SOME FACTORS INFLUENCING THE BEHAVIOUR OF THE OPTICAL PROPERTIES OF CARBONISED MACERALS

VOLUME I

TEXT

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Thesis submitted for the Degree of

Doctor of Philosophy

University of Newcastle upon Tyne

MARCH 1975

TO MY FATHER

PRESENTATION OF THESIS

The general contents are listed at the beginning of Volume I which, with Volume II, contains text, figures, references, etc. Each main part in Volumes I and II, of which there are 10 has a detailed list of contents.
Volume III contains Appendices, Plates and detailed descriptions of morphological changes during heat-treatment of macerals.

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(a) Abstract

This Thesis considers certain factors whose influence on the optical properties of coal macerals heated over a range of temperatures and under varying conditions, have not been examined in detail. Reflectivity measurements in two media have allowed derivation of the fundamental optical parameters, refractive and absorptive indices, which, along with bireflectance, have been related to changes in the molecular structure of the heated macerals. The factors studied here are heating rate, prolonged constant heating below the decomposition point, the effect of mixing vitrinites and sporinites before carbonisation, as compared with the optical properties of each maceral carbonised separately, the effect of pressure on carbonised vitrinite and finally heating at elevated temperatures in the range 1000° to 2500°C. The following conclusions were drawn:-

1. On the basis of the variations in the optical properties of six vitrinites of different rank carbonised at three different heating rates, the anisotropy (through bireflectance) and the aromaticity (through reflectivity and absorptive index) at any specific temperature are the higher as the heating rate rises, particularly for graphitising vitrinites. The form of the refractive index curves differs for softening and non-softening vitrinites, indicating changes in the rate of the build-up and breakdown of crystallites with

the varying heating rates. Increased bireflectance and size of mosaic structure reflect increasing fluidity with rising heating rate.

2. Progressive increase of holding time up to 8 months during heating below the decomposition point of six vitrinites varying in rank causes an increase in aromaticity which is reflected in the optical properties of the vitrinites. Influence of holding time on the optical properties is the greater the lower is the maceral rank and the higher is the temperature. Mosaics can develop at 350°C after treatment for 8 months.

3. Carbonisation of sporinites produces optical properties in these chars similar to those of carbonised vitrinites. Depending on rank, these also display similar trends, but the sporinite chars always possess a mosaic. The optical properties of carbonised mixtures of sporinite and vitrinite differ from those of the carbonised individual macerals, lying approximately intermediate to the trends for the carbonised individual macerals.

4. Carbonisation of a coking-coal vitrinite under hydraulic pressure shows that above the resolidification temperature, the higher is the pressure the lower is the reflectivity and the smaller is the mosaic size. In the plastic stage the position is reversed. For this rank of vitrinite at least, there is no clear-cut relationship between the optical

properties of the maceral carbonised under pressure, in a bomb and in an 'open boat'.

5. In an attempt to continue the earlier trends of optical properties of carbonised vitrinites established below 1000°C, three vitrinites were heat-treated in the range 1000° to 2500°C. The chars show anomalous trends of optical data, if the starting ranks are bituminous. The anomalies appear to be due to a gradual deterioration in surface quality caused by molecular structural changes in the semi-graphitising to graphitising zone. The optical properties of anthracite behave more normally, showing a gradual increase in structural ordering towards that of graphite.

The results. of these several studies should assist in the interpretation of the thermal histories of semi-cokes and cokes.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to:-

Dr. D. G. Murchison, who supervised this research project for his valuable advice and discussion during the research and also devoting so much of his valuable time in preparation of the manuscript.

Dr. N. H. Battey of the University of Newcastle upon Tyne, Department of Geology for instruction in the techniques of X-ray diffraction.

Mr. J. Allan of Organic Geochemistry Unit, Department of Geology, The University of Newcastle upon Tyne, for supplying the sporinites and corresponding vitrinite samples.

Mrs. A. Summerbell, Miss B. Arnold and Mr. K. Hall for their technical assistance.

Miss G. Hermon for undertaking the carbonisation of all samples under pressure and for valuable discussion of the experimental work; to Dr. H. Marsh for guidance in this work and discussion of several aspects of this Thesis; and to Professor D. Whiffen, F.R.S., Honorary Director of the Coke Research Laboratories for permission to make use of the laboratory facilities.

Mr. R. E. Goddard, Chief Scientist, National Coal Board (Kent) and the National Coal Board Executive for access to Whitonstall Opencast Site, Northumberland.

ACKNOWLEDGEMENTS (contd)

Mr. C.Cornford and Mr. J. Gibbons, Mrs. G. Kavari, Mr. E. Scott, for many useful and detailed discussions.

Mrs. E.M.Gannie for typing this thesis.

Finally, I would like to express my sincere gratitude to my father for encouragement and help throughout this project.

This programme of research was partially financed by the Phalavi Foundation.

* * *

GENERAL INTRODUCTION AND STATEMENT OF PROBLEM

The optical properties of semi-coke and cokes are dependent on many factors, some of which have received detailed attention, others which have not. The present research programme was designed to study the influence of several factors on the optical properties of different ranks of vitrinites primarily, but also sporinites, to which little attention has been given. These factors are heating rate, holding time below active decomposition, interaction and effect of different macerals (vitrinite and sporinite) on one another, pressure and the extension of the temperature range above 1000°C.

The work in this Thesis rests on a basis of earlier optical studies on carbonised vitrinites in these laboratories. The optical properties of carbonised vitrinites have been studied in the Organic Geochemistry Unit by Davies (1965); Marshall (1968) and Goodarzi (1971). Davies (1965) examined the variation of the optical properties of laboratory carbonised vitrinites up to 600°C, Marshall (1968) determined the dispersion curves of optical properties of three vitrinites carbonised up to 750°C over the range 403nm to 709nm. These researches essentially only considered the influence of rank on the optical properties of carbonised vitrinites, Goodarzi (1971) extended the carbonisation temperature up to 950°C and in addition to the influence of rank, studies the effect of pre-oxidation on the optical properties of carbonised vitrinites, relating the optical data to molecular changes in the residues (see also Goodarzi and Murchison 1972, 1973). The influence of rank then on the optical properties of carbonised vitrinites is understood, so also from the work of other investigators is the effect of grain size, 'soak period' and oxidation. One major gap in possible factors affecting optical properties appeared to lie in variable heating rates. Another area that required study was the possible effect of long-term heating below the decomposition points of the vitrinites. Each of these factors has a geological bearing.

Since little is known about the optical behaviour of carbonised macerals, other than vitrinite, the important maceral sporinite has been carbonised and its optical properties in relation to molecular structural changes examined and compared. The optical properties of mixed vitrinite/sporinite blends have also been studied, since such changes have a bearing on the properties of that part of cokes developed from reactive constituents.

In these first three studies of this Thesis, the influence of time, temperature and constituent composition is considered. The fourth Part of the Thesis covers the effect of pressure on a single vitrinite carbonised under hydraulic pressure in a gold capsule in a 'bomb'. These data are compared with results for the same vitrinite carbonised under atmospheric pressure.

The final Part of the Thesis extends the earlier work of Goodarzi (1971) to higher temperature levels (1000°C). Patterns of variation of the optical properties of vitrinites of three rank levels are examined in relation to changing molecular structure over a temperature range of approximately 1400°C and compared with the variations observed in the range 0° to 1000°C.

Although the various sections of this Thesis are discrete in themselves, they are also closely related and have a bearing on the response of the organic matter under both laboratory controlled and natural conditions, with consequent effect on the optical properties.

PART I <u>PREVIOUS RELATED STUDIES</u>

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1. OPTICAL PROPERTIES OF COAL MACERALS

(a) Introduction

Reflectivity of coals is now used extensively and regarded as a valuable parameter in coal science; directly or indirectly it may be employed to determine degree of coalification (rank), conditions of carbonisation, including carbonisation temperature, level of oxidation, aspects of molecular structure and petrological characters for coking plants. The optical properties of coal macerals are now well known and satisfactory relationships between the optical constants of vitrinites and other macerals with their chemical parameters, for example, volatile-matter yield, carbon and hydrogen contents and the atomic ratio H/C are well established. Optical properties of coal constituents are more sensitive parameters and are also in some respects more widely applicable and easier to determine than chemical properties.

In this section the relation between the optical properties of vitrinites and sporinites with rank will be discussed.

(b) Reflectivity

(i) Vitrinite The reflectivity of vitrinite increases with progressive rise of coalification; the increase is slow up to carbon content 89.0% (daf), but then it rises at a greater rate with further increase in rank (Fig. 1). According to Mackowsky

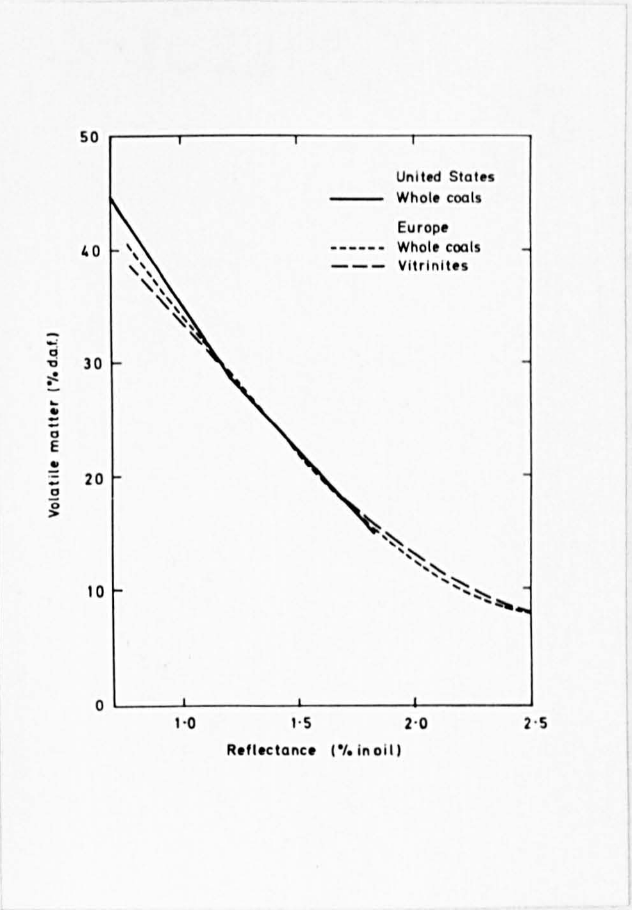


Fig 1 Variation of oil reflectivity of vitrinite with volatile matter (after McCartney and Teichmuller 1972)

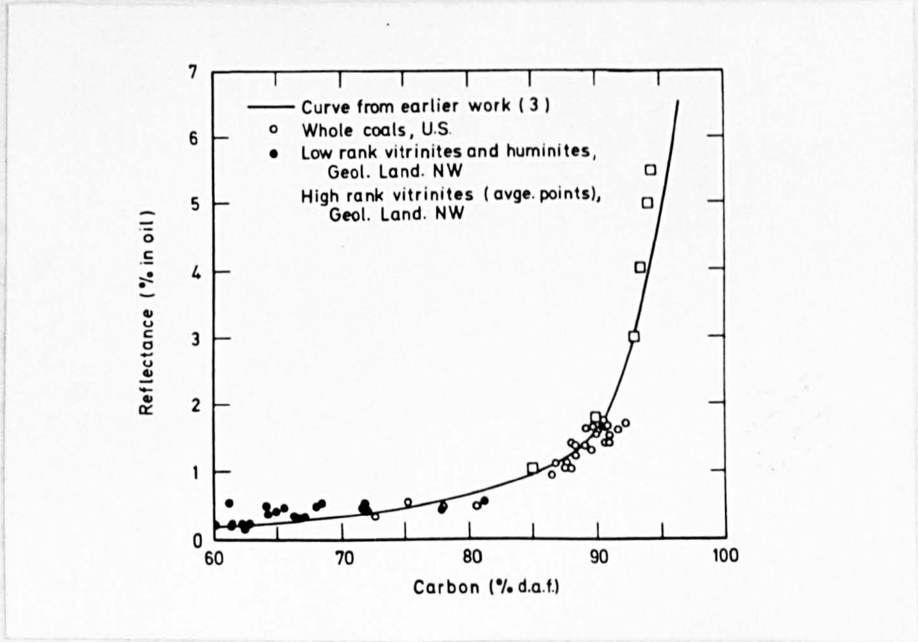


Fig 2 Variation of oil reflectivity of vitrinite with rank (after McCartney and Teichmuller 1972).

(1961), reflectivity variations in coals are a function of the number of aromatic lamellae and the changes in number and form during coalification.

McCartney and Teichmüller (1972) have recently classified coals on the basis of the reflectivity of their vitrinitic components and have discussed the relationships between reflectivity and volatile matter (Fig. 1), carbon (Fig. 2), hydrogen and moisture contents at different ranks. They conclude that a relationship exists between reflectivity and rank, which is poor for sub-bituminous coals and lignites (Roil ∠ 0.5%), satisfactory for low-rank bituminous coals, excellent for high-rank bituminous coals and good for anthracitic coals. Bituminous and anthracitic coals can be subdivided according to their different reflectivity ranges.

