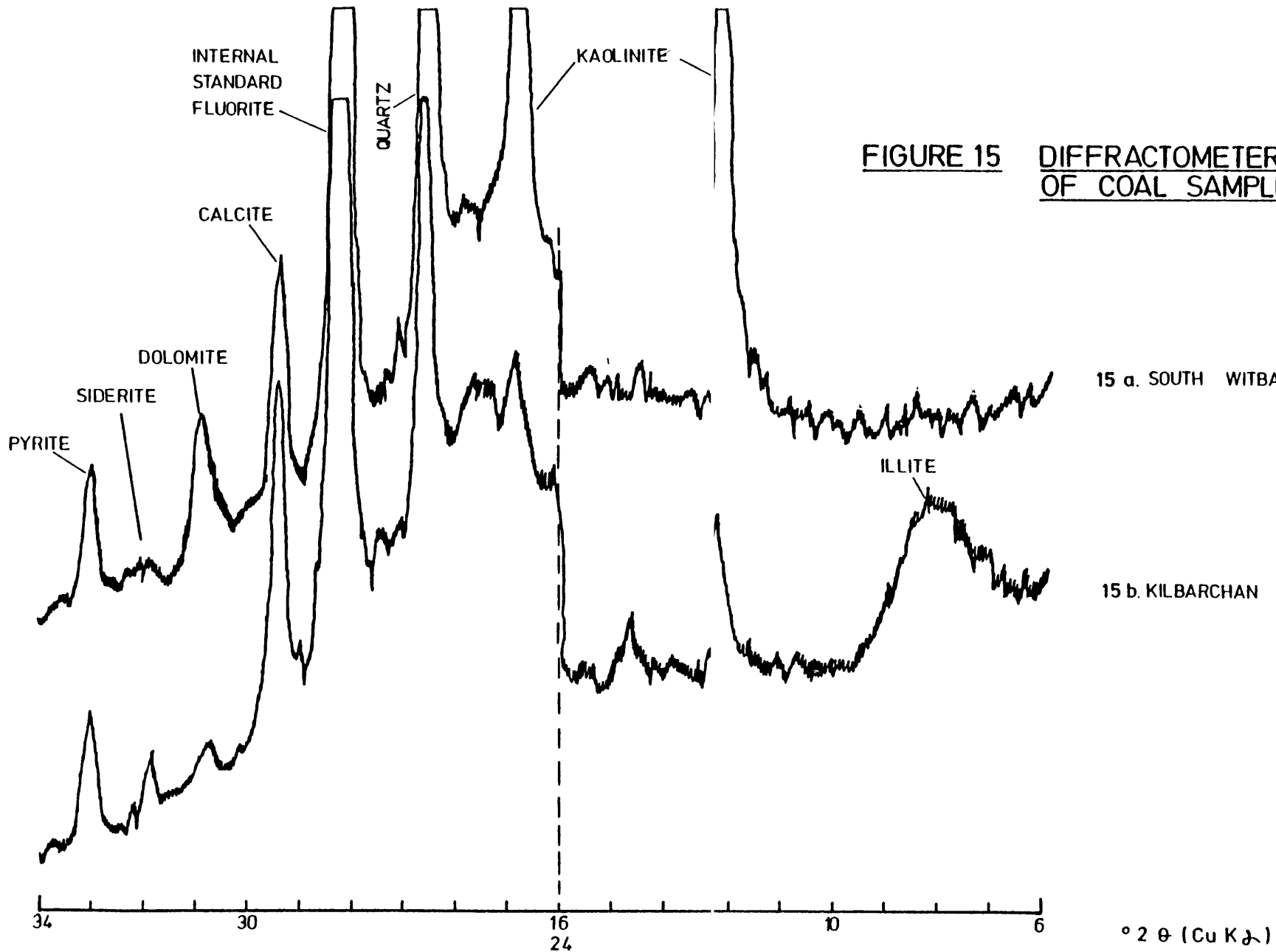


FIGURE 15 DIFFRACTOMETER TRACES
OF COAL SAMPLES.

15 a. SOUTH WITBANK

15 b. KILBARCHAN

$^\circ 2\theta$ (Cu K α)

All X-ray diffraction work was carried out with a Siemens D500 automated X-ray powder diffractometer using copper K α -radiation at 40 kV and 30 mA. A graphite monochromator was used in the diffracted beam to suppress fluorescence and eliminate K β -radiation, and a scintillation counter with pulse height analysis was used as detector.

Although a number of diffraction peaks overlapped with one another (pyrite 3,13 Å with fluorite 3,15 Å; kaolinite 3,37 Å with quartz 3,34 Å; dolomite 2,67 Å with pyrite 2,71 Å; calcite 2,85 Å with dolomite 2,89 Å and the third order basal spacing of illite with the quartz position at 3,34 Å) only the pyrite-fluorite and kaolinite-quartz overlaps were considered to affect the results significantly. Because of the low concentrations of dolomite and pyrite (generally less than 2 per cent) a relatively narrow interval of 0,8 °2 θ was stepscanned which afforded adequate resolution to exclude the dolomite overlap on the pyrite peak position. In the case of calcite, a peak with only about 1 per cent of the intensity of the 3,04 Å calcite peak overlaps with the dolomite position and since calcite is usually only a minor constituent in the coal, this correction could be neglected. The third order basal spacing of illite overlapping on the quartz position was broad, and was thought not to influence the intensity of the quartz peak.

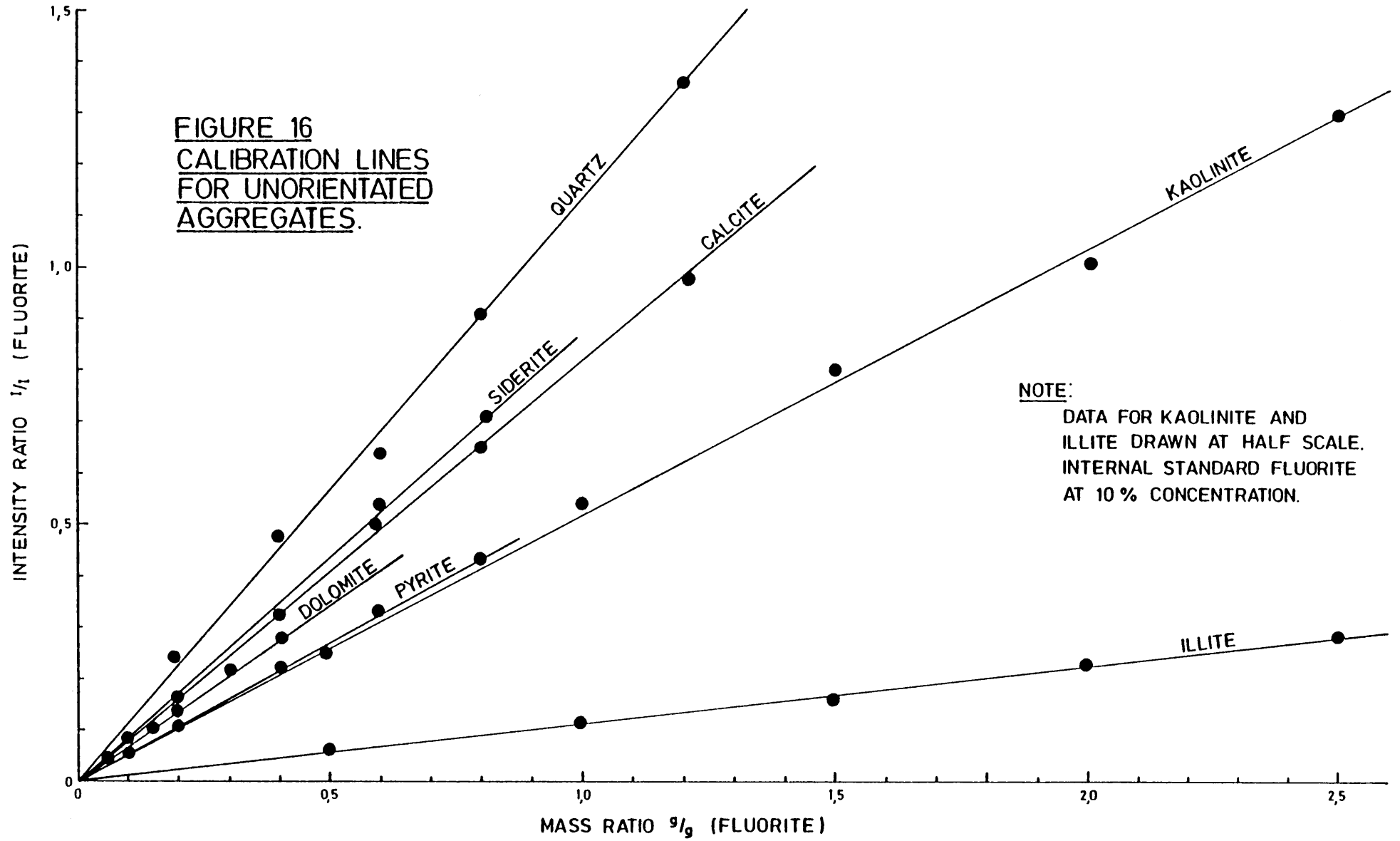
The intensity ratios of the overlapping peaks were determined experimentally on the samples used as standards: 33,0 per cent of the pyrite 2,71 Å peak intensity was subtracted from the fluorite peak intensity at 3,15 Å and 1,55 per cent of the kaolinite 001 peak intensity was subtracted from the 3,34 Å quartz peak intensity.