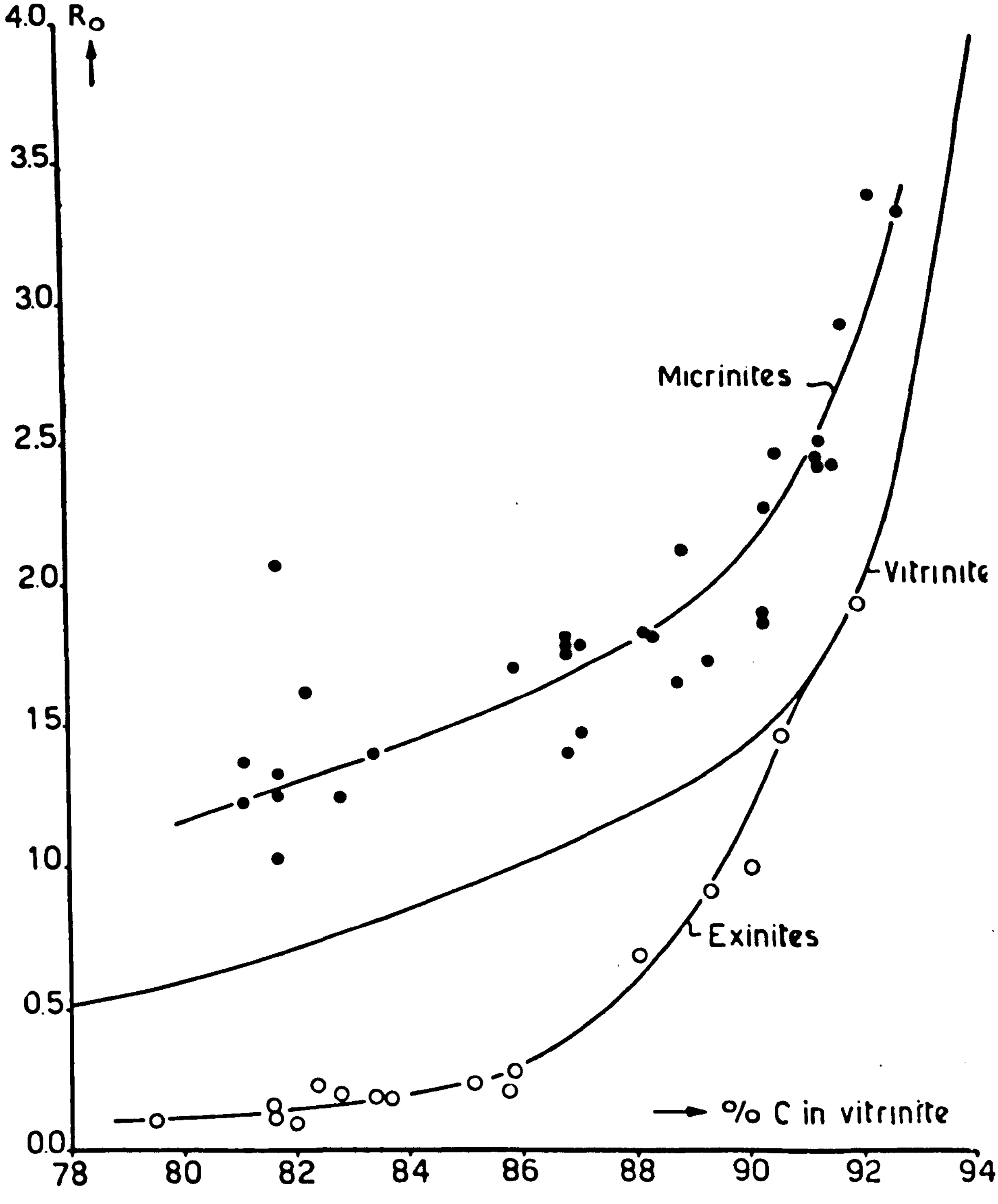
<u>TABLE I</u> (from McCartney and Teichmüller 1972)

Coal Rank	Reflectivity
High-volatile bituminous	0.50 - 1.12 per-cent
Medium-volatile bituminous	1.12 - 1.51 per-cent
Low-volatile bituminous	1.51 - 1.92 per-cent
Semi-anthracite	1.92 - 2.50 per-cent
Anthracite	2.50 per cent

There are natural rank boundaries which are:

1. The coalification jump Roil = 1.20%
   or at 29% volatile matter

Fig. 3 Variation with rank (carbon content) of oil reflectivity of macerals, vitrinite, exinite and micrinite (after Dormans *et al.* 1957).



4.0
R_o
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
78
80
82
84
86
88
90
92
94
Micrinites
Vitrinite
Exinites
% C in vitrinite

2. the disappearance of exinite Roil = 1.50 – 1.55%
   20 – 22% volatile matter
3. boundary between bituminous-semi anthracite and
   anthracitic coal Roil = 2.50 – 2.55%

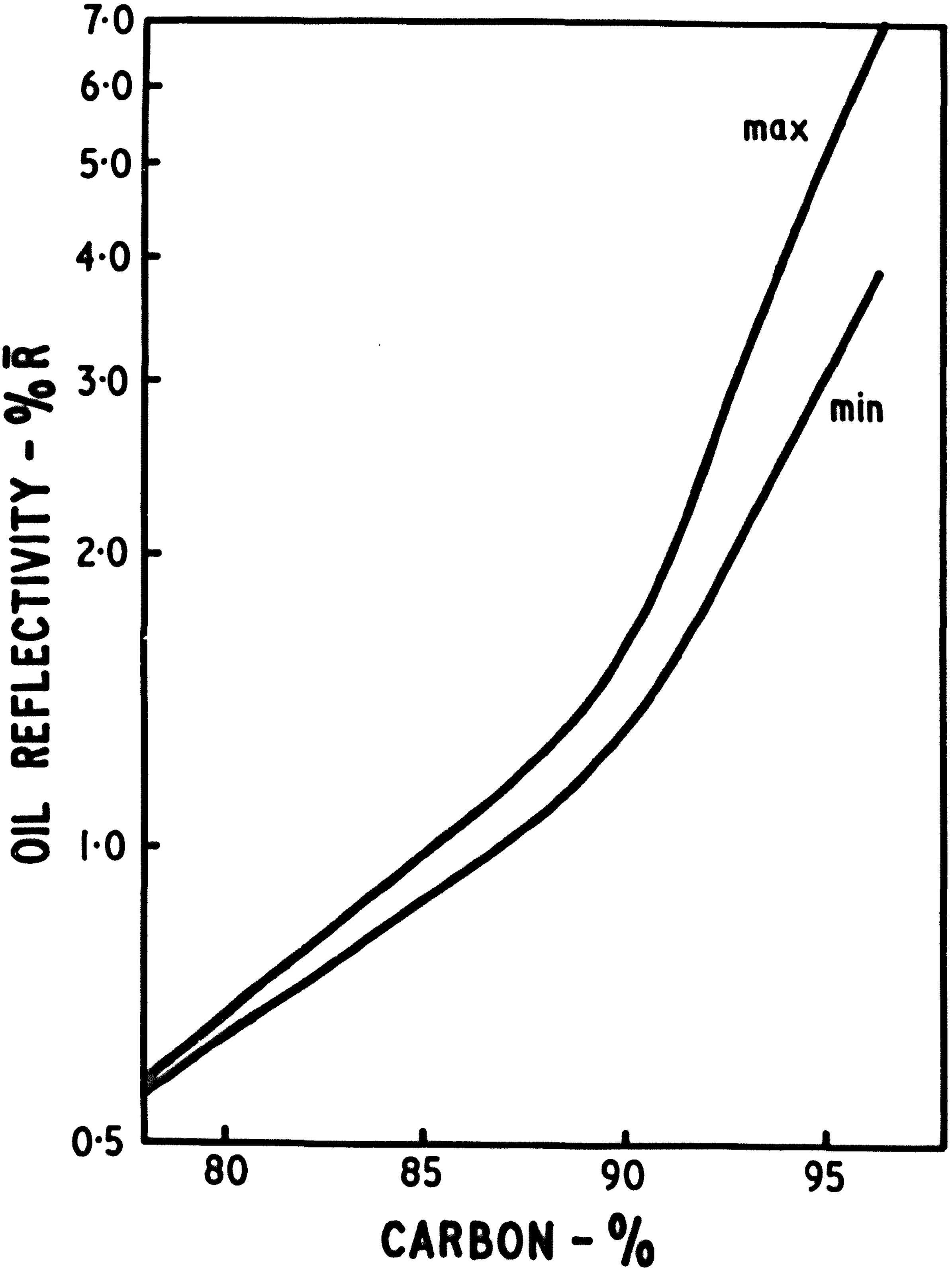
(ii) Sporinite According to Stach (1955); Dormans *et al.* (1957) and van Krevelen (1961), the reflectivity of sporinite (exinite) only increases slightly with rise in rank and at a lower rate than that of vitrinites up to 86% carbon content, after which the reflectivity rises more quickly up to approximately 91% carbon content (18% volatile-matter yield), when the sporinite track coincides with that of vitrinite then follows the same trend (Fig. 3).

(c) Bireflectance ($R_{max} - R_{min}$)

(i) Vitrinite The difference between the maximum reflectivity of vitrinite (or other appropriate maceral) in a section parallel to the bedding and the minimum reflectivity in the same section perpendicular to the bedding is an expression of the degree of orientation of the structural elements of the vitrinite and is termed the 'bireflectance'.

Anisotropy in vitrinite has been observed by many workers (e.g. Hirsch 1954; Broadbent and Shaw 1955; Murchison 1958; van Krevelen 1961 and McCartney and Ergun 1967). Hirsch (1954) studied a series of thin sections of vitrinite (carbon = 78.3 to 94.7% daf) by X-ray diffraction methods and inferred that

Fig 4 Relationship between carbon content and maximum and minimum oil reflectivity of vitrinite illustrating bireflectance (redrawn after I.C.C.P. 1963).


7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·5
OIL REFLECTIVITY - %R̄
max
min
80
85
90
95
CARBON - %

the rise of optical anisotropy with coalification was probably due to increase in the degree of ordering of the molecules.

According to van Krevelen (1961), vitrinite of 81.5% carbon content is the lowest rank vitrinite which displays anisotropy, but with the use of oil immersion anisotropic effects may be observed at ranks even lower than 80.0% carbon content. Lowry (1963) stated that bireflectance becomes strong at around 88% carbon content, but even at 96% carbon content, the degree of orientation of structural elements is far from perfect (Fig. 4).

(ii) Sporinite To the author's knowledge there is no report of the anisotropy of fresh sporinite, which generally does not show any anisotropy, even in coals of 88% carbon content, probably because the spores possess larger amounts of amorphous material and fewer aromatic layers; also the degree of preferred orientation is lower than that of the corresponding vitrinite at any rank level.

(d) Refractive Index

Refractive index is one of the fundamental optical properties which can be derived from the measured reflectivities. Refractive index increases with rise of rank slowly up to 92% carbon content and then remains constant or decreases slightly in fresh vitrinites. It has been suggested that the decrease of refractive index at about 92% carbon content is due to the slackening of the crystallite packing caused by better orientation of the aromatic layers and an increase of their diameter (see Hirsch 1954; Broadbent and Shaw 1955; McCartney and Ergun 1959; van Krevelen 1961 and McCartney and Ergun 1967). McCartney and Teichmüller (1972) state that the refractive index of coal is a function of the atomic density and increases with the increasing degree of aromatization.

(ii) Sporinite The refractive indices of sporinites lack systematic investigation, but the results of Dormans *et al.* (1957) and van Krevelen (1961) show that the refractive index of sporinite increases with rising rank, but at a lower rate than that of vitrinite up to 91% carbon content, until it reaches a value of approximately 1.96, after which there is convergence of the two tracks.

(c) Absorptive Index

(i) Vitrinite Absorptive index is also a fundamental optical constant which is calculated from determined reflectivities. The absorptive index increases slowly with rise of rank up to 90% carbon content and then more rapidly with further increase of rank. The rapid rise of absorptive index after 90% carbon content is related to electronic absorption in the aromatic layers (Hirsch 1954). According to McCartney and Teichmüller (1972), absorption is dependent on the number and the mobility of delocalised electrons. Increase in the size and in the degree of condensation of aromatic structures in coal results in an increase in the electron mobility and a rise of the absorptive index.

(ii) Sporinite Dormans et al. (1957) state that the absorptive index of sporinite is negligible (some negative values of the square of the absorptive index were obtained in the calculation of their results) which could be due to small errors in reflectivity measurement). However, the absorptive indices of sporinite seem to follow a similar but a lower trend than those of vitrinites of equivalent rank range.

2. OPTICAL PROPERTIES AND MOLECULAR STRUCTURE OF COAL MACERALS

(a) Introduction

All molecules which are not entirely symmetrical are optically anisotropic. Random orientation of asymmetric molecules in the amorphous state excludes the possibility of an anisotropy, but with increase in the ordering of such molecules, optical anisotropy will increase. Coal macerals possess a polymeric structure more or less similar to this summarised description.

(b) Vitrinite

The possible correlation between the anisotropy of vitrinite and its molecular structure is considered by Dahme and Mackowsky (1951), who suggest that coal (vitrinite), depending on rank, has a layered structure, because of the presence of stratified lamellae. Anisotropy increases with development in the size of crystallites composing the lamellae. Alignment of the crystallites is caused originally by pre-orientation of the vegetable tissue, and the later effects of overburden pressure and loss of volatile matter during coalification allows the lamellae to pack more closely. Williams (1953) supported the above opinions, believing that the overburden pressure and tectonic forces are responsible for the development of anisotropy in coal.

Data on the molecular arrangement of coal constituents can be obtained directly by study of X-ray diffraction patterns of coal macerals. Comprehensive X-ray diffraction studies have been made since 1944 on coal macerals, mainly vitrinite, by Blayden et al (1944); Nelson (1954 a and b); Hirsch (1954); Cartz et al. (1956); Ergun (1958) and Cartz and Hirsch (1960).

Blayden and his co-workers (1944) suggest a 'turbostratic lamellar structure' for coal (vitrinite), qualitatively confirmed by Hirsch (1954). According to Blayden et al. (1944), coal contains stacked polycondensed aromatic layers. Coalescence of a number of lamellae with roughly parallel orientation forms 'crystallites'. The degree of ordering and the average dimensions of the aromatic layers increase with rise in coalification.

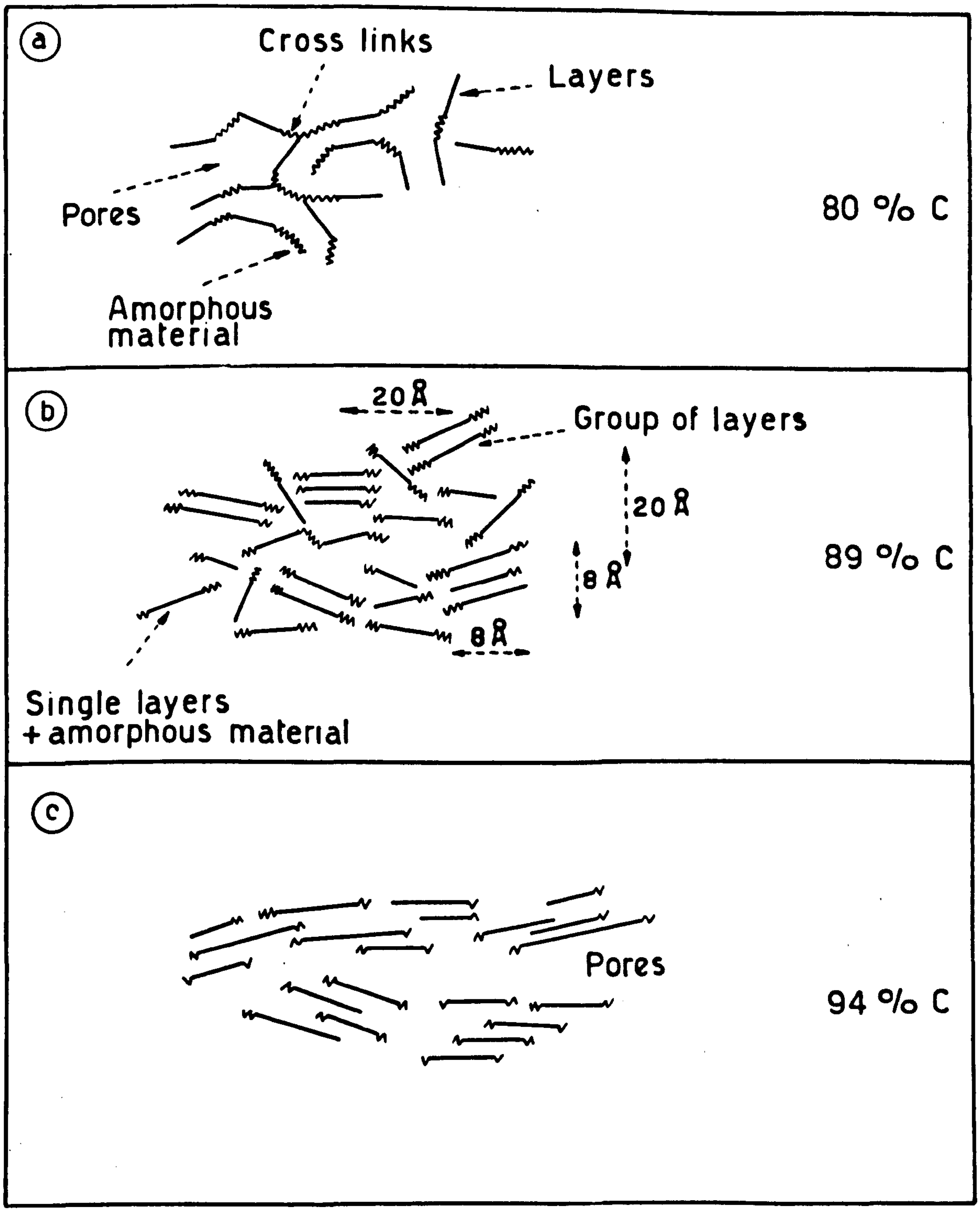
Hirsch (1954) and Cartz and Hirsch (1960) report detailed X-ray studies of a series of vitrinites of different rank (carbon = 78.3 - 94.1% daf), drawing the following conclusions about basic vitrinite structure (Fig 5).

(1) Coal with less than 85% carbon content possesses an 'imperfect sheet structure', or 'open structure'. There is no preferred orientation and the aromatic layers are connected to each other with cross links, producing a highly porous system.

(2) 'Liquid packing' is found in coals between 85 and 91% carbon content. The lamellae show some preferred orientation with crystallites consisting of

Fig 5 Change of molecular structure with rank (from van Krevelen 1961; after Hirsch 1954).

(a) 'open' structure
(b) 'liquid' structure
(c) anthracitic structure.


a
Cross links
Layers
Pores
Amorphous material
80 % C
b
20 Å
Group of layers
20 Å
8 Å
8 Å
Single layers + amorphous material
89 % C
c
Pores
94 % C

groups of two to three layers of about 8 Å diameter and an interlayer spacing of approximately 20 Å.

(3) 'Anthracitic structure' occurs in coals with more than 91% carbon content. The degree of orientation of the lamellae increases and layers are connected directly by C – C bonds; the pore structure also becomes orientated.

The following relationships between the optical properties of vitrinites and their molecular structures also received comment from Hirsch (1954).

(4) Increase of coal bireflectance with rank is due to degree of ordering.

(5) The sharp increase of the absorption coefficient with rise of rank at about 90% carbon is caused by the rapid increase of polycondensed aromatic lamellae and their electronic absorption. There is a similarity between the variation of the layer diameter and absorption coefficient with the rank.

(6) Gradual increase of refractive index with rank of coal is related to improvement in the stacking and increase in layer diameter.

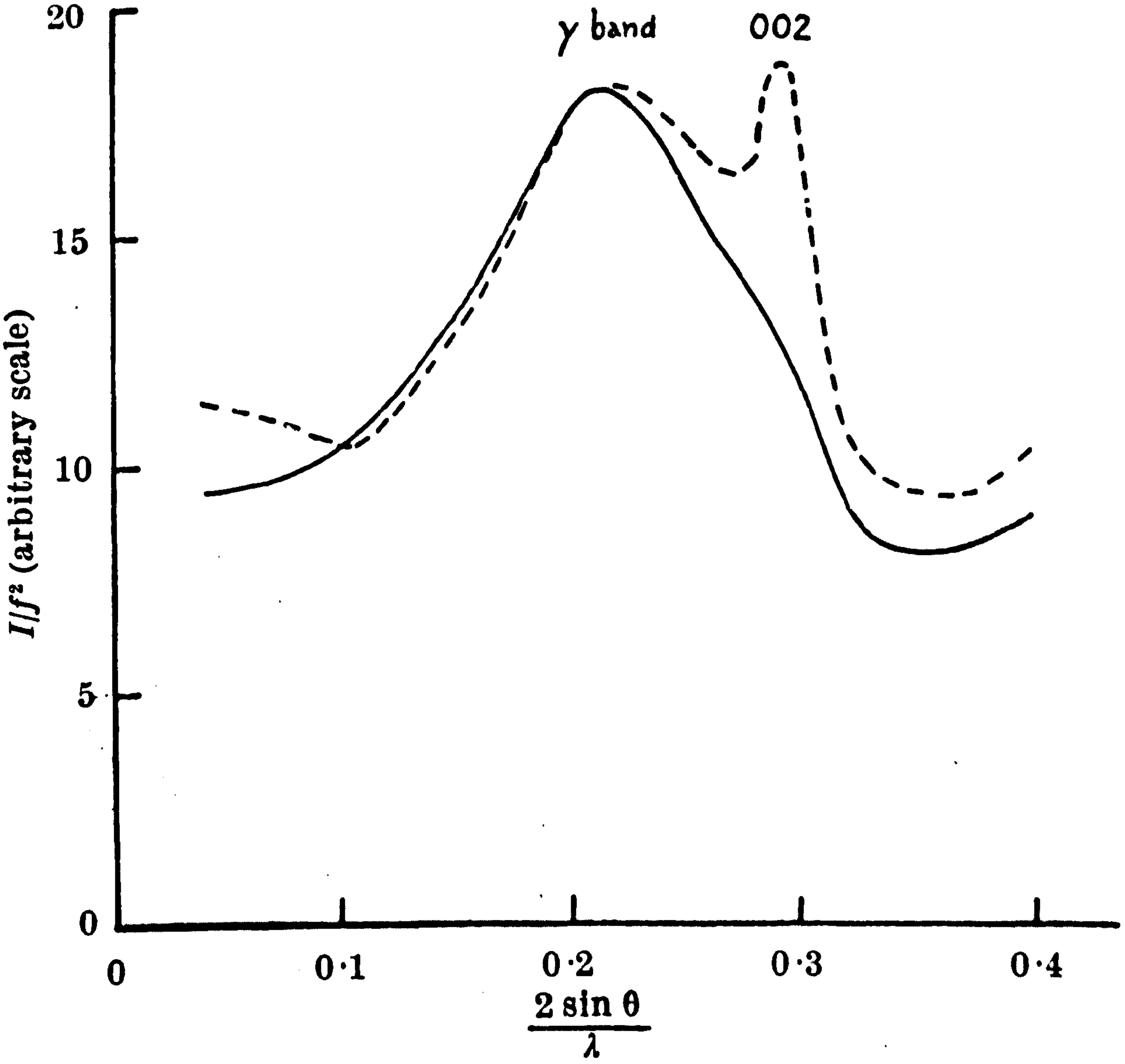
(c) Sporinite

Blayden *et al.* (1944); Nelson (1954); Cartz *et al.* (1956);

Ergun et al. (1958) and Cartz and Hirsch (1960) studies the X-ray diffraction patterns of sporinite (exinite) or exinite-rich material. They report the occurrence of a broad band at about 4-5 Å instead of or in addition to the 002 band. This band at 4-5 Å has been indexed the 'gamma band' (Fig 6). Generally all hydrogen-rich coals or coal macerals display the gamma band.

Blayden et al. (1944) were first to report the existence of a broad band, referred to as the gamma band, in a coking coal vitrinite (carbon = 88.4% daf). The intensity of this band decreases with rising rank. Later, Nelson (1954) attributed the band to the presence of spore-rich material. Nelson examined a vitrinite from the same coal which was previously used by Blayden et al., but failed to detect any trace of the band. Instead, a concentration of spore-rich material (exinite = 90% and vitrinite etc = 10% by volume) exhibited the gamma band with a peak value of 4-8 Å. Cartz and Hirsch (1956) also clearly demonstrated the relationship between the gamma band and spore-rich material by studying the low-angle scattering of a black durain and a spore-rich concentrate. The black durain shows the gamma band in addition to the 002 band, but the exinite-rich concentrate shows only the gamma band with a much-reduced 002 band (Fig. 6). High-angle scattering of spore-rich material showed that its structure is similar to that of vitrinites, i.e. mostly carbon consisting of polycondensed aromatic lamellae, but with important differences in the diameter and arrangement of the layers. The gamma band is

Fig 6 Low-angle scattering intensities of black durain (dashed curve) and exinite-rich concentrate (solid curve) as a function of 2 $\sin\theta/\lambda$, where 2 $\sin\theta$ is the angle of scattering and λ is the X-ray wavelength (after Hirsch 1956).


20
15
10
5
0
I/f² (arbitrary scale)
γ band
002
0
0·1
0·2
0·3
0·4
2 sin θ / λ

thought to be caused by a larger interlayer spacing and irregular stacking of layers due to the presence of more edge groups (aliphatic etc) or alternatively to buckling of layers. Cartz and Hirsch further state that exinites are composed of small aromatic layers which pack imperfectly and contain more aliphatic material and hydrogen than the vitrinites. Ergun (1958), however, attributes the gamma band in coal to parallel alicyclic layers in exinite material.

The above studies show that the molecular structure of vitrinites consist basically of aromatic (ordered) and amorphous (disordered) carbon. With increase of rank the proportion of aromatic carbon increases and the amount of amorphous (aliphatic and/or alicyclic) carbon falls. The layer diameter (L_a) and stack height (crystallite height or L_c) increase with rising rank. Sporinite (or exinite-rich concentrates) show a molecular structure similar to vitrinite, but is composed of smaller aromatic layers of even lower ordering.