Any gypsum in the samples would be partially dehydrated to form bassanite (CaSO₄·½H₂O) by the drying at 105°C and its diffraction peaks at 3,00 Å (100) and 2,80 Å (50) - JCPDS, 1974 - would enhance the intensities of calcite and siderite

diffraction peaks at 3,04 Å and 2,79 Å respectively. Although attempts were made to apply correction factors using the 6,01 Å (95) peak of bassanite as a basis, its intensity was low due to the low content of bassanite and data corrected for the presence of bassanite were thought not to be necessarily superior to the uncorrected data. Where bassanite (original gypsum) is present in a sample, the proportions of calcite and siderite will be slightly overestimated.

In Figure 16 the calibrations used for quantitative X-ray diffraction on the unorientated aggregates are given. The internal standard fluorite was held at 10 per cent concentration and mixtures of the various minerals were made up to accommodate the expected range of mass proportions of minerals in the coal samples, (i.e. quartz and calcite less than 12 per cent, siderite and pyrite less than 8 per cent and dolomite less than 4 per cent) by dilution with amorphous Al_2O_3 . Mixtures of the clay minerals kaolinite and illite, whose data are shown at half scale in Figure 16, were made up to cover the concentration range of 10 to 50 per cent in order to compensate for their relatively weaker diffraction intensities, although they seldom reached such high concentration in the coal samples. Five mixtures were used for each mineral and the calculated regression lines passed close to the origin - fully in agreement with Chung's work (1974), which was discussed in Section VI. Following Chung (op. cit.) the calculated slopes of the regression lines (coefficient of regression) give the reference intensities of the various minerals relative to fluorite, which are as follows:

Fithian illite (API No. 35) 0,112; Lewistown kaolinite (API No. 17) 0,513; quartz 1,135; calcite 0,823; dolomite 0,684; siderite 0,872 and pyrite 0,548. Thus, for each sample, diffraction peak intensities were determined at 10 Å (illite); 7 Å (kaolinite); 3,34 Å (quartz); 3,15 Å (fluorite); 3,04 Å (calcite); 2,89 Å (dolomite); 2,79 Å (siderite) and 2,71 Å (pyrite).



B. Results and discussion

Quantitative results on the unorientated aggregates are given in Table VI. The duplicates refer to different diffractometer mounts and give an indication of the reproducibility of the X-ray diffraction method and sample homogeneity. Any possible weighing errors, and the absolute accuracy of the measurements cannot be estimated from these data.

Except for the weakly crystalline illite the reproducibility of the X-ray diffraction method appears to be good (standard error $\pm 0,3$ mass per cent for kaolinite and $\pm 0,2$ mass per cent for quartz). Although illite was detected in the orientated aggregates of the low temperature ash of all the product samples (Table III) only the relatively more crystalline illite could be detected in the coal samples directly. These results were expected. It also appears that the expandable clays retain a relatively "open" and variable basal spacing in the coal and cannot be detected in the unorientated aggregates - for example the products from Umgala and Zimbutu collieries (58 and 44 per cent expandable clays in Table III) contained no detectable illite (Table VI) whereas, if the clay structures had been collapsed, this would not have been the case.

In Table VII the mineral matter composition of the coals are recalculated from the radio-frequency data (Table II) to equal 100 per cent. Except for Balgray, Brockwell and Aloe products (all anthracites) the total from the X-ray diffraction determinations (Table VI) is less than the total amount of mineral matter determined by radio-frequency ashing (Table II). The difference must be ascribed to amorphous "inorganic" phases present in the coal, to quantities of minerals below detection limits, to poorly crystalline illite and probably also to the expandable clays as well as errors. For the three anthracites the higher totals in Table VI compared with Table II, must be due to the use of a Fithian illite (poorly crystalline) in the calibrations, which results in the amount of well crystallized illite in the coal being overestimated.

TABLE VI
DUPLICATES AND AVERAGE DATA FOR MINERAL MATTER FROM UNORIENTATED AGGREGATES
(MASS % OF COAL, AIR-DRY)

Colliery	Illite ⁽¹⁾		Kaolinite ⁽²⁾		Quartz	Calcite	Dolomite	Siderite	Pyrite	Total					
Witbank No. 2 Seam															
Elkeboom	ND ⁽³⁾	-	5,05 5,18	5,12	0,63 0,68	0,66	0,15 0,09	0,12	0,21 0,27	0,24	0,06 0,09	0,08	0,32 0,21	0,26	6,48
Springbok	2,98 2,95	2,96	6,16 6,10	6,13	0,34 0,36	0,35	ND	-	0,82 0,84	0,83	0,30 0,24	0,27	0,98 0,96	0,97	11,51
New Clydesdale	2,30 2,74	2,52	5,60 5,83	5,72	ND	-	0,85 0,79	0,82	1,49 1,39	1,44	0,25 0,19	0,22	1,60 1,45	1,52	12,24
Albion	4,10 3,79	3,95	5,52 5,65	5,58	0,45 0,51	0,48	1,63 1,79	1,71	1,24 1,27	1,26	1,13 1,13	1,13	0,91 0,91	0,91	15,02
Delmas	ND	-	7,09 7,31	7,20	3,55 3,89	3,72	1,25 1,31	1,28	0,51 0,67	0,59	0,22 0,25	0,24	1,29 1,31	1,30	14,33
Witbank No. 4 Seam															
South Witbank	ND	-	6,68 6,82	6,75	4,45 4,32	4,38	1,19 1,19	1,19	1,10 1,08	1,09	ND	-	0,97 0,97	0,97	14,38
Anglo Power (Kriel)	ND	-	6,63 6,86	6,74	4,89 4,88	4,88	1,89 2,01	1,95	1,07 0,91	0,99	0,10 0,18	0,14	1,15 0,97	1,06	15,76
Witbank No. 5 Seam															
Blesbok	1,28 1,38	1,33	3,22 3,41	3,32	5,38 5,37	5,38	ND	-	0,40 0,37	0,38	ND	-	0,49 0,37	0,43	10,84
Springbok	0,70 0,89	0,80	2,75 3,06	2,90	4,28 4,46	4,37	ND	-	ND	-	ND	-	0,28 0,36	0,32	8,39
Greenside	0,49 0,65	0,57	4,03 4,19	4,11	2,37 2,39	2,38	0,63 0,69	0,66	0,51 0,43	0,47	0,03 0,04	0,04	0,37 0,25	0,31	8,54
Navigation	0,20 0,69	0,44	3,62 3,81	3,72	3,68 3,90	3,79	0,22 0,18	0,20	0,11 0,16	0,14	ND	-	0,07 0,09	0,08	8,37
Breyten-Ermelo															
Union	ND	-	4,82 5,17	5,00	2,11 2,13	2,12	0,62 0,49	0,56	0,35 0,40	0,38	ND	-	0,74 0,89	0,82	8,88
Spitzkop	ND	-	3,49 3,74	3,62	3,07 3,10	3,08	0,62 0,49	0,56	0,35 0,45	0,40	ND	-	1,16 1,30	1,23	8,89
Usutu (S & E)	ND	-	4,78 4,85	4,82	4,26 4,31	4,28	0,52 0,23	0,38	0,60 0,84	0,72	0,13 0,12	0,12	1,78 2,01	1,90	12,22
South Rand & OFS															
Grootvlei	ND	-	11,13 11,84	11,48	4,36 4,77	4,56	2,16 2,05	2,10	0,59 0,65	0,62	ND	-	0,74 0,80	0,77	19,53
Cornelia Bertha I	ND	-	9,73 9,73	9,73	7,90 8,20	8,05	1,05 0,88	0,96	0,45 0,72	0,58	0,20 0,29	0,24	0,90 1,05	0,98	20,54
Sigma	ND	-	11,81 12,18	12,00	8,23 8,15	8,19	1,26 1,36	1,31	0,34 0,32	0,33	0,14 0,16	0,15	0,55 0,46	0,50	22,48
Coalbrook No. 2	ND	-	10,33 10,87	10,60	2,11 3,02	2,56	2,11 2,09	2,10	0,07 0,27	0,17	0,43 0,46	0,44	0,93 0,87	0,90	16,77
Vierfontein	ND	-	8,79 8,21	8,50	4,69 4,37	4,53	0,47 0,42	0,44	0,03 0,21	0,12	ND	-	1,74 1,47	1,60	15,19

TABLE VI (continued)