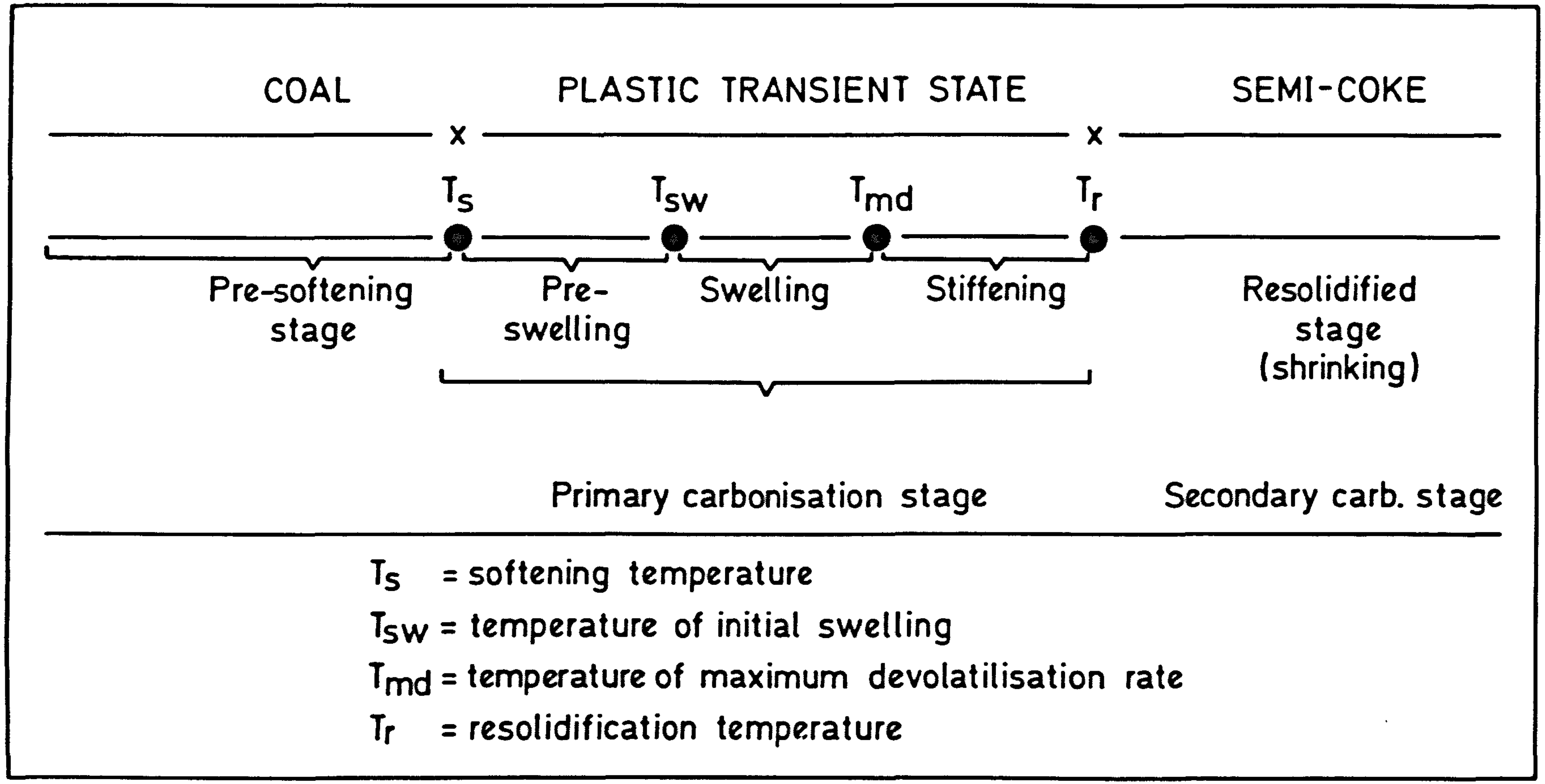
2. CARBONISATION OF COAL

(a) Introduction

The carbonisation process refers to a progressive depolymerisation in which the carbon content of coal rises due to destructive distillation of other components in the absence of air and involving a continuous interrelated, complex sequence of physical and chemical processes. This physicochemical transformation produces tar and gas (volatile matter), resulting in the accumulation and aggregation of the remaining carbon.

There have been numerous investigations to study the behaviour of coals carbonised in the laboratory and thermally metamorphosed coals and natural cokes produced by intrusions of igneous rock into coal seams. The thermal reaction of coal depends upon many factors, including coal rank, maximum temperature of carbonisation, rate of heating, the presence or absence of pressure, oxidation, the length of time for which the coal is heated and the particle size. These same factors influence the development of optical properties during carbonisation. The effect of certain of these factors is already well known from the work of other authors; the influence of several others is examined in this thesis. First, however, a brief generalised description of the carbonisation process is given below.

Fig. 7 Different stages of carbonisation process (after van Krevelen 1961).



T_s = softening temperature
T_{sw} = temperature of initial swelling
T_{md} = temperature of maximum devolatilisation rate
T_r = resolidification temperature

Temperature stages in phase 2 of the carbonisation process (after van Krevelen)

(b) The Carbonisation Process

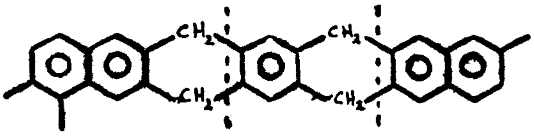
Coals of coking rank when subjected to heat, soften, pass through a plastic stage, swell on decomposition and resolidify into a fused mass. Degasification is a continuous reaction during the carbonisation process. During carbonisation dehydrogenation becomes active immediately in the case of all coals and thereafter deoxygenation takes place.

Van Krevelen (1961) divides the carbonisation process into two successive stages based on characteristic temperatures: primary carbonisation which produces mainly tar (below 500°C) and secondary carbonisation in which only gas diffuses (Fig. 7). Berkowitz (1967) studied the chemical changes and mechanisms of the coal-carbon transformation by dividing the carbonisation process into three stages based on characteristic chemical changes, which in coals, other than anthracites, do not differ much from one coal to another.

(i) In the first stage, up to about 400°C, the changes caused by carbonisation are similar to natural maturation of coal, involving only limited depolymerization and condensation. Decarboxylation and dehydroxylation start at about 350°C, but do not appear to play an active role at this time; if decarboxylation or dehydroxylation occur, they would affect only low-rank coals, since the proportion of edge groups is higher in such coals. According to Brooks and Maher

(1957), interaction between carboxyl and hydroxyl groups at temperatures lower than 300°C in brown coal results in direct C–C linkages.

(ii) In the second stage, extending from 400°C to 650°C and with active decomposition occurring, coal undergoes a destructive distillation and an extensive degasification which produces tar. According to Given (1960), tar-forming materials are actually alicyclic bridges, rather than aliphatic structures, which connect the aromatic structures to each other. The appearance of a small amount of material of aromatic origin in low-temperature tar is attributed to this reaction (see below), but condensation of aromatic material in coal increases with rise of temperature, despite the loss and by 600°C, the coal is fully aromatised.



Oxygen content groups other than hydroxyl will survive this stage, which means that two thirds of the oxygen groups will remain.

(iii) The third stage begins at approximately 600°C and ends at about 1000°C. This stage is accompanied by severe physical rather than chemical changes and is characterised by intermolecular peripheral reactions, e.g. removal of hydrogen from the periphery of aromatic lamellae, resulting in an increase in size of the aromatic layers.

4. OPTICAL PROPERTIES OF CARBONISED VITRINITE

(a) Introduction

The optical properties of laboratory-carbonised vitrinites have been studied in numerous investigations (Bond *et al.* 1958; Chandra 1963; 1965; Davis 1965; de Vries *et al.* 1968; Ghosh 1968; Marshall and Murchison 1971; Goodarzi and Murchison 1972 and Melvin 1974). As stated earlier, the optical properties of carbonised vitrinites depend on several factors; among the more important are the original rank of the vitrinite, the temperature level, duration of heating, rate of heating, pressure, occurrence of oxidation and particle size. Not all of these factors have been studied exhaustively in relation to optical properties. Those factors which have been examined in depth by other workers, and hence are not part of the experimental work in this thesis, will be discussed in this section and others, in particular, duration of heating, rate of heating and the effect of pressure will be discussed later, in the appropriate sections, being part of the project. Some of the earlier investigations used vitrinite-rich coals rather than comparatively pure selected vitrinite; the word 'coal' is used by these earlier authors, but in fact reflectivity measurements were carried out on vitrinites as in the present study.

(b) Rank and Temperature

That the optical properties of carbonised vitrinites are related to the original rank of the vitrinites has been clearly demonstrated by Bond et al. (1958), Davis (1965), Ghosh (1968), de Vries et al. (1968), Marshall and Murchison (1971), Goodarzi (1971) and Goodarzi and Murchison (1972).

In the first of these studies, Bond et al. (1958) examined the carbonised residues of three vitrinites (carbon = 83.6, 84.6 and 92.0% dmmf) at temperatures between 100°C and 900°C (intervals of 100°C up to 700°C and then 200°C between 700° and 900°C). Reflectivities in air and oil were measured and refractive and absorptive indices calculated. The oil reflectivities of the two low-rank vitrinites increased after 300°C to a lower level at 900°C than did the reflectivities of the residues from the high-rank vitrinite which began to rise at 400°C. The high-rank coal showed increasing anisotropy with rise of carbonising temperature, but the two low-rank vitrinites remained almost isotropic during carbonisation. Errors in the reflectivity measurements were stated to be as great as 10% but the measurement of reflectivities was apparently made in white light.

The refractive indices of the two low-rank vitrinite residues rose with temperature up to 700°C and then decreased with further increase in temperature. The high-rank vitrinite showed the least variation in refractive index, increasing between 400° and 500°C, decreasing at 600°C and then maintaining this reduced level up to 900°C. Absorptive index rose continuously with increase of temperature, but some negative values of the squares of the absorptive indices were obtained, suggesting a substantial error in reflectivity measurement. Rise in the anisotropy of the carbonised vitrinite was also reported with rise of temperature.

Davis (1965) carbonised a wider rank range of vitrinites (carbon = 76.8 up to 93.3% daf) at temperatures between 200° and 600°C using a 50°C interval. Dispersion of reflectivities between 400 and 600 nm were also measured. The reflectivities in air and oil at 532 nm did not increase up to 300°C for most of the vitrinites of this series, but an increase in reflectivity occurred between 350° and 400°C and was the greater the lower the initial rank of the vitrinite. High-rank/anthracitic vitrinites (carbon = 91.4 and 93.3% daf) did not show a reflectivity increase before 450°C.

Bireflectance of Davis' carbonised low-rank vitrinites showed no increase or a slight increase up to 600°C, whereas caking and coking vitrinites showed a rapid increase in bireflectance after an initial decrease between 300° and 400°C. High-rank vitrinite also showed a rise in bireflectance between 400° and 600°C, but the anisotropy of anthracitic vitrinite did not change up to 600°C. The refractive indices of the vitrinites increased up to 600°C, but the increase was irregular in anthracitic vitrinite, while the refractive index of one of the coking coal vitrinites (carbon = 88.1% daf)initially decreased at 200°C and then increased up to 550°C before decreasing again to 600°C. Davis related the drop of refractive index to some inaccuracy in reflectivity measurement.

An important point emerging from Davis' results was the decrease of the bireflectance of caking and coking vitrinites in the temperature range between 300° and 400°C, which was not reported by Bond _et al._ (1958). Also Davis' finding confirmed the findings of Bond _et al._ in which the bireflectance is one of the more sensitive parameters of rank variation in carbonisation. However, Davis' work was never published, although presented as a doctorate thesis.

Ghosh (1968) reported on four vitrinites (carbon = 76.2, 83.5, 86.5 and 91.1% daf) carbonised up to 1000°C. The reflectivity curves of the vitrinites plotted against carbonising temperature follow almost similar trends, the uppermost curve being for the highest-rank vitrinite (Fig. 8). A plot of reflectivity against the carbon content of the carbonised residues (Fig. 9) clearly demonstrates that the original rank of the vitrinite influences the pattern of reflectivity change.

De Vries _et al._ (1968) examined the effects of temperature level on the reflectivity of a range of vitrinites (carbon = 78.8, 87.5, 88.5, 89.6, 89.7, 91.3 and 92.3% daf) at four different temperatures (450°, 520°, 600° and 1000°C). The reflectivity-temperature variation of each of the above vitrinites

Fig 8 Variation with temperature of oil reflectivity of four vitrinites carbonised between 100° and 1000°C (after Ghosh 1968).

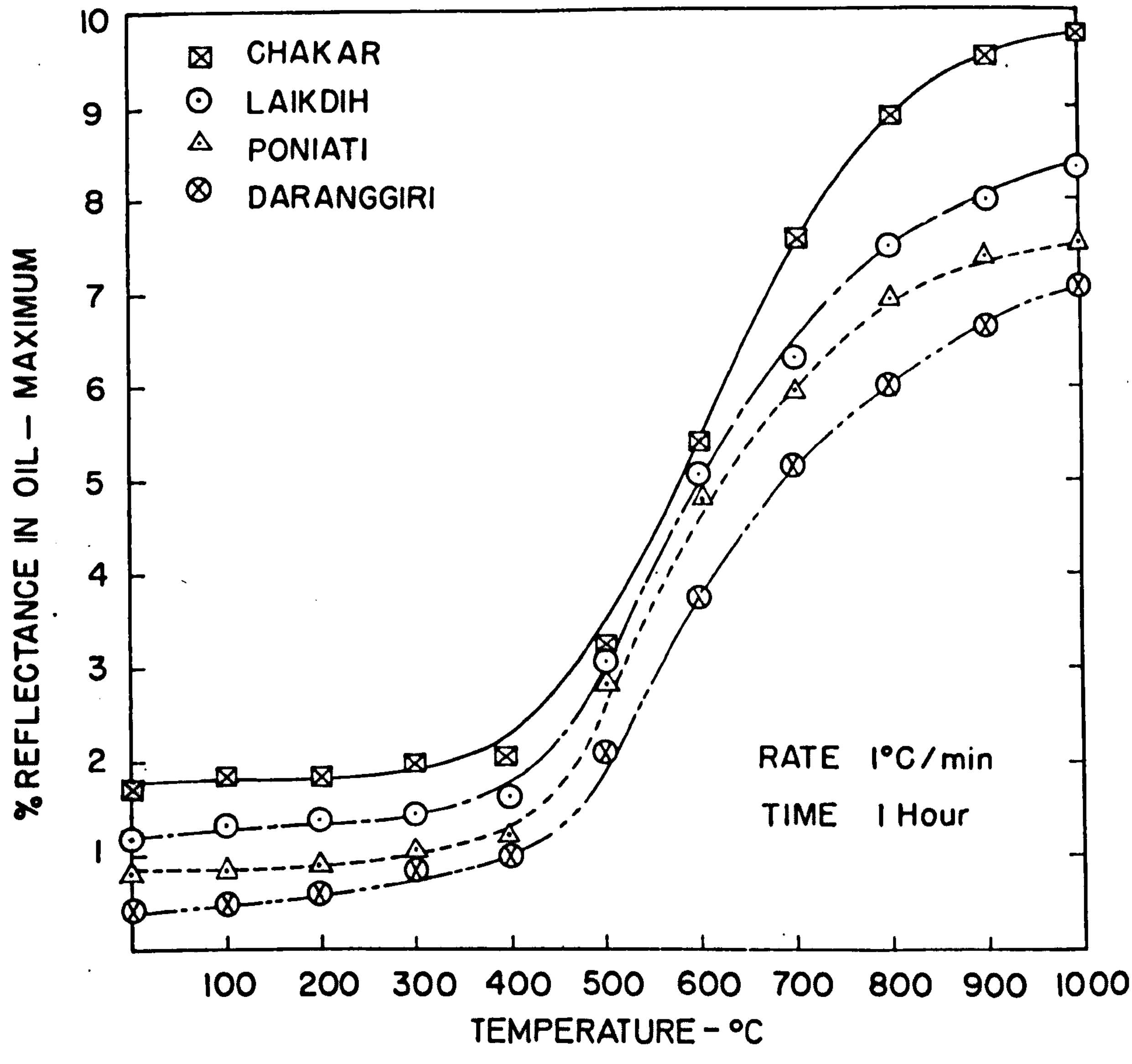
Carbon content % daf

Daranggiri = 76.2%

Poniati = 83.5%

Laikdih = 86.5%

Chakar = 94.1%

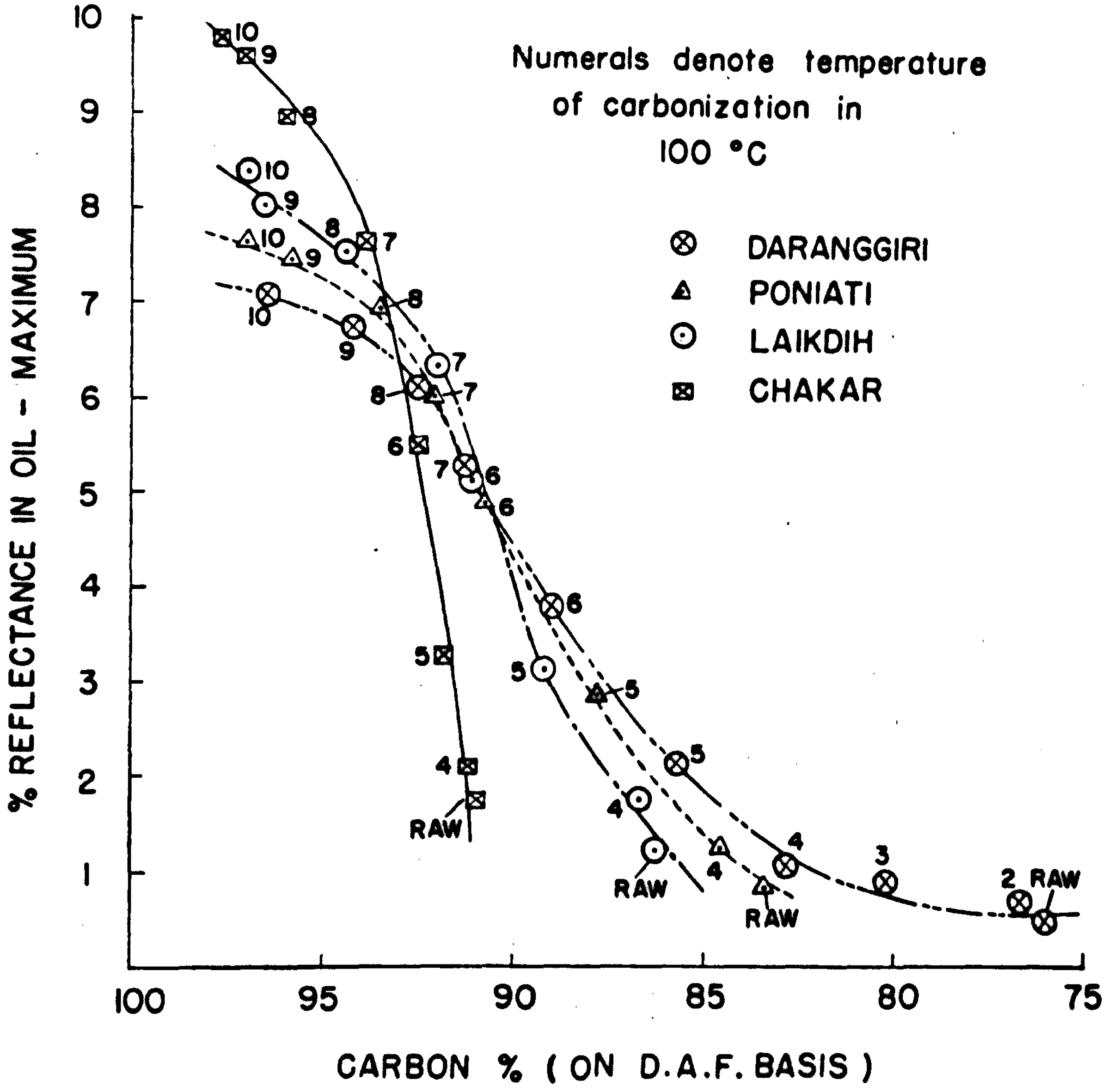


CHAKAR
LAIKDIH
PONIATI
DARANGGIRI
RATE 1°C/min
TIME 1 Hour
% REFLECTANCE IN OIL – MAXIMUM
TEMPERATURE – °C
1
2
3
4
5
6
7
8
9
10
100
200
300
400
500
600
700
800
900
1000

Fig 9 Variation with carbon content of oil reflectivity of four vitrinites carbonised between 100° and 1000°C (after Ghosh 1968).

Carbon content % daf

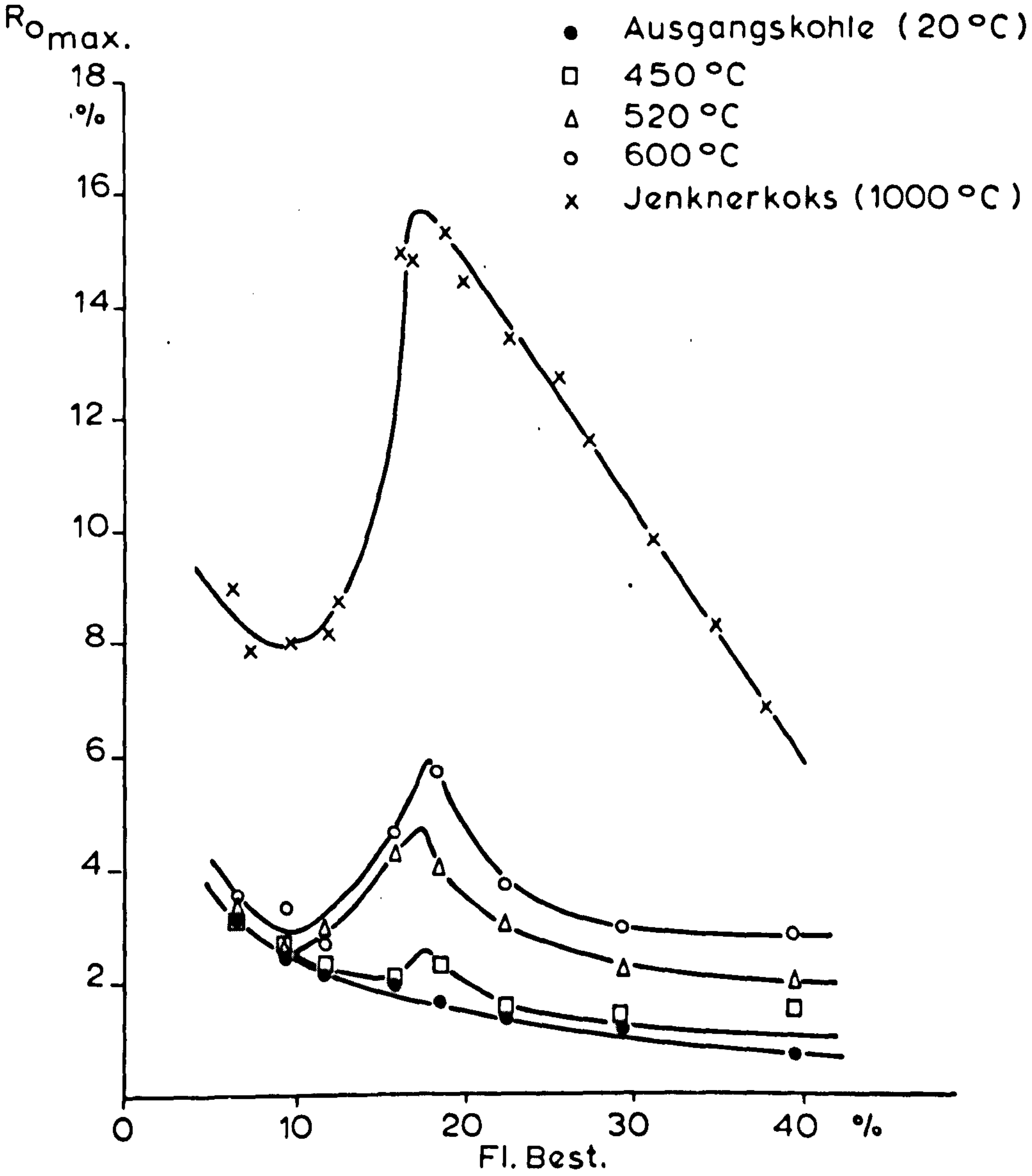
Daranggiri = 76.2%
Poniati = 83.5%
Laikdih = 86.5%
Chakar = 94.1%


Numerals denote temperature of carbonization in 100 °C
⊗ DARANGGIRI
△ PONIATI
⊙ LAIKDIH
⊠ CHAKAR
% REFLECTANCE IN OIL - MAXIMUM
CARBON % (ON D.A.F. BASIS)
10
9
8
7
6
5
4
3
2
1
100
95
90
85
80
75
RAW

was plotted against volatile-matter content (Fig. 10). Reflectivity rises with decrease of the volatile-matter content at all four of the above carbonisation temperatures, but after passing through a maximum at about 17 to 18% volatile-matter content before finally increasing once again with further drop in volatile-matter. The rate of rise and fall of the reflectivity is dependent on the temperature of carbonisation and on the rank of vitrinite, the fluctuation of the reflectivity being greater the higher is the temperature of carbonisation. The reflectivity of vitrinite carbonised at 1000°C was about three times as great as those taken to lower temperatures. The reflectivity rose, particularly in the range between 17 and 18% volatile-matter content, the maximum reflectivity coinciding with the end of plastic range. These results are interesting because the reflectivity-temperature curves for different ranks of vitrinites after resolidification (about 520°C) do not follow a sequential trend as was shown by earlier authors. In the coking range vitrinites also exhibit much higher reflectivity value than either lower rank or anthracitic vitrinite.

De Vries and his co-workers also carbonised three coking coal vitrinites (carbon = 87.5, 88.6 and 89.6% daf) at temperatures ranging from 350° to 600°C. (Fig. 11). The reflectivity held constant up to 400°C and then increased slowly up to approximately 450°C and sharply to about 500°C, after which the rate of increase of the reflectivity decreased up to approximately

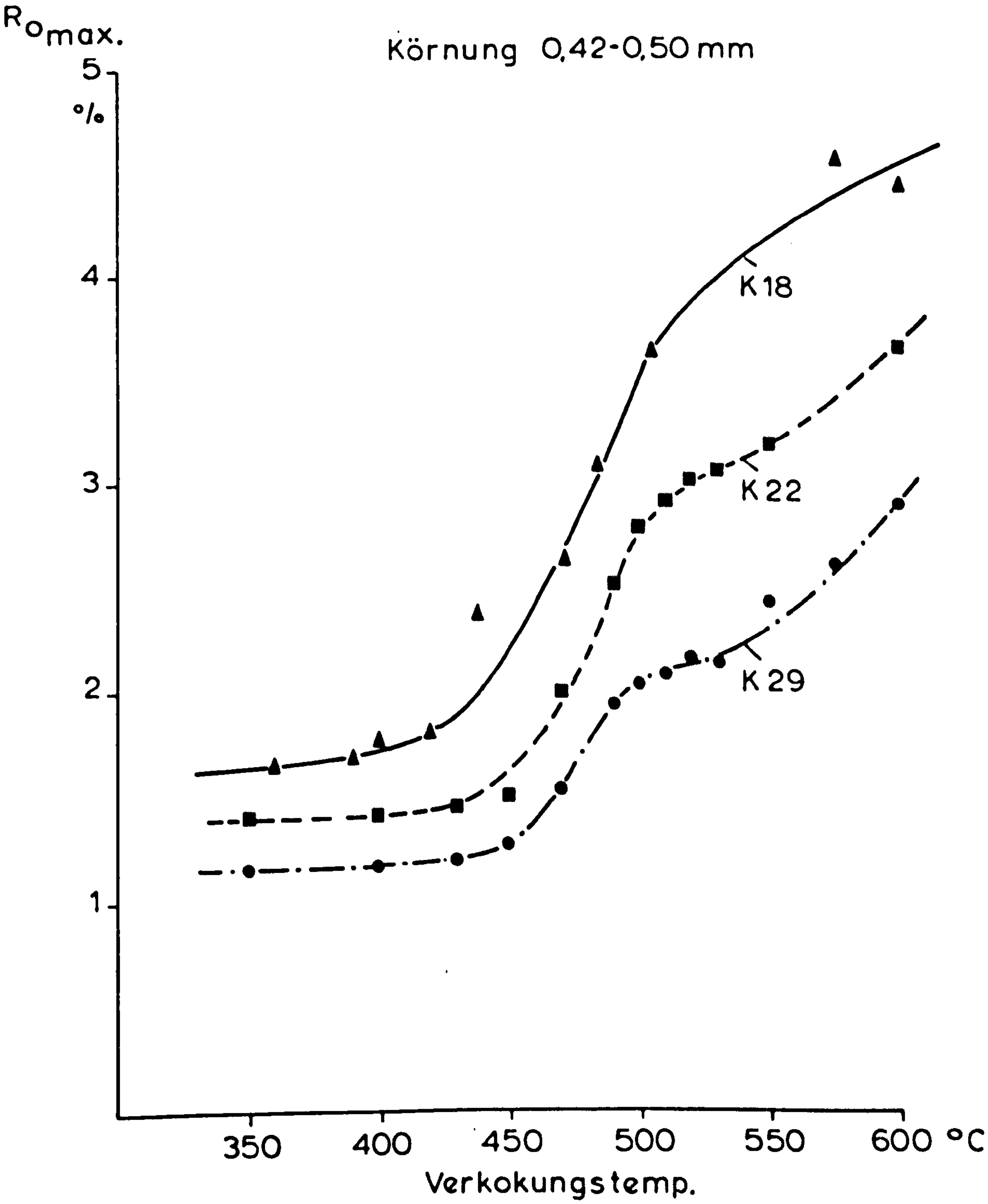
Fig 10 Variation of oil reflectivity with volatile matter for a range of vitrinites carbonised at 450°, 520°, 600° and 1000°C (after de Vries *et al.* 1968).