Colliery	Illite ⁽¹⁾		Kaolinite ⁽²⁾		Quartz		Calcite		Dolomite		Siderite		Pyrite		Total
<u>Klip River, Natal</u>															
Kilbarchan	21,05}	20,68	2,03}	1,94	2,82}	2,82	2,09}	2,18	0,17}	0,22	0,12}	0,10	1,05}	1,13	29,07
	20,32}		1,86}		2,82}		2,28}		0,27}		0,08}		1,21}		
Ballengeich	7,11}	6,50	2,56}	2,62	0,83}	0,86	0,58}	0,59	0,08}	0,08	ND	-	0,89}	0,86	11,51
	5,89}		2,68}		0,89}		0,60}		0,09}				0,84}		
Durban Navigation	4,71}	5,36	2,20}	2,03	0,40}	0,42	0,59}	0,56	0,07}	0,10	ND	-	0,88}	0,94	9,41
	6,02}		1,86}		0,44}		0,52}		0,13}				1,00}		
Natal Navigation	7,39}	6,94	2,22}	2,08	1,42}	1,40	ND	-	ND	-	ND	-	1,47}	1,42	11,84
	6,48}		1,95}		1,39}								1,36}		
Indumeni	7,23}	7,14	0,84}	0,94	0,32}	0,32	0,87}	0,83	0,36}	0,44	0,09}	0,06	0,95}	0,93	10,66
	7,04}		1,03}		0,32}		0,79}		0,51}		0,02}		0,91}		
Newcastle-Platberg	12,64}	13,76	3,44}	3,68	2,40}	2,51	ND	-	ND	-	ND	-	2,24}	2,22	22,17
	14,89}		3,92}		2,62}								2,19}		
<u>Utrecht</u>															
Balgray	10,83}	10,09	1,96}	1,90	1,84}	1,84	4,70}	4,92	ND	-	ND	-	0,95}	0,96	19,71
	9,35}		1,83}		1,85}		5,14}						0,96}		
Utrecht	5,22}	5,78	1,38}	1,28	1,01}	1,02	2,99}	2,98	0,18}	0,19	0,23}	0,12	1,66}	1,70	13,07
	6,34}		1,18}		1,04}		2,98}		0,20}		0,02}		1,75}		
Umgala	ND	-	1,37}	1,32	1,93}	1,88	1,71}	1,73	0,39}	0,34	0,15}	0,10	1,37}	1,46	6,83
			1,27}		1,84}		1,75}		0,29}		0,05}		1,56}		
Zimbutu	ND	-	1,94}	2,06	1,69}	1,74	1,33}	1,28	0,30}	0,30	0,15}	0,12	1,75}	1,74	7,24
			2,19}		1,79}		1,23}		0,30}		0,08}		1,74}		
<u>Paulpietersburg-Vryheid</u>															
Dumbe	0,22}	0,75	3,08}	2,99	1,94}	2,03	ND	-	ND	-	ND	-	1,07}	1,05	6,82
	1,28}		2,90}		2,12}								1,03}		
Brockwell	14,68}	13,54	0,85}	0,76	1,88}	1,77	ND	-	ND	-	ND	-	0,43}	0,41	16,48
	12,41}		0,68}		1,66}								0,39}		
Tendega	1,40}	1,30	3,21}	3,10	1,39}	1,37	0,26}	0,28	ND	-	ND	-	0,99}	0,98	7,03
	1,20}		3,00}		1,35}		0,31}						0,96}		
Hlobane	2,72}	2,72	2,80}	2,77	1,21}	1,22	ND	-	ND	-	ND	-	0,33}	0,32	7,03
	2,73}		2,74}		1,22}								0,32}		
Vryheid Coronation	3,98}	4,34	2,53}	2,52	1,53}	1,53	ND	-	ND	-	ND	-	0,67}	0,68	9,07
	4,69}		2,51}		1,53}								0,68}		
Aloe	14,44}	15,21	0,62}	0,60	1,64}	1,61	ND	-	ND	-	ND	-	0,29}	0,28	17,70
	15,98}		0,59}		1,58}								0,28}		

NOTES: (1 Relatively well crystallized, relative to Fithian illite (API No. 35)

(2 Relative to Lewistown kaolinite (API No. 17)

(3 ND = concentration too low to be detected

TABLE VII
COMPOSITION OF MINERAL MATTER IN COAL (MASS %)

Colliery	Illite	Kaolinite	Quartz	Calcite	Dolomite	Siderite	Pyrite	Amorphous ⁽¹⁾	Total ⁽²⁾
Witbank No. 2 Seam									
Eikeboom	-	44,9	5,8	1,1	2,1	0,7	2,3	43,1	100,0
Springbok	18,2	37,6	2,1	-	5,1	1,7	6,0	29,3	100,0
New Clydesdale	13,2	29,9	-	4,3	7,5	1,2	7,6	36,3	100,0
Albion	19,3	27,2	2,3	8,3	6,1	5,5	4,4	26,9	100,0
Delmas	-	30,8	15,9	5,5	2,5	1,0	5,6	38,7	100,0
Witbank No. 4 Seam									
South Witbank	-	27,8	18,0	4,9	4,5	-	4,0	40,8	100,0
Anglo Power (Kriel)	-	26,6	19,3	7,7	3,9	0,6	4,2	37,7	100,0
Witbank No. 5 Seam									
Blesbok	8,7	21,8	35,4	-	2,5	-	2,8	28,8	100,0
Springbok	6,2	22,5	33,9	-	-	-	2,5	34,9	100,0
Greenside	4,2	30,0	17,4	4,8	3,4	0,3	2,3	37,6	100,0
Navigation	3,3	27,6	28,1	1,5	1,0	-	0,6	37,9	100,0
Breyten-Ermelo									
Union	-	30,1	12,8	3,4	2,3	-	4,9	46,5	100,0
Spitzkop	-	22,5	19,1	3,5	2,5	-	7,6	44,8	100,0
Usutu (S & E)	-	23,5	20,9	1,9	3,5	0,6	9,3	40,3	100,0
South Rand & OFS									
Grootvlei	-	35,8	14,2	6,5	1,9	-	2,4	39,2	100,0
Cornelia Bertha I	-	30,9	25,6	3,0	1,8	0,8	3,1	34,8	100,0
Sigma	-	34,4	23,5	3,8	0,9	0,4	1,4	35,6	100,0
Coalbrook No. 2	-	34,6	8,4	6,9	0,6	1,4	2,9	45,2	100,0
Vierfontein	-	24,1	12,9	1,2	0,3	-	4,5	57,0	100,0
Klip River, Natal									
Kilbarchan	70,6	6,6	9,6	7,4	0,8	0,3	3,9	0,8	100,0
Ballengelch	34,4	13,9	4,6	3,1	0,4	-	4,6	39,0	100,0
Durban Navigation	40,6	15,4	3,2	4,2	0,8	-	7,1	28,7	100,0
Natal Navigation	43,6	13,1	8,8	-	-	-	8,9	25,6	100,0
Indumeni	56,2	7,4	2,5	6,5	3,5	0,5	7,3	16,1	100,0
Newcastle-Platberg	51,9	13,9	9,5	-	-	-	8,4	16,3	100,0
Utrecht									
Balgray	51,2	9,6	9,3	25,0	-	-	4,9	-	100,0 ⁽³⁾
Utrecht	34,6	7,7	6,1	17,8	1,1	0,7	10,2	21,8	100,0
Umgala	-	7,9	11,3	10,4	2,0	0,6	8,7	59,1	100,0
Zimbutu	-	13,0	11,0	8,1	1,9	0,8	11,0	54,2	100,0
Paulpietersburg-Vryheid									
Dumbe	6,0	23,7	16,1	-	-	-	8,3	45,9	100,0 ⁽³⁾
Brockwell	82,2	4,6	10,7	-	-	-	2,5	-	100,0
Tendega	9,4	22,3	9,9	2,0	-	-	7,1	49,3	100,0
Hlobane	18,5	18,8	8,3	-	-	-	2,2	52,2	100,0
Vryheid Coronation	30,6	17,7	10,8	-	-	-	4,8	36,1	100,0 ⁽³⁾
Aloe	85,9	3,4	9,1	-	-	-	1,6	-	100,0

NOTES: (1) Determined by difference and includes poorly crystalline and expandable clays and errors.

(2) Relative to mineral matter determined by radio-frequency ashing (Table II).

(3) Relative to total in Table VI.

In view of the uncertainty about the illite standard, and whether the same clay standard may be used for coals of different rank, it is not certain whether the Natal coals do, on average (Table VIII), contain less amorphous material than for example the OFS coals, i.e. whether there is any relationship between the amount of non-crystalline phases in the coal and its rank.

After the clay minerals and amorphous material, quartz is the predominant mineral in many South African coal products which confirms the conclusion of Kunstmann and Kerkovius (1968) who determined free quartz chemically. Quartz contents are extremely variable: the products from three collieries mining the Witbank No. 2 Seam in the centre of the coalfield (Albion, New Clydesdale and Springbok) have the lowest quartz contents (nil to 2 per cent of the mineral matter) whereas the Witbank No. 5 Seam contains rather high proportions of quartz (17 to 35 per cent of mineral matter) and in Natal the quartz content in the mineral matter is generally moderate at 3 to 16 per cent.

The content of carbonates (calcite, dolomite and siderite) is variable. In the Paulpietersburg-Vryheid area of Natal it is low, varying from nil to 2 per cent of the mineral matter, but in the adjoining Utrecht area values are rather high, varying from 12 to 25 per cent in the four collieries. Nearly all the Witbank No. 2 Seam samples contained dolomite and siderite in addition to calcite, each individually comprising less than 10 per cent of the total mineral matter. The high value (6 per cent) for siderite in the Albion product is not reflected in the chemical analysis on the coal ash (Table IX), where the ferric iron content was moderate, but an anomalously high P_2O_5 content of 4 per cent in the ash indicates that apatite was probably mistaken for siderite.

Siderite is generally associated with coal formed under fresh water conditions according to Kemezys and Taylor (1964) and dolomite with coal influenced by marine invasions (Mackowsky,

1968a), but these criteria cannot be applied to the present series of samples, since it is not known what proportion of the minerals determined by X-ray diffraction were syngenetic. The apparent absence of carbonates in some of the low ash Natal coals may not necessarily be significant since carbonates may very well be present, but below the detection limits when determined by X-ray diffraction on the coal samples directly.

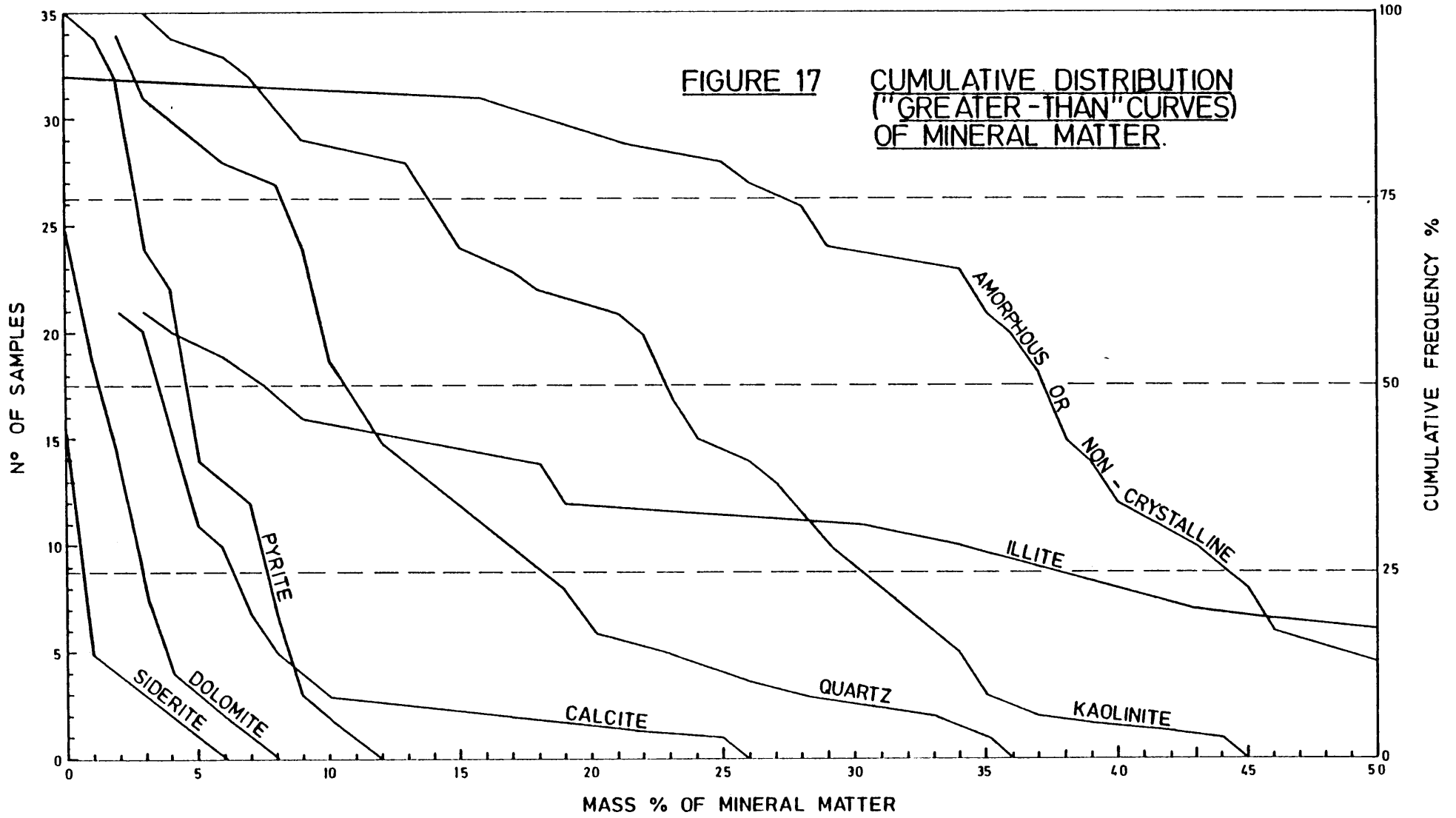
Pyrite, with which any possible marcasite would be included, is present in all the product samples. Samples from the Utrecht coalfield contain relatively high proportions of pyrite in the mineral matter varying from 5 to 11 per cent, compared with the overall average of about 5 per cent for South African coal products.

Average data for the various seams and areas and the overall average for all the product samples are given in Table VIII. In Figure 17 the cumulative distributions ("greater-than" curves) for the mineral matter occurring in the coal products are given. The median coal sample contains more than 23 per cent of kaolinite, 7 per cent of illite, 37 per cent of amorphous material, 10 per cent of quartz, 3 per cent of calcite, 1 per cent of dolomite and 4 per cent of pyrite, but siderite is absent.

TABLE VIII

AVERAGE DATA FOR THE COMPOSITION OF MINERAL MATTER (MASS %)

Seam or Area	No. of samples	Illite	Kaolinite	Quartz	Calcite	Dolomite	Siderite	Pyrite	Amorphous
Witbank No. 2 Seam	5	10,1	34,1	5,2	3,8	4,7	2,0	5,2	34,9
Witbank No. 4 Seam	2	-	27,2	18,7	6,3	4,2	0,3	4,1	39,2
Witbank No. 5 Seam	4	5,6	25,5	28,7	1,6	1,7	0,1	2,0	34,8
Breyten-Ermelo	3	-	25,4	17,6	2,9	2,8	0,2	7,3	43,8
OFS and South Rand	5	-	32,0	16,9	4,3	1,1	0,5	2,9	42,3
Klip River, Natal	6	49,6	11,7	6,4	3,5	0,9	0,1	6,7	21,1
Utrecht	4	21,4	9,6	9,4	15,3	1,2	0,5	8,7	33,9
Paulpietersburg- Vryheid	6	38,8	15,1	10,8	0,3	-	-	4,4	30,6
Transvaal and OFS	19	3,8	25,6	16,6	3,6	2,8	0,7	4,1	42,8
Natal	16	38,5	12,4	8,8	5,3	0,7	0,2	6,3	27,8
Overall for S.A. coal products	35	19,7	19,6	13,0	4,4	1,8	0,5	5,1	35,9



IX. CHEMICAL ANALYSES OF COAL ASH

From time to time chemical analyses of major and some minor elements in the ash of South African coal product samples are published by the Fuel Research Institute in annual reports (e.g. FRI: 1975, 1976, 1977), in various bulletins (Savage: 1965, 1976, 1978) and also in the literature (Kunstmann et al., 1960; Savage et al., 1977).

In addition, surveys have been carried out on some minor and trace elements occurring in South African coals, e.g. germanium, titanium, arsenic, boron and fluorine, vanadium, and manganese (Kunstmann and others: 1955, 1957, 1961, 1963, 1967, 1968).

Results of the chemical determination of free quartz in coal ash have also been reported (Kunstmann and Kerkovius, 1968; FRI, 1970).

Gluskoter et al. (1977) have recently published data on sixty chemical elements occurring in coal, mainly from the Illinois basin.

A. Major and minor elements

Chemical analyses on the present samples were included in a report on 135 ash analyses (Savage et al., 1977) and are given in Table IX together with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Smoothed frequency curves are given in Figure 18 (major elements) and Figure 19 (minor elements) and are compared with the earth's crustal averages of Taylor (1964). Cumulative frequency curves appear in Figure 20.

The chemical analyses of the coal ash show the coal residue to have features of a hydrolysate sediment, modified by the element collecting activities of the plants and low Eh pH conditions.

The paucity in SiO_2 , MgO , Na_2O and K_2O of coal ash with median values of 48; 1,2; 0,4 and 1,8 per cent respectively (Figure 20), compared with crustal averages (Taylor, 1964) of

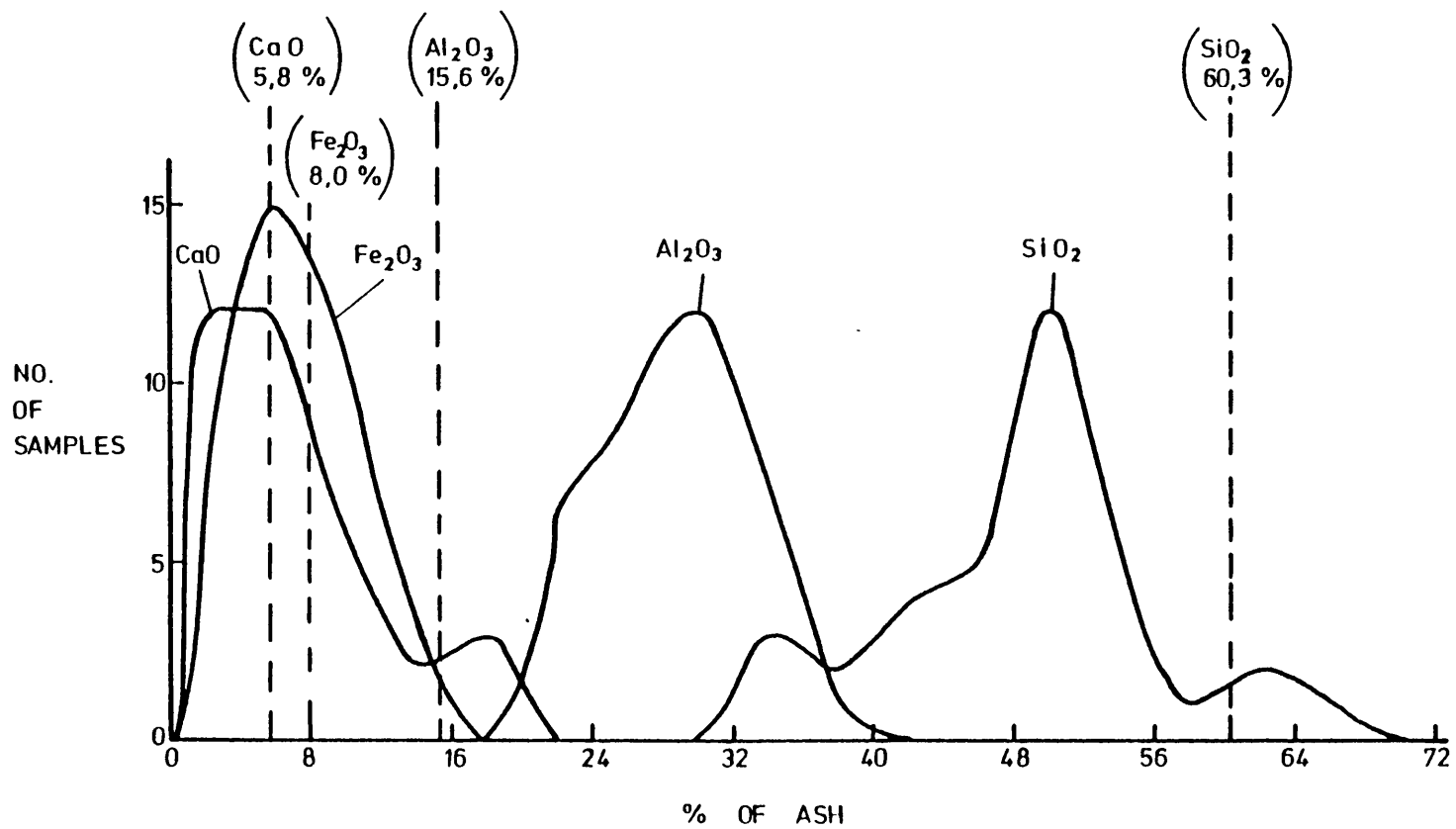
TABLE IX
CHEMICAL ANALYSES (1) OF COAL ASH (MASS %)