$R_{o\,max.}$
%
18
16
14
12
10
8
6
4
2
0
10
20
30
40
%
Fl. Best.
● Ausgangskohle (20 °C)
□ 450 °C
△ 520 °C
○ 600 °C
× Jenknerkoks (1000 °C)

Fig 11 Variation of oil reflectivity with temperature of coking coal vitrinites (after de Vries *et al.* 1968).

K18: carbon = 89.6% daf
K22: carbon = 88.6% daf
K29: carbon = 87.5% daf


Romax.
%
Körnung 0,42-0,50 mm
5
4
3
2
1
K18
K22
K29
350
400
450
500
550
600 °C
Verkokungstemp.

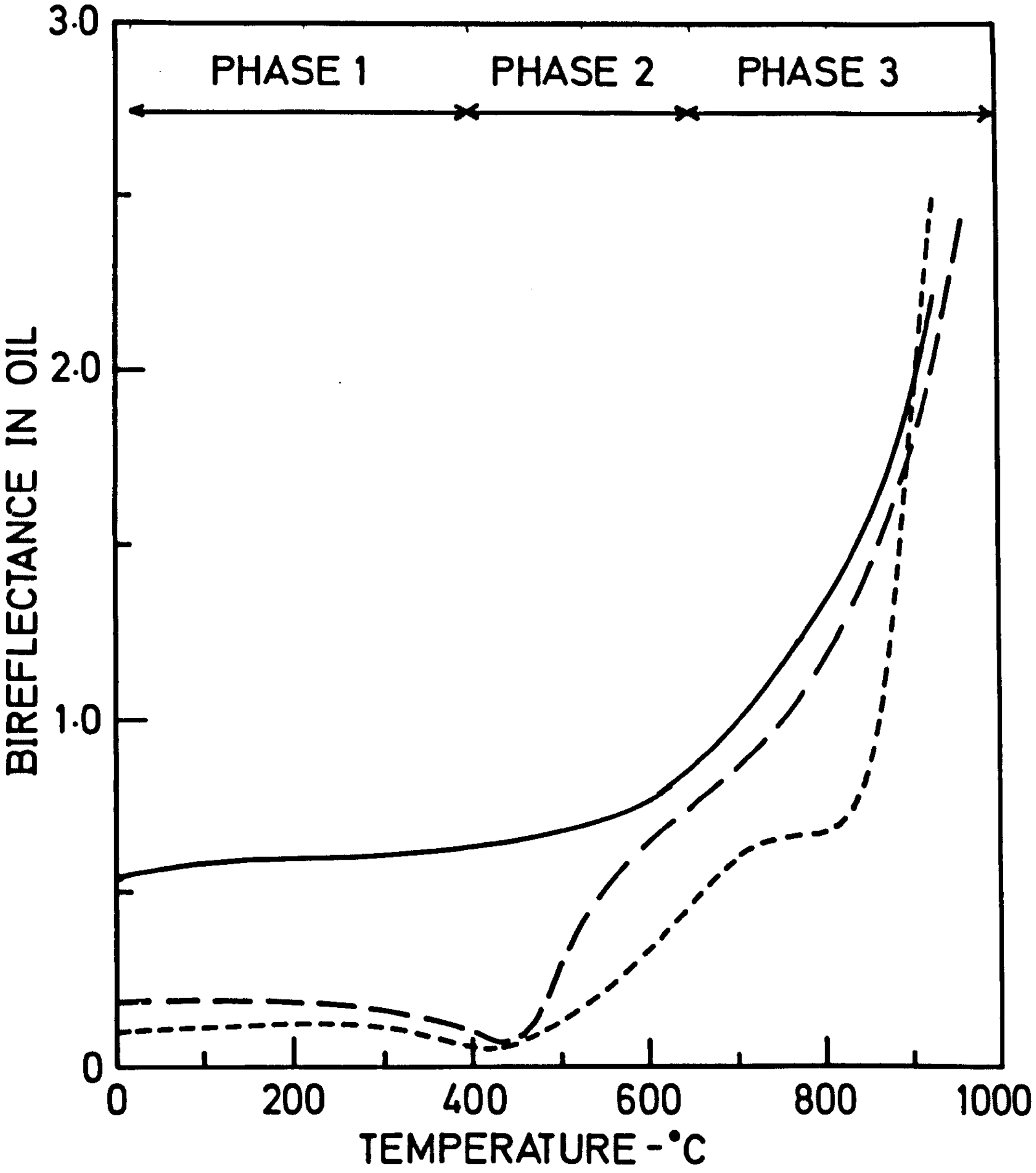
540°C; then again the reflectivity rose at an enhanced rate between approximately 540° and 600°C.

Marshall and Murchison (1971) and Goodarzi and Murchison (1972) also studied the influence of rank on the optical properties of vitrinites over approximately the same rank range (carbon = 82.5 to 93.3% daf), although these studies were more aimed at the relationship between optical properties and molecular structure of the carbonised residues. Marshall and Murchison studied the dispersion of the optical properties at three carbonisation temperatures, 450°, 600° and 750°C. Bireflectance at 546nm rose with increase of carbonisation temperature and is greater the higher the initial rank of the vitrinite until at 750°C the coking coal vitrinite has developed a similar anisotropy to that of the anthracitic vitrinite. Goodarzi and Murchison have also shown the importance of bireflectance in carbonisation experiments. The bireflectance of two bituminous-rank vitrinites, after an initial decrease at about 400°C (confirming Davis' results), increased with rise of temperature; the uppermost curve is that of anthracitic vitrinite. The low-rank vitrinite followed a much lower curve up to about 875°C (Fig. 12) before rising sharply to 950°C.

Refractive index can also indicate the basic structural differences between different ranks of vitrinite, e.g. softening or non-softening vitrinites (this aspect will also be discussed in more detail later).

Fig 12 Generalised curves for the variation with temperature of oil bireflectance of three vitrinites from:-

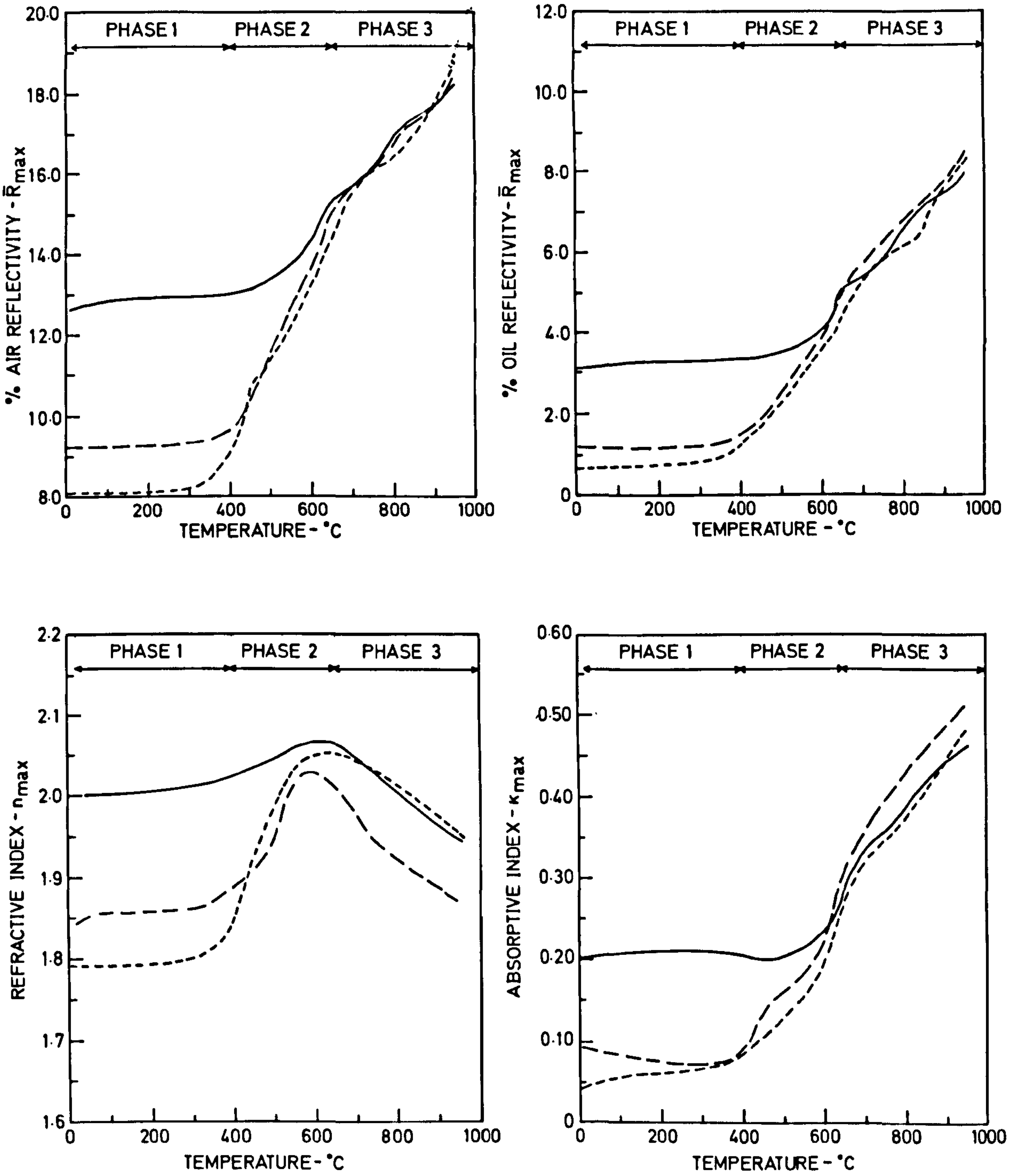
anthracite (carbon = 93.1% daf) ————————
high-rank bituminous (carbon = 88.0% daf) — — —
low-rank bituminous (carbon = 82.5% daf) - - - -
(after Goodarzi and Murchison 1972).


3.0
2.0
1.0
0
PHASE 1
PHASE 2
PHASE 3
BIREFLECTANCE IN OIL
0
200
400
600
800
1000
TEMPERATURE - °C

The earlier findings of Bond et al. (1958) do not agree with the later similar sets of data of Marshall and Murchison (1971) and Goodarzi and Murchison (1972). The refractive indices of all three carbonised vitrinites in these later studies rose to a maximum at about 600°C and also the anisotropy of low-rank vitrinite increased with carbonisation temperature, whereas vitrinites of similar rank were suggested by Bond et al. as being isotropic and remaining so during carbonisation, while the refractive indices of low-rank vitrinites reached a maximum at about 750°C and very low maximum in the high-rank vitrinite at the same temperature.

The influence of original rank on the optical properties of carbonised vitrinite is clearly demonstrated by the behaviour of the bireflectance (Fig 12) the trends of refractive index and to some degree by the variation of reflectivity (Figs. 10 and 13). The influence of rank is displayed in the increase of reflectivity but the most recent studies of Marshall and Murchison and also Goodarzi and Murchison show less distinct differences between the reflectivity curves of different ranks of vitrinite carbonised beyond 600°C than in earlier studies, e.g. Bond et al. (1958) and Ghosh (1968). The results of Goodarzi and Murchison only partially agree with the findings of de Vries et al. (1968) which show the coking range of vitrinites with higher reflectivity than those of caking or non-coking vitrinites (Fig 10). It is useful if the bireflectance is used in conjunction with the reflectivity to indicate the original rank of the vitrinite, because the

Fig 13 From Goodarzi and Murchison 1972.



Generalized curves for the variation with temperature of the optical properties at 546nm of carbonised vitrinites from three coals of different rank

——— From anthracite (carbon = 93.1% d.a.f.)
— — — From high-rank bituminous coal (carbon = 88.0% d.a.f.)
- - - - - From low-rank bituminous coal (carbon = 82.5% d.a.f.)