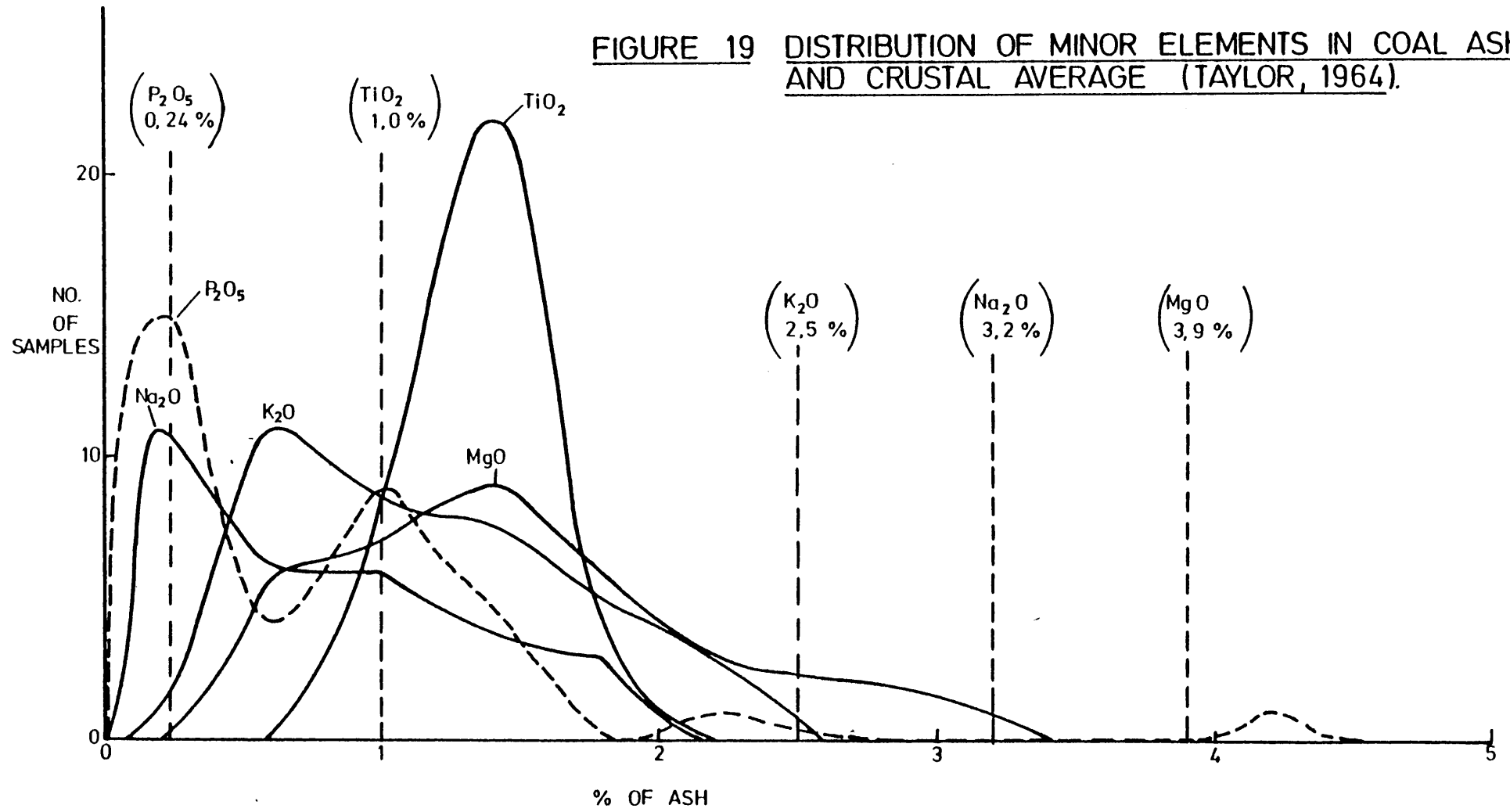
Colliery	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Total	SiO ₂ /Al ₂ O ₃
Witbank No. 2 Seam												
Eikeboom	46,4	36,4	2,9	1,51	1,87	4,97	0,94	0,50	0,12	1,43	96,97	1,27
Springbok	41,8	34,7	6,1	2,21	1,58	6,51	1,81	0,40	0,25	2,97	98,32	1,20
New Clydesdale	36,2	32,9	9,5	1,51	1,34	11,33	3,00	0,40	0,56	3,29	100,00	1,10
Albion	34,0	29,6	4,8	4,06	1,49	16,24	2,50	0,80	0,25	3,90	97,60	1,15
Delmas	48,7	27,8	8,9	0,10	1,42	7,12	1,57	0,40	0,36	3,53	99,88	1,75
Witbank No. 4 Seam												
South Witbank	52,0	27,1	4,0	1,06	1,52	8,42	1,86	0,62	0,34	2,24	99,14	1,92
Anglo Power (Kriel)	47,5	23,7	4,2	1,12	1,74	12,93	2,45	0,44	0,47	3,23	97,75	2,00
Witbank No. 5 Seam												
Blesbok	63,2	21,7	4,4	0,09	1,10	2,29	1,22	1,77	0,19	1,47	97,34	2,91
Springbok	64,7	24,0	3,7	0,08	1,36	0,84	0,74	1,58	0,19	0,58	97,73	2,70
Greenside	51,5	28,0	3,9	0,99	1,40	7,72	1,51	0,86	0,16	2,27	98,29	1,84
Navigation	61,5	26,9	1,9	0,33	1,22	2,60	0,95	1,22	0,16	1,13	97,91	2,29
Breyten-Ermelo												
Union	50,6	29,7	5,9	0,25	1,53	5,21	1,88	0,70	0,21	2,28	98,25	1,70
Spitzkop	50,2	25,9	10,3	0,10	1,20	6,31	1,68	0,74	0,19	3,64	100,25	1,94
Usutu (S & E)	47,6	22,4	11,1	0,81	1,31	8,62	2,28	0,50	0,50	4,25	99,35	2,13
South Rand & OFS												
Grootvlei	50,0	30,5	3,2	0,34	0,93	7,82	1,30	0,80	0,53	2,88	98,28	1,64
Cornelia Bertha I	53,8	24,2	4,1	0,85	1,46	7,82	1,80	0,40	0,81	3,67	98,89	2,22
Sigma	55,6	27,3	3,4	0,22	1,54	5,84	1,44	0,52	0,86	2,34	99,02	2,04
Coalbrook No. 2	43,8	32,1	4,5	1,42	1,60	9,62	1,16	0,27	0,65	2,58	97,68	1,36
Vierfontein	54,8	28,2	5,3	0,09	1,14	3,81	0,92	0,99	0,60	2,58	98,42	1,94
Klip River, Natal												
Kilbarchan	49,4	28,5	5,8	0,32	1,19	6,81	1,24	1,89	1,52	1,98	98,64	1,73
Ballengeich	47,1	31,2	6,1	0,52	1,31	4,94	1,32	1,33	1,68	2,77	98,23	1,51
Durban Navigation	45,2	32,3	7,0	0,67	1,30	6,23	0,99	1,65	1,03	1,85	98,19	1,40
Natal Navigation	50,5	31,5	10,0	0,30	1,31	1,43	0,58	1,49	0,70	0,98	98,76	1,60
Indumeni	39,1	28,2	8,4	1,42	1,07	10,72	1,93	0,96	1,64	4,10	97,52	1,39
Newcastle-Platberg	51,4	31,0	10,5	0,15	1,12	0,59	0,73	2,00	0,80	0,72	98,92	1,66
Utrecht												
Balgray	35,9	20,4	11,4	1,18	1,14	19,85	2,03	1,10	1,68	3,87	98,50	1,77
Utrecht	35,9	22,4	14,0	0,77	0,98	16,04	2,30	1,43	1,46	4,35	99,59	1,60
Umgala	40,7	22,6	10,5	1,17	1,18	13,54	2,80	1,33	0,54	4,19	98,51	1,80
Zimbutu	42,2	25,6	12,5	0,96	1,10	8,62	1,47	1,35	0,55	3,31	97,64	1,65
Paulpietersburg-Vryheid												
Dumbe	50,6	27,5	12,9	0,09	1,21	2,04	1,04	1,49	0,41	1,58	98,82	1,84
Brockwell Anthracite	50,8	30,0	8,9	0,42	1,35	1,69	1,20	1,65	1,24	1,46	98,62	1,69
Tendega	48,6	32,3	9,3	0,05	1,54	3,55	0,83	0,86	0,94	1,38	99,30	1,50
Illobane	53,8	33,8	4,9	0,06	1,38	0,72	0,60	1,89	0,60	0,63	98,36	1,59
Vryheid Coronation	50,7	33,9	6,6	0,10	1,68	1,26	0,62	2,14	0,80	1,37	99,10	1,50
Aloe Anthracite	56,4	29,4	5,2	0,08	1,40	0,60	0,73	2,18	1,31	0,50	97,80	1,92
Crustal average (Taylor, 1964)	60,3	15,6	7,2 ⁽²⁾	0,24	1,0	5,8	3,9	2,5	3,2	-	100,54	3,87