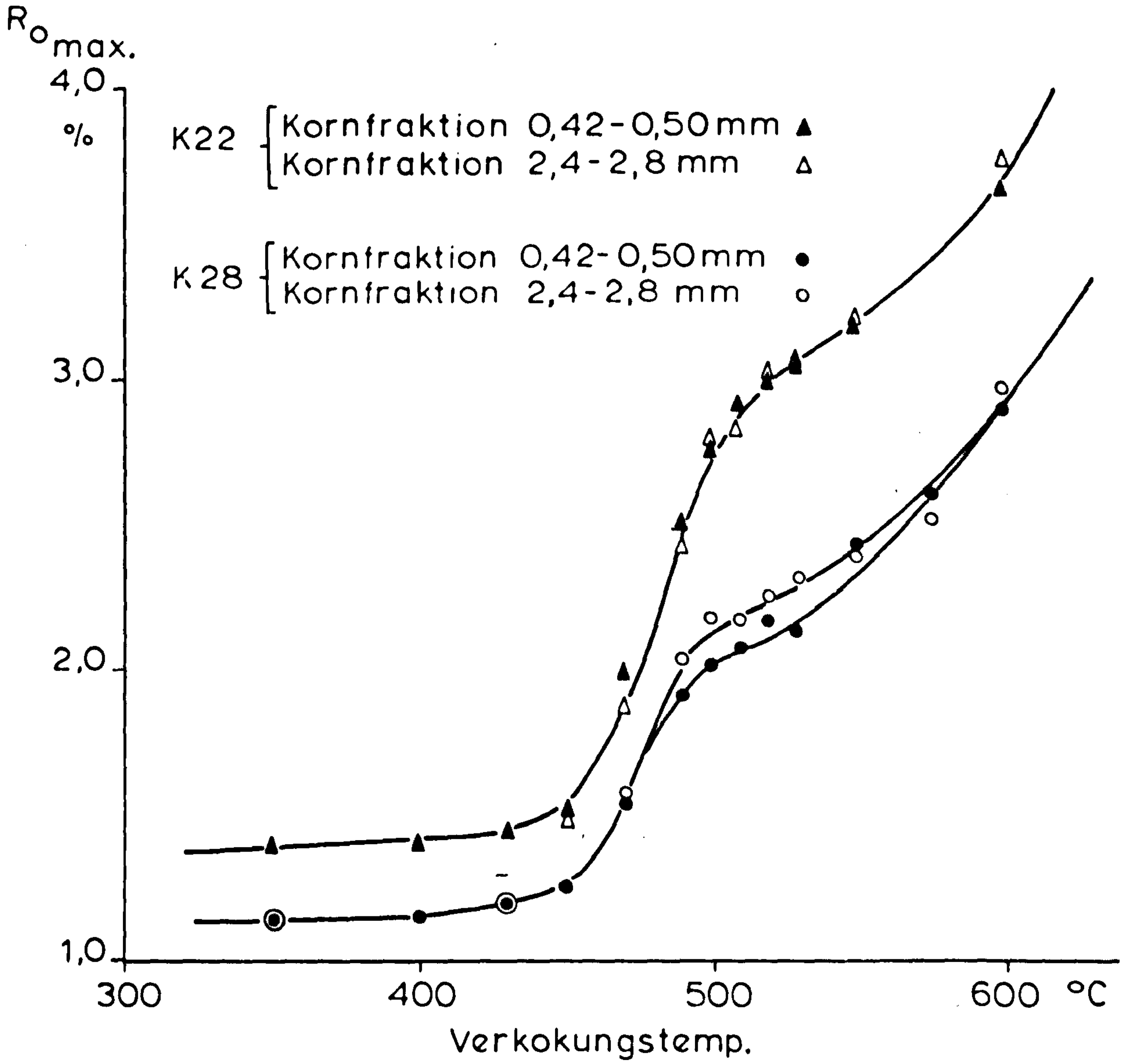
reflectivity of softening vitrinites exhibit different trends to those of non-coking vitrinites (Fig 10). The bireflectances of vitrinites of different rank also follow different trends.

(c) Particle Size

The influence of particle size on the reflectivity of carbonised coals has only been examined by de Vries *et al.* (1968). Two coals (carbon = 87.5 and 88.6% daf) were carbonised over the temperature range from 350° to 600°C using two different grain sizes of between 0.42 to 0.50 mm and 2.4 to 2.8 mm. The reflectivity of the coking coal vitrinite showed little, if any, variation with particle size on heating at different temperatures up to 600°C, but the reflectivity of the low-ranking coking coal exhibited some differences, the reflectivity being higher the smaller the particle size. Difference between the reflectivities of the residues with two different particle sizes began to show at 475°C and increased with rise of temperature, with the reflectivity curves for the smaller grain-size residues always lying above that of the larger grain-size residues. The difference between the reflecitivity curves for the two grain sizes reached a maximum at 500°C and then decreased with further rise of temperature to 600°C. (Note: There seems to be a discrepancy between the graph (Fig. 14) representing this data and the text of the paper, because there is a reversal of the symbols for the residues from the two grain-sizes). De Vries *et al.* (1968) conclude that the influence of the particle size is very small in coking coal and only slight in low-rank caking coal, Fig 14 Variation of oil reflectivity with particle size of two coking-coal vitrinites carbonised up to 600°C (after de Vries *et al.* 1968).

K22: carbon = 88.6% daf
K29: carbon = 87.5% daf

NOTE: the K28 in figure is quoted as K29 in the text.



R_{o} max.
%
4,0
3,0
2,0
1,0
300
400
500
600 °C
Verkokungstemp.
K22 { Kornfraktion 0,42-0,50 mm ▲
Kornfraktion 2,4-2,8 mm △
K28 { Kornfraktion 0,42-0,50 mm ●
Kornfraktion 2,4-2,8 mm ○

even if it could be determined at all. However, since the particle size apparently has some effect on the behaviour of the optical properties of carbonised vitrinites, during the course of this research programme a constant grain size of approximately BSS72 was used (see 'Experimental Details').

5. MOLECULAR STRUCTURE OF SEMI-COKES AND COKES (± 1000°C)

(a) Introduction

The molecular structure of semi-cokes and cokes has been studied by many investigators using different methods. These methods include morphological studies of mosaic structures using optical microscopy and/or electron microscopy (Stereoscan), measurements of optical properties and X-ray diffraction studies. In this section various aspects of the mosaic structures that develop in semi-cokes and cokes and which have been discussed by other workers are considered. Later in this thesis, the effect of different factors on mosaic structures will be recognised.

Coke made from vitrinite in the coking coal range and also from hydro-carbons with a relatively high atomic ratio of hydrogen to non-carbon elements (e.g. coal-tar pitch, petroleum-tar pitch) exhibit a three-dimensional mosaic structure. The term 'mosaic' is applied to isotropic material which has been converted totally to a coalesced mesophase at temperatures around the resolidification temperature (Brooks and Taylor 1965).

Graphitisability or non-graphitisability of carbonaceous materials can be determined by their physico-chemical behaviour during the early stages of carbonisation (carbonisation and graphitisation are two consecutive processes). Commonly, if a carbonaceous material forms a liquid phase during the early stages of carbonisation, it will produce a graphitised carbon at higher temperatures (e.g. 2500°C); otherwise it remains non-graphitised.

During the course of carbonisation, the graphitised carbon softens and produces an anisotropic phase. Spherical bodies slowly appear in this isotropic matrix. The components of the spheres possess some degree of ordering compared with that of the surrounding isotropic material. The growth of the spherical bodies (the 'mesophase' or intermediate state) in number and size is in reverse proportion to that of isotropic matrix. This mesophase or 'liquid crystals' refers to materials which have liquid properties and are anisotropic. Such a system is not truly crystalline, but has greater structural ordering than that of the normal isotropic liquid. There are several types of liquid crystal, but the mesophase produced during the carbonisation of carbonaceous materials has many typical characteristics of nematic liquid crystals. The ordering of the molecules in a nematic mesophase is such that all molecules are oriented parallel to each other without any stacking sequence with their long axes parallel to the layer planes. A nematic mesophase shows strong anisotropy. Commonly, the conversion of isotropic carbonaceous compounds to a mosaic structure is as follows:-

Isotropic ⟶ anisotropic mesophase which coalesces
mosaic,

but there also exist some intermediate stages between the above stages.

(b) The Mesophase - Its Morphology and Optical Behaviour

One of the earliest studies of the progressive changes of optical properties of vitrinite during low-temperature carbonisation was given by Taylor (1961), who stated that change to isotropic vitrinite takes place over a range of 40°C which differs slightly for different ranks of vitrinite, commonly being higher for vitrinites of higher rank. Loss of optical anisotropy is an indication of loss of structural anisotropy and is caused by physical rather than chemical change. After this stage, the optical properties of plastic vitrinite increase steadily but slowly, spherical bodies of approximately 0.5 micron diameter begin to appear in the isotropic mass, the minute spheres enlarging with further increase of temperature at the expense of the isotropic matrix. Finally, the spherical bodies coalesce to form a three-dimensional mosaic texture. Taylor concludes that the resolidification of the liquid phase and the subsequent formation of semi-coke closely resembles crystallisation.

The spherical mesophase described by Taylor is strongly pleochroic. The mesophase behaviour is similar to a single crystal and between crossed polars it lightens and darkens four times on a full rotation of the microscope stage. This phenomenon is thought to be due to shrinkage stresses during the cooling of the semi-coke. The pleochroism becomes more complex with growth of the mesophase. Taylor's investigation is important because it was the first detailed microscopical study of plastic vitrinite, for the first time explaining the formation of the anisotropic mesophase from the plastic isotropic vitrinite and demonstrating a lamellar structure within mesophase.

Brooks and Taylor (1965) studied in more detail the earlier findings of Taylor (1961) on the mesophase, giving additional support to the earlier results by use of the reflected-light microscope and the electron microscope. Taylor's original work was carried out on thin sections by transmitted-light microscopy. Later, Brooks and Taylor studied the behaviour of a number of substances, for example, vitrinites from bituminous coals, coke, oven-pitch and petroleum bitumen during the early stages of carbonisation. They found that the material which became plastic and formed an isotropic pitch-like material during carbonisation produced spherical bodies which enlarged with increase of temperature and/or holding time. The spheres then began to coalesce to form a mosaic. The mosaic structure is complete only when the isotropic material is replaced entirely by the anisotropic mesophase. The conversion of the mesophase to solid semi-coke is gradual, but develops over a few degrees centigrade.

Electron diffraction patterns of the spherical bodies by Brooks and Taylor indicate that these materials are not crystallite, but that they possess either a fibrous or lamellar-type structure. Since there is no evidence of fibrous structure, the structure ought to be a lamellar type and this is supported by observation under polarised light. The bodies exhibit complete extinction when the lamellae are sectioned perpendicular to the median plane of the sphere and show an extinction cross when the section is parallel to the median plane of the sphere. The cross remains stationary during a complete revolution of the stage. Each individual sphere consists of planar aromatic material of high molecular weight with some degree of ordering. The aromatic lamellae are stacked in parallel order normal to the median plane of the spheres, but they also curve in a manner which makes them perpendicular to the surface of the sphere. (Fig. 15).

Neither Taylor nor Brooks and Taylor commented on the optical structure of the mesophase, apart from its lamellar structure. More recently Honda et al. (1971) examined critically the mesophase formed by carbonisation of coal-tar and noptha-tar pitches in the temperature range between 350° and 500°C using reflected-light and crossed polars with a gypsum plate. Honda and his colleages believe that the mesophase behaves as a uniaxial positive material and belongs to the hexagonal system.

Marsh (1973) examined a residue from a coking coal carbonised under pressure (carbon=89.1% daf) using a Stereoscan microscope. Marsh maintains that the anisotropic liquid crystals do not coalesce but grow, fuse and maintain their individuality and are termed 'botryoidal'. A high-resolution electron micrograph, taken in the phase-contrast mode of the above vitrinite, carbonised without pressure to about 1860°C, reveals

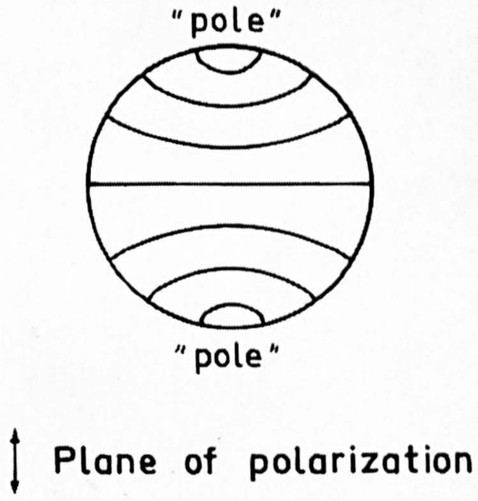


Fig 15 Structure of sphere, section parallel to main axis of symmetry. (after Brooks and Taylor 1965).

a layered structure which was thought to be related to the layered structure of the mesophase.

The above investigations show how the anisotropic mesophase forms, that it possesses a lamellar structure and has a most interesting optical behaviour, thought to be uniaxial positive and analogous to the hexagonal systems. The mesophase formed by carbonisation of vitrinite is suggested as being morphologically very similar to that from coal-tar pitch, so when the latter behaves as a uniaxial positive material, it is a direct corollary to believe that the former behaves similarly. There seems no reason why thermal treatment should not result in the formation of a uniaxial positive mesophase from uniaxial negative vitrinite. Furthermore, carbonisation under pressure can apparently prevent coalescence of the mesophase in vitrinite and so, if the project is concerned with the development and size of mesophase, carbonisation under pressure may be very useful.