NOTES: (1) From Savage et al., 1977

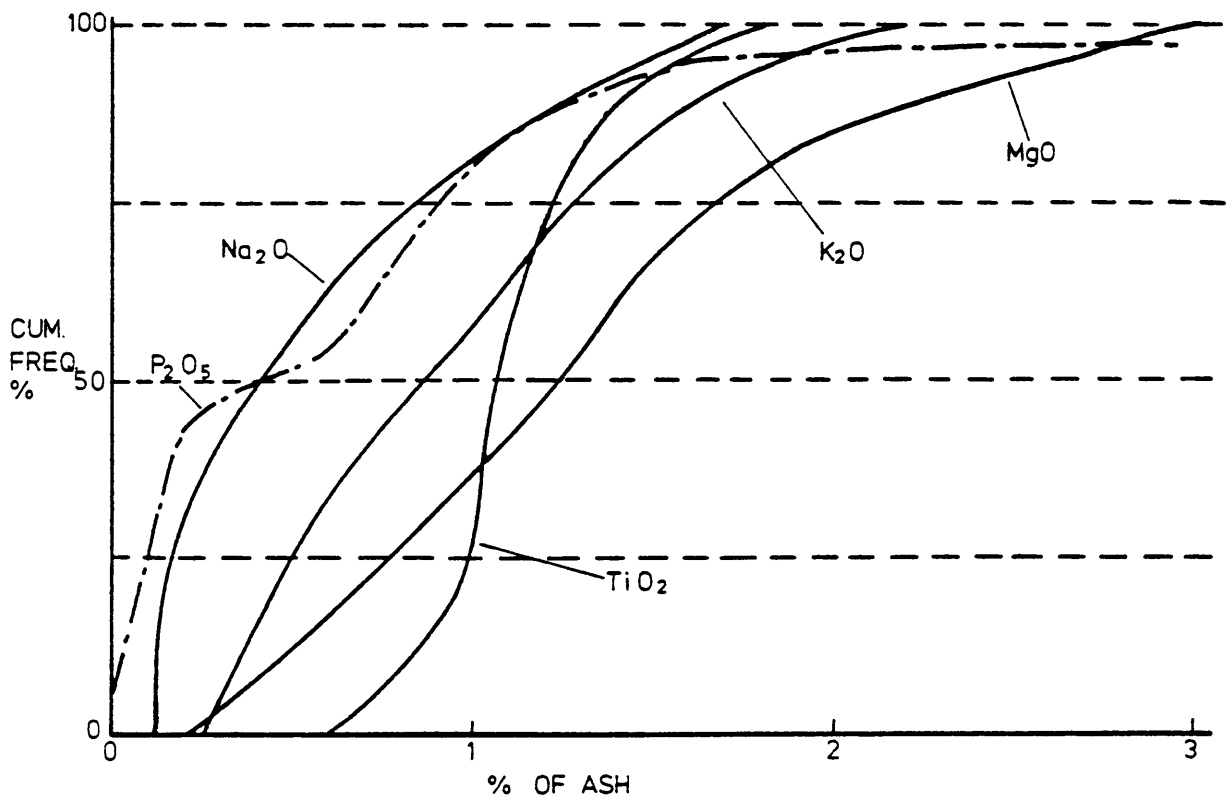
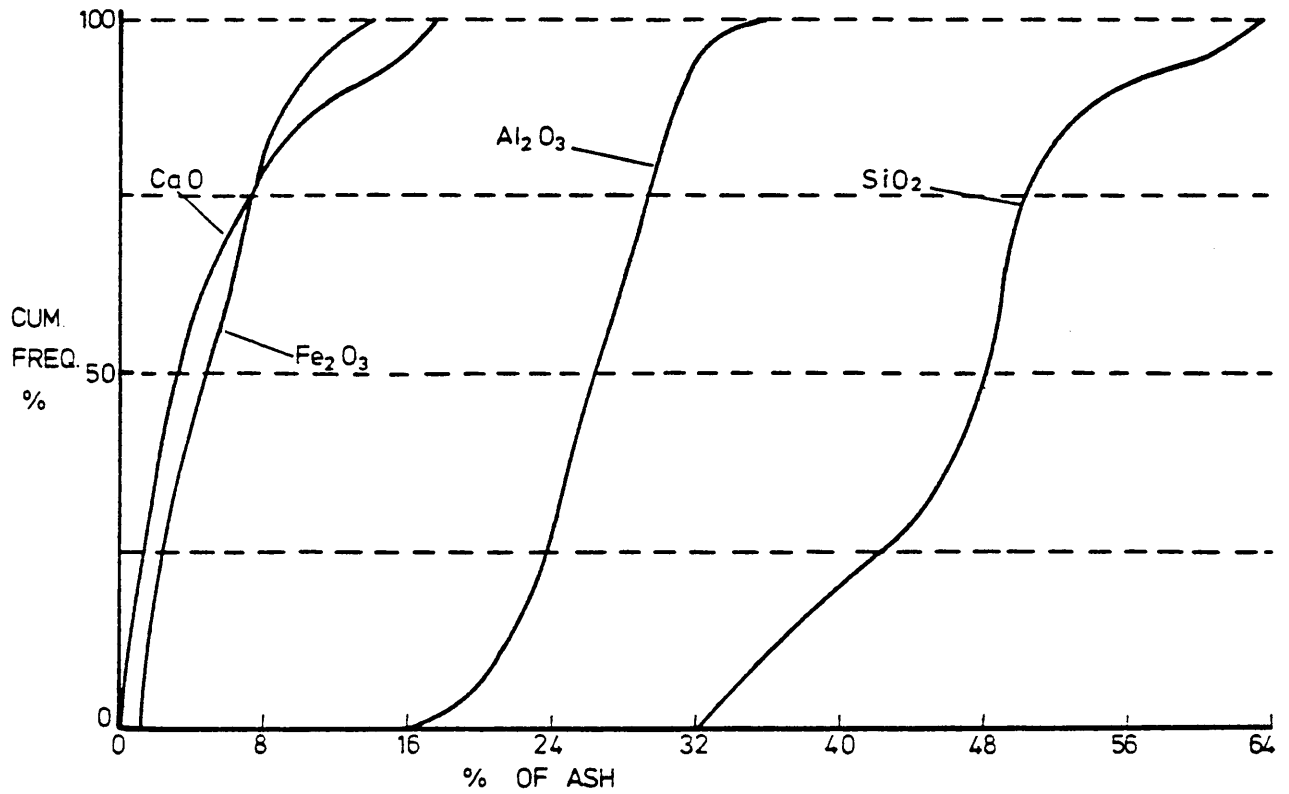
(2) 7,2% FeO = 8,0% Fe₂O₃

FIGURE 18 DISTRIBUTION OF MAJOR ELEMENTS IN COAL ASH AND CRUSTAL AVERAGE (TAYLOR, 1964).





**FIGURE 20 CUMULATIVE DISTRIBUTION OF ELEMENTS
IN COAL ASH.**



60,3; 3,9; 3,2 and 3,5 per cent, is probably due to their relative solubility under humid, acid-leaching conditions (Goldschmidt, 1954: p.371, 220, 146, 158). Although magnesium and potassium are indispensable to plant life (Goldschmidt, op. cit., p.220, 158) the severity of the leaching conditions precluded their enrichment in coal ash.

Alumina and titania are enriched in coal ash with median values of 26 and 1,2 per cent respectively, compared with only 15,6 and 1 per cent for the earth's crust (Taylor, 1964), probably as a result of leaching conditions and element accumulation by the plants (Goldschmidt, op. cit., p.302). Goldschmidt (op. cit., p.421) has noted that the titania in the ash of certain vitrains from the Northumberland coalfields may attain as much as 24 per cent.

Titania, alumina and ferric oxide in the coal ash show normal distributions with single maxima (Figures 18 and 19), but the curves for soda and potash are skewed and seem to follow each other rather closely. Phosphorus pentoxide in the coal ash has a wide distribution varying from 0,05 to 4 per cent.

B. Trace elements

Trace element determinations by emission spectroscopy and by atomic absorption spectrometry were carried out on six of the present coal samples during a study of trace element losses during the ashing of coal. Some of Watling and Watling's data (1976, p.162, Table 2) referring to the ashed coal and recalculated to an ash basis are given in Table X, together with Taylor's (1964) estimate of abundances of chemical elements in the continental crust.

Due to the rather limited data, the variability of the concentrations of trace elements between the various coalfields and seams cannot be considered as proven, but the coal ash appeared to be enriched in tungsten, gallium and sometimes strontium with enrichment ratios of 1 000, 10 and 3 to 5 respectively, relative to the earth's crust.

TABLE X

TRACE ELEMENT CONCENTRATIONS ($\mu\text{g/g}$ ASH), RECALCULATED AFTER WATLING AND WATLING (1976)

Colliery	Zn	Cd	Cu	Pb	Mn	Ni	Co	Cr	W	Sr	Ga	V
<u>Witbank No. 2 Seam</u>												
Springbok	29	1,5	58	22	102	80	44	109	1015	1394	139	285
New Clydesdale	52	<0,6	39	19	130	45	26	84	1045	1695	130	52
Delmas	63	0,5	42	26	316	89	21	53	1000	958	100	247
<u>Witbank No. 5 Seam</u>												
Greenside	43	<0,9	43	26	209	70	35	70	922	1009	148	252
<u>OFS</u>												
Cornelia Bertha I	15	<0,4	34	19	61	31	11	61	1130	859	107	61
<u>NATAL</u>												
Newcastle-Platberg	52	<0,4	34	47	43	43	22	56	819	293	116	125
Crustal average (Taylor, 1964)	70	0,2	55	12,5	950	75	25	100	1,5	375	15	135

The high tungsten values (800 to 1 100 ppm) are particularly interesting because its close crystallochemical relative, molybdenum, may also be present in relatively high concentration in South African coals, as has been found for Northumberland coals where molybdenum concentrations attained 0,05 per cent of the ash (Goldschmidt, 1954, p.559).

These data underline the views of Falcon (1978) and Snyman (1978) that a thorough investigation of the elements present in coal ash and their possible economic recovery, is long overdue.

X. NORMATIVE CALCULATIONS

Since no standard procedure for the direct determination of the minerals in coal is followed by the different laboratories concerned with coal analysis and because ash analyses are readily available, it was attempted to recalculate the ash analyses in terms of standard minerals. A comparison between the mineral matter in coal from data of different sources would thus be facilitated.

The "argillaceous norm" of Nicholls (1962) was used as a basis, with some important deviations. Because values for the free silica (quartz) are not usually available and as coal ash differs from an argillaceous rock in not containing carbonates, sulphides or moisture, the calculation method had to be amended. The scheme of recalculation is as follows:

A. Method of recalculation

1. The ash analysis is recalculated to a "coal basis" by multiplying the various oxides by the proportion of ash divided by the total of the ash analysis.
2. Sulphate is then ignored since the amount of sulphur fixed depends on the available calcite and ashing conditions. It is excluded from all further calculations.
3. The mass proportions are divided by the appropriate molecular weights to convert the constituent oxides to molecular proportions, except TiO_2 which is reported as such.
4. All the Fe_2O_3 is reserved for pyrite (FeS_2).
5. CaO is combined with P_2O_5 in the ratio 10 : 3 to form apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$.
6. Remaining CaO is combined with MgO in the ratio 1:1 and reserved for dolomite $\text{CaMg}(\text{CO}_3)_2$.

7. Usually CaO is left over after MgO has been used up and it is then reserved for calcite (CaCO_3). If CaO is deficient for converting all the MgO to dolomite, the remaining MgO is reported as excess MgO.
8. Na_2O and K_2O are combined with Al_2O_3 and SiO_2 in the ratio 1 : 3 : 6 to build eventual paragonite $\text{Na}_2\text{Al}_4(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4$ and muscovite $\text{K}_2\text{Al}_4(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4$ for normative "illite".
9. Remaining Al_2O_3 , combined with SiO_2 in the ratio 1:2, is reserved for kaolinite $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$. Excess SiO_2 is reported as quartz. Where not enough SiO_2 is present to satisfy the Al_2O_3 , no normative quartz would be present and excess Al_2O_3 is reported as such.

In these calculations sulphur, carbon dioxide and moisture were ignored. Allowance is made for them in the next step, by multiplying the molecular proportions by the adjusted molecular weights of the relevant minerals viz. pyrite, dolomite, calcite, mica and kaolinite. An example, (the Eikeboom product with 9,6 per cent of ash) is given in Table XI.

Although titanium and phosphorus often tend to become concentrated in the low ash fraction of coal since they show strong organic affinities (Gluskoter, 1975), it was decided to apply Nicholls's scheme as far as possible and report titanium as TiO_2 (rutile) and combine phosphorus with calcium, oxygen and hydroxyl to form apatite.

B. Results and discussion

Mineral matter in coal calculated by the argillaceous norm and the mineral matter determined by radio-frequency ashing (Table II) as well as the amount of mineral matter determined by X-ray diffraction on unorientated aggregates (Table VI) are given in Table XII. In order to compare the calculated data with the experimentally determined data, ratios were formed and in Table XIII, the average ratio of the former divided by the latter, and their standard deviations are given

TABLE XI

EXAMPLE OF RECALCULATION OF CHEMICAL ANALYSIS (EIKEBOOM PRODUCT; 9,6% ASH)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Total	Adjusted mole- cular weight	Mass % of coal	Argillaceous norm			
Molecular weight	60,06	101,9	159,7	142,0	-	56,08	40,32	94,19	61,99	-	-						
Mass % ash	46,4	36,4	2,9	1,51	1,87	4,9	0,94	0,50	0,12	1,43	96,97						
Mass % "coal"	4,59	3,60	0,29	0,150	0,190	0,485	0,093	0,050	0,012	-	9,46						
Molecular proportion x 10 ⁴	764	353	18	11	-	87	23	5	2	-	1263						
Pyrite	-	-	18	-	-	-	-	-	-	-	-	240	0,43	Pyrite			
Apatite	-	-	-	11	-	37	-	-	-	-	-	355	0,37	Apatite			
Dolomite	-	-	-	-	-	23	23	-	-	-	-	184	0,42	} Carbonates			
Calcite	-	-	-	-	-	27	-	-	-	-	-	100	0,27				
Excess MgO	-	-	-	-	-	-	-	-	-	-	-	40	-	Excess MgO			
Muscovite	30	15	-	-	-	-	-	5	-	-	-	796	0,40	} Clay			
Paragonite	12	6	-	-	-	-	-	-	2	-	-	764	0,15				
Kaolinite	664	332	-	-	-	-	-	-	-	-	-	258	8,57				
Quartz	58	-	-	-	-	-	-	-	-	-	-	60	0,35	Quartz			
Excess Al ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	102	-	Excess Al ₂ O ₃			
TiO ₂	-	-	-	-	-	-	-	-	-	-	-	-	0,19	TiO ₂			
Totals	764	353	18	11	-	87	23	5	2	-	1263	-	11,15				

NOTE: (1 Adjusted to element used for calculating mass per cent.

TABLE XII
 MINERAL MATTER (COAL BASIS, AIR-DRY) CALCULATED ACCORDING TO THE ARGILLACEOUS NORM,
 AND DETERMINED EXPERIMENTALLY BY RADIO-FREQUENCY ASHING AND BY QUANTITATIVE X-RAY DIFFRACTION

Colliery	Argillaceous norm (mass %)								Total mineral matter %	X-ray diffraction % ⁽²⁾			
	Clay	Quartz or excess Al ₂ O ₃ ⁽³⁾	Car-bonates	Pyrite	Apatite	TiO ₂	Excess HgO	Total		Clay	Quartz	Car-bonates	Pyrite
Witbank No. 2 Seam													
Elkeboom	9,12	0,35	0,69	0,43	0,37	0,19	-	11,15	11,4	5,12	0,66	0,44	0,26
Springbok	12,45	0,03 ⁽³⁾	1,40	1,27	0,74	0,22	-	16,11	16,3	9,09	0,35	1,10	0,97
New Clydesdale	11,97	0,34 ⁽³⁾	3,53	2,20	0,54	0,21	-	18,79	19,1	8,24	-	2,48	1,52
Alhlon	12,58	0,12 ⁽³⁾	4,24	1,25	1,64	0,26	-	20,09	20,5	9,53	0,48	4,10	0,91
Delmas	13,40	3,02	3,00	2,54	0,03	0,27	-	22,26	23,4	7,20	3,72	2,11	1,30
Witbank No. 4 Seam													
South Witbank	14,00	4,06	3,34	1,22	0,50	0,31	-	23,43	24,3	6,75	4,38	2,28	0,97
Anglo Power (Kriel)	12,52	4,08	5,33	1,32	0,54	0,36	-	24,15	25,3	6,74	4,88	3,08	1,06
Witbank No. 5 Seam													
Biesbok	7,57	5,27	0,44	0,91	0,30	0,15	0,07	14,71	15,2	4,65	5,38	0,38	0,43
Springbok	7,00	4,29	0,28	0,65	0,03	0,16	0,03	12,44	12,9	3,70	4,37	-	0,32
Greenside	8,23	2,21	1,69	0,68	0,27	0,16	-	13,24	13,7	4,68	2,38	1,17	0,31
Navigation	8,21	3,66	0,70	0,35	0,10	0,15	-	13,17	13,5	4,16	3,79	0,34	0,08
Breyten-Ermelo													
Union	9,90	2,09	1,67	1,18	0,07	0,20	-	15,11	16,0	5,00	2,12	0,94	0,82
Spitzkop	8,57	2,63	1,93	2,04	0,03	0,16	-	15,36	16,1	3,62	3,08	0,96	1,23
Usutu (S & E)	9,48	3,59	3,09	2,81	0,30	0,22	-	19,49	20,5	4,82	4,28	1,22	1,90
South Rand & OFS													
Grootvlei	20,97	3,82	4,34	1,31	0,20	0,25	-	30,89	32,1	11,48	4,56	2,72	0,77
Cornelia Bertha I	16,27	6,71	4,18	1,64	0,50	0,39	-	29,69	31,5	9,73	8,05	1,78	0,98
Sigma	20,97	7,22	3,91	1,56	0,17	0,47	-	34,30	34,9	12,00	8,19	1,79	0,50
Coalbrook No. 2	20,33	1,51	4,09	1,70	0,84	0,40	-	28,87	30,6	10,60	2,56	2,71	0,90
Vierfontein	21,76	6,70	2,58	2,44	0,07	0,35	-	33,90	35,2	8,50	4,53	0,56	1,60
Klip River, Natal													
Kilbarchan	18,21	3,91	3,48	2,18	0,20	0,30	-	28,28	29,3	22,62	2,82	2,50	1,13
Ballengeich	12,93	1,70	1,68	1,50	0,20	0,22	-	18,23	18,9	9,12	0,86	0,67	0,86
Durban Navigation	9,10	0,83	1,29	1,18	0,17	0,15	-	12,72	13,2	7,39	0,42	0,66	0,94
Natal Navigation	10,97	1,85	0,41	2,08	0,10	0,18	-	15,59	15,9	9,02	1,40	-	1,42
Indumeul	7,51	0,67	2,09	1,34	0,37	0,11	-	12,09	12,7	8,08	0,32	1,33	0,93
Newcastle-Platberg	18,58	3,46	0,20	3,70	0,10	0,26	0,12	26,42	26,5	17,44	2,51	-	2,22
Utrecht													
Balgray	7,87	1,87	5,69	2,64	0,44	0,18	-	18,69	18,2	11,99	1,84	4,92	0,96
Utrecht	7,59	1,34	4,29	2,86	0,23	0,13	-	16,44	16,7	7,06	1,02	3,29	1,70
Ungala	7,69	1,97	3,70	2,15	0,37	0,16	-	16,04	16,7	1,32	1,88	2,17	1,46
Zimbutu	8,36	1,61	2,09	2,45	0,30	0,14	-	14,95	15,8	2,06	1,74	1,70	1,74
Paulpietersburg-Vryheid													
Dumbe	7,45	2,02	0,59	2,10	0,03	0,13	-	12,32	12,6	3,74	2,03	-	1,05
Brockwell	10,45	2,15	0,48	1,85	0,13	0,19	0,06	15,31	15,5	14,30	1,77	-	0,41
Tendega	9,92	1,31	0,94	1,70	0,03	0,19	-	14,09	13,9	4,40	1,37	0,28	0,98
Hlobane	11,22	1,85	0,24	0,96	0,03	0,18	0,03	14,51	14,7	5,49	1,22	-	0,32
Vryheid Coronation	10,81	1,38	0,41	1,25	0,03	0,21	-	14,09	14,2	6,86	1,53	-	0,68
Aloe	8,94	2,66	0,17	0,95	0,03	0,17	0,05	12,97	12,7	15,81	1,61	-	0,28

NOTES: (1) Total amount of mineral matter determined by radio-frequency ashing (Table II).

(2) From Table VI.

(3) Excess Al₂O₃, other values denote quartz.

for Transvaal and OFS; and Natal coals, separately.

The total of the argillaceous norm corresponds rather closely with the amount of mineral matter in coal determined experimentally by radio-frequency ashing (Table II), but is generally slightly lower: the average ratio of the calculated mineral matter to the determined mineral matter is 0,96 for Transvaal and OFS; and 0,98 for Natal coals, with standard deviations of single ratios of well within ± 3 per cent.

However, with the exception of the quartz values, the argillaceous norm almost always overestimates the amount of the various minerals in coal by an average factor of 1,8. This is hardly surprising since apart from the approximations inherent in the recalculation scheme (Table XI) which must lead to some minerals being overestimated (e.g. forming pyrite from all the Fe_2O_3 in the analysis) - the difficultly definable amorphous and poorly crystalline class of mineral matter (Tables VII and VIII) which includes the ash-forming part of gels and salts of humic acids - are given distinct mineral identities.

The systematic deviations in the quartz values where the amount of calculated quartz in Transvaal and OFS coals is almost always less than the determined values (ratio 0,84), whereas for the Natal coals there was generally more calculated quartz relative to determined quartz (average ratio 1,4), are probably due to the fact that most Natal coals contain illite as their principal clay mineral (Table III). According to Grim (1968, p.580) the silica to alumina ratio of illite varies from 1,7 to 2,4 whereas in the norm calculations a constant 2 to 1 molecular relationship (silica to alumina ratio of 1,18 by mass) was used for calculating normative "illite" (muscovite and paragonite), as well as for kaolinite. It is evident that for the calculated data, the "extra" quartz in Natal coals is an occult mineral in the illite.

TABLE XIII

AVERAGE RATIOS AND THEIR STANDARD DEVIATIONS OF THE ARGILLACEOUS
NORM DIVIDED BY THE DETERMINED DATA, CALCULATED FROM TABLE XII

	Total mineral matter	Clay	Quartz	Carbonates	Pyrite
<u>TRANSVAAL AND OFS</u>					
No. of samples	19	19	17	18	19
Average ratio:					
<u>calculated data</u> <u>determined data</u>	0,964	1,84	0,844	1,84	1,87
Standard deviation %	+1,50	+16,5	+32,9	+43,6	+40,2
<u>NATAL</u>					
No. of samples	16	16	16	9	16
Average ratio:					
<u>calculated data</u> <u>determined data</u>	0,983	1,72	1,35	1,80	2,08
Standard deviation %	+2,43	+81,8	+29,3	+40,1	+42,7

From the standard deviations listed in Table XIII, (± 30 to 40 per cent for minerals other than clay) variations in individual ratios of calculated data to X-ray diffraction data are shown to be considerable. The ratios for the clay contents in the Transvaal and OFS coals (mainly kaolinite) are less variable with a standard deviation of ± 17 per cent, than for the Natal coals (standard deviation ± 82 per cent). The poor agreement of the Natal values must be partly due to the quantitative X-ray diffraction determinations on the unorientated aggregates either overestimating the amount of clay present in the anthracitic and lean coals (viz. Kilbarchan, Balgray, Brockwell and Aloe products) due to the use of a Fithian illite in the calibrations, or underestimating the amount of clay where a relatively high proportion of expandable clays is present (e.g. Umgala and Zimbutu products).

XI. SUMMARY AND CONCLUSIONS

The occurrence and distribution of mineral matter in 35 commercial grade coals originating from thirty-four collieries in the Transvaal, OFS and Natal were determined using relatively new methods of radio-frequency ashing and automated powder X-ray diffractometry.

By means of radio-frequency ashing the total amount of "inorganic" material, and hence also the amount of material not shown by X-ray diffraction, was determined. On average this amorphous material made up at least 40 per cent of the mineral matter in the low rank OFS and Ermelo coals, but less than 30 per cent for the high rank Natal coals. The apparent relationship between coal rank and amount of amorphous material may be due to the use of a Fithian illite in the calibrations, or it may indicate that neoformation of minerals had occurred during coalification.

The amount of radio-frequency ash residue (mineral matter) was always higher than the ash determination due to many of the minerals occurring in coal being decomposed during ashing. Ash yields varied from 10 to 30 per cent with mineral matter to ash ratios varying from 1,08 to 1,25. The median coal sample yielded 13,4 per cent of ash, 16,0 per cent of mineral matter and a mineral matter to ash ratio of 1,19.

X-ray diffraction on orientated aggregates of low temperature (350°C) ash showed the average clay mineral composition for Transvaal and OFS coals to resemble Australian Permian coal with somewhat more illite and less expandable clays, whereas the average clay mineral composition for the Natal coals falls within the field of the Herrin (No. 6) coal member of the Illinois basin. Kaolinite is prevalent (greater than 80 per cent of the clay minerals) in the low rank coals (dry ash-free carbon content less than 82 per cent). Conversely the Natal anthracites (average of 90 per cent of dry ash-free carbon) contain more than 80 per cent of illite in the clay. Montmorillonite, mixed-layer and regularly interlayered illite-montmorillonite are also present and on average, the Transvaal and also the Natal coking coal products contain at

least 20 per cent of expandable clays (relative to Wyoming bentonite), a fact which may be significant. Although the maceral composition of the low rank coals influences the clay mineral composition, the high illite content of Natal coals is thought to be due to neoformation during late diagenesis, caused by the dolerites.

The amount of mineral matter was determined directly on the coal samples by X-ray diffraction. Illite is the most variable constituent (0 to 86 per cent of the mineral matter). The mineral matter in the median coal sample consists of more than 37 per cent amorphous material (including poorly crystalline and expandable clays), 23 per cent kaolinite, 10 per cent quartz, 7 per cent illite, 4 per cent pyrite, 3 per cent calcite, 1 per cent dolomite and siderite is absent from over half of the samples.

The chemical analyses on the coal ash showed it to have features of a hydrolysate sediment (deficiency in SiO_2 , MgO , K_2O and Na_2O relative to the earth's crust) modified by the element concentrating activities of the plants (excess Al_2O_3 and TiO_2). Of the trace elements, tungsten is enriched about 1 000 times over the crustal average in the six coal ashes analysed. A detailed study of trace element concentrations in South African coals may be economically rewarding and is long overdue.

The chemical analyses were recast into normative minerals and the total agrees remarkably well with the total mineral matter determined experimentally by radio-frequency ashing. However, clay, carbonates, pyrite, and quartz (in Natal coals) are usually overestimated in the argillaceous norm relative to the determined values, often by a factor of 1,8 with standard deviations of the factors of \pm 30 to 40 per cent.

ACKNOWLEDGEMENTS

Although the author must bear responsibility for any views expressed, the permission of the Acting Director and Board of the Fuel Research Institute, Pretoria, in allowing this work to be published in the form of a thesis is gratefully acknowledged. The support of the Research Advisory Committee to the Institute in making funds available for the purchase of apparatus used in this study is acknowledged with thanks.

Prof. C.P. Snyman and Dr. E. Förtsch are thanked for their guidance and encouragement, without which, the project would not have been completed within a reasonable period of time.

The author is indebted to Dr. P.G. Sevenster for suggesting and supporting this project in the first instance and to Mr. W.H.D. Savage for granting access to his collection of samples and for his interest in the work. Finally the author wishes to express his thanks to Dr. W.T.E. von Wolff, the late Mr. B. Moodie, and the author's colleagues at the Institute for their interest; the library, drafting and technical staff for their cheerful assistance and Mrs. S.M. Duursema for the extremely accurate typing of the manuscript.

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