(c) Transition between Mesophase and Mosaic

Having considered the formation of the mesophase and its optical behaviour, the microstructure of the coalesced mesophase will now be further discussed. White *et al.* (1967) and Honda *et al.* (1971) studied the structure of coalesced mesophase.

White *et al.* (1967) examined the coalesced mesophase formed by carbonisation of coal-tar pitch at 450°C by polarised-light and electron microscopy. The predominant features of the coalesced mesophase were nodal points which remained stationary when the microscope stage was rotated. Two types of nodal structure were observed:-

(i) a co-rotating nodal structure which has a simple arch structure, with the curved layers lying either concave or radially relative to the position of the nodes and

(ii) a counter-rotating nodal structure which has a more complex delta-shaped structure and possesses a three-fold symmetry. The layer planes lie perpendicular to each other at the node.

Examination by electron microscopy of pitch graphitised to 2800°C also revealed the existence of nodal structure. Further carbonisation of the coalesced mesophase leads to formation of two types of texture, namely, 'fibrous' and 'mosaic'.

More recently, the studies of Honda <u>et al.</u> (1971) threw more light on the understanding of the coalesced mesophase.

Coalescence of the mesophase first results in the formation of a 'cross-type' extinction, but further plastic deformation, due to degasification and formation of gas bubbles, causes the deformation of the 'cross-type' extinction to a 'node-type' extinction.

The foregoing studies demonstrate the complexity of the coalesced mesophase which eventually forms the mosaic structure. It can be deduced that the mosaic, having such a complex structure, cannot behave in the same way as a single mesophase, i.e. it will probably not display in bulk a uniaxial positive behaviour.

(d) Mosaic structure in coke

Coke made from vitrinite of the coking range exhibits a three-dimensional structure. One of the earliest studies was by Abramski and Mackowsky (1952) who described the optical anisotropy on polished surfaces of manufactured cokes. The optical orientation of the mosaic units differed from one another and each mosaic structure consisted of many anisotropic units. The dimensions of these units measure less than a micron up to several microns, depending on the rank of the original coal. Coal with approximately 35% vm produced a fine mosaic structure (units of ± 1 micron diameter). The mosaic size reaches a maximum at about 22% V.M. The size of the mosaic units is finally determined during the plastic stage and further carbonisation, even at a high temperature, does not change the form of the mosaic structure.

Alpern (1956) described the mosaic texture of cokes from coals of different rank (V.M. = 18.3 to about 36% daf). Coal with 18 to 22% V.M. produced a fibrous texture and showed undulose anisotropy, whereas coal with about 25% V.M. formed a coarse-grained mosaic texture of about 2 to 6 micron diameter. Low-rank coal (V.M.= 34%) developed a fine-grained mosaic of approximately 1 micron diameter and finally coal of higher than 35% V.M. remained isotropic during carbonisation. These results supported the earlier findings of Abramski and Mackowsky (1952). This was one of the earlier attempts to classify coke by mosaic size. Later de Vries <u>et al.</u> (1968), using polarised-light microscopy, studied a range of vitrinites (carbon = 78.8 to 92.4% daf) and described their mosaic texture. Non-coking vitrinite (carbon = 78.8% daf), which was isotropic, remained isotropic on heating, whereas caking vitrinite developed a fine-grained mosaic. Coking coal vitrinites (carbon = 88.6 and 89.6%) developed a coarse-grained and/or fibrous mosaic. Anthracitic vitrinites (carbon = 91.3 and 92.4%) maintained their original anisotropy, but the intensity of the anisotropy increased on heating. The size of the mosaic increased with rise of temperature, but once the resolidification stage was reached, no size alteration with further increase of temperature took place. These findings again support the earlier findings of Ambramski and Mackowsky (1952).

Sugimura <u>et al.</u> (1969) and (1970) described different anisotropic textures, e.g. as fine-to coarse-grained mosaic, fibrous and leaflet textures in residues of Japanese coal (carbon 77.8 to 89.8% daf) carbonised up to 900°C. The isotropic texture remained the predominant feature of non-coking and weakly coking coal, whereas it changed to a fine-grained mosaic texture in strongly caking coal (carbon = 86.2 to 87.2% daf), remaining almost unchanged with rising temperature. The coking coal (carbon = 89.8%) developed a mosaic and fibrous texture, with the percentage of fibrous texture increasing with rise of temperature. Finally, these authors concluded that the variation of anisotropic texture is rank dependent and that there is a correlation between anisotropic texture and coke qualities.

Marshall and Murchison (1971) observed that the orientation of the mosaic structure of coking coal vitrinite (carbon = 88% daf) became more regular and developed stronger anisotropy with increase of temperature.

More recently attempts have been made to determine original rank by the measurement of the mosaic size. Goldring (1973) states that the size of mosaic units in carbonised vitrinites with a mean maximum oil reflectivity of 0.8% can only just be seen with the optical microscope. The size of the mosaic units, however, increases with reflectivity up to an oil reflectivity of 1.2%, after which the mosaic units tend to coalesce; at about 1.7% oil reflectivity, they develop a 'lamellar' rather than a mosaic structure. Goldring suggests that the size of the mosaic units can be used in addition to reflectivity to study rank as well as the carbonisation conditions, microlithotypes, the presence of sulphur (locally) and finally interactions between blend components.

In a paper similar to that by Sugimura *et al.*, Patrick et al. (1973) discussed the use of mosaic size as a useful tool in the classification of the carbonised products of different ranks of vitrinites (carbon = 82.6% to 92.0% daf. The diameters of the anisotropic grains (fine grain = 0.3 micron, medium grain = 0.7 microns and coarse grain = 1.3 microns) follow a sequence which depends on the initial rank of vitrinites: basic anisotropy → isotropic → fine grain mosaic → medium grain mosaic → coarse grain mosaic → flow-type mosaic.

According to Patrick et al. the conversion of isotropic or anisotropic vitrinite to a fine grained mosaic is direct without the formation of any intermediate spherical bodies and/or development of an isotropic phase. Vitrinites of different rank are divided on the basis of their mosaic sizes. Weakly-caking and strongly-caking vitrinites (carbon = 82.6 and 84.7% daf) produce no mosaic larger than fine grain: very strongly-caking vitrinites (carbon = 87.2 and 87.8% daf) also exhibit the sequential transformation from isotropic vitrinite, but the final grain size does not exceed medium grain. Prime-coking vitrinite (carbon = 89.1 and 90.2% daf) exhibit the full consecutive transformation of mosaic size from fine grain to flow-type with rise of temperature. Finally, semi-anthracitic vitrinite (carbon = 91.5% daf), which is basically anisotropic, remains so, but its anisotropy intensifies with increase of temperature without exhibiting any mosaic structure. Furthermore, the total anisotropic content of cokes produced at 1000°C, irrespective of the type and size of mosaic grain or the rank of the starting vitrinite, is said to be dependent on the volatile-matter yield (Fig. 16). Anisotropy decreases markedly with increase of volatile-matter yield at about 35% and is also accompanied by a decrease in the plastic properties of the vitrinite.

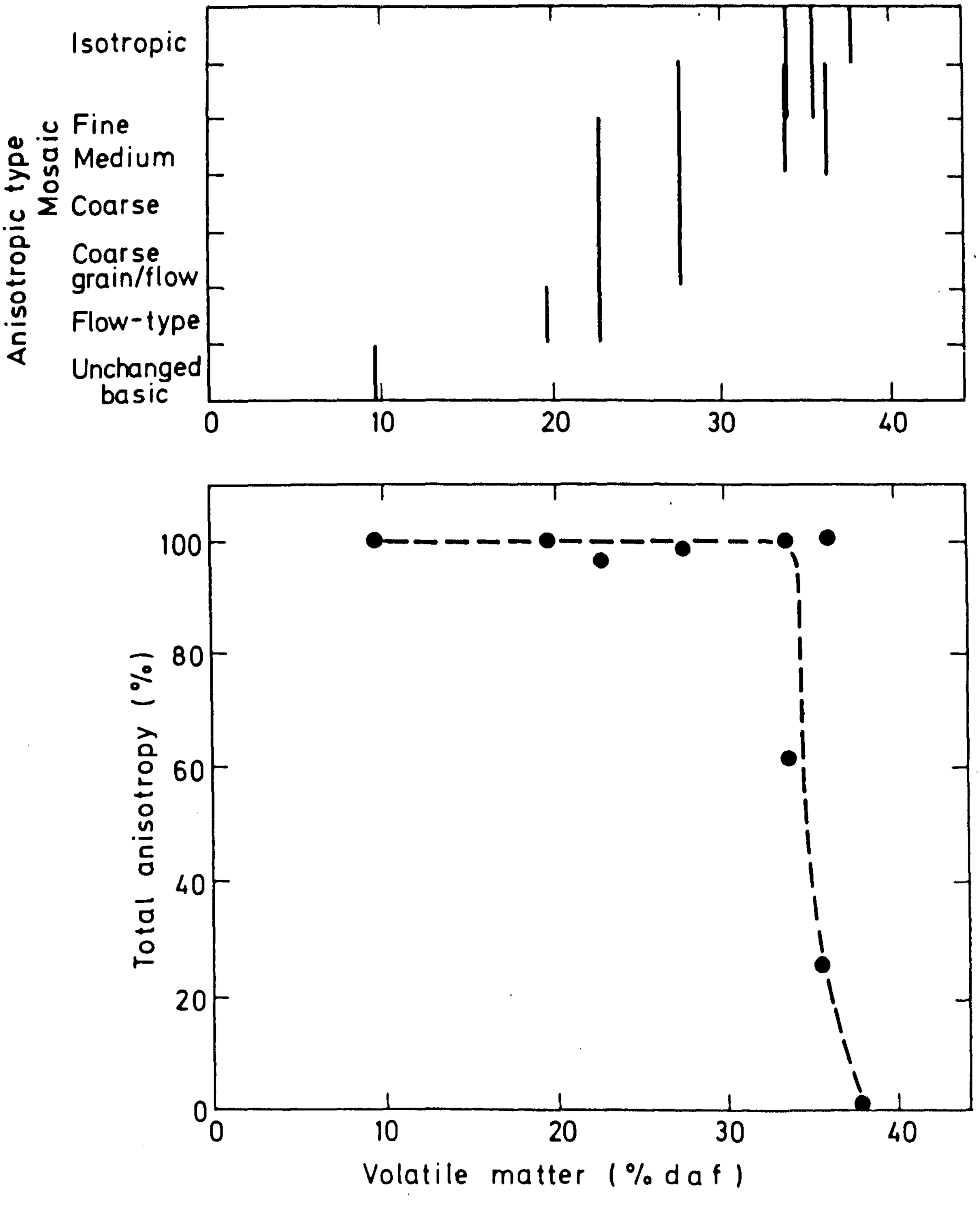
The above investigation, by Patrick *et al.* contradicts apparently what are well established facts about fresh and carbonised vitrinites. First, it classifies vitrinites of different rank (carbon = 82.6 to 89.1% daf) as being isotropic under polarised light when, in fact, these vitrinites are anisotropic, the degree of anisotropy varying from weak to medium. Also a vitrinite of higher rank (carbon = 92% daf) is suggested as being isotropic, whereas a second vitrinite of similar carbon content was classified as being anisotropic. It is well-known that vitrinite of even 80% carbon content shows some degree of anisotropy when it is examined with oil immersion under polarised light. (van Krevelen 1961, Lowry 1963 and many other authors). Patrick *et al.* also did not observe the isotropic stage commonly developed during the carbonisation of softening vitrinites, assuming that its absence was due to insufficient thermal treatment. In fact, the absence is only due to too large a temperature interval being employed.

The investigations above suggest that it is possible to use mosaic size, in addition to some other features to determine the rank of the parent constituents of cokes and also to predict the potential of a coal to graphitise at higher temperatures.

Fig 16 Variation with volatile-matter content of fresh vitrinites with anisotropic structure of carbonised residues at 1000°C

(a) type of anisotropic structure and
(b) total anisotropic structure

(after Patrick *et al.* 1973)


Anisotropic type
Isotropic
Mosaic
Fine
Medium
Coarse
Coarse grain/flow
Flow-type
Unchanged basic
0
10
20
30
40
Total anisotropy (%)
100
80
60
40
20
0
0
10
20
30
40
Volatile matter (% daf)

Non-graphitising vitrinite, excluding anthracite, does not develop a mosaic structure and the degree of being a prime coking or good graphitising vitrinite is related to the size and type of mosaic produced.

(e) Factors Affecting the Development of the Mosaic Structure

Mosaic units produced by coking of vitrinites of the coking range are commonly much smaller than the mosaic units developed during the carbonisation of pure aromatic hydrocarbons. Investigations have been carried out by many workers, e.g. Kipling et al. (1964, 1966); Marsh et al. (1973, a, b, c, d); Sanada et al. (1973) to establish a relationship between the size of the mosaic units and different factors; for example, purity of aromatic structure, oxygen content and sulphur content.

Kipling et al. (1964) carbonised polyvinyl chloride in the presence of nitrogen up to 500°C, and the residues displayed distinct optical anisotropy which was preserved, even on graphitisation to 2700°C. Initial oxidation of the same material results in reduced optical anisotropy and even further graphitisation 2700°C did not change the appearance of the oxidised material. Kipling and Shooter (1966) state that addition of sulphur or oxygen alters the structure of the carbon, probably by increasing the degree of cross-linkage within the decomposing polymer. The addition of sulphur causes reduction in the development of anisotropic areas and produces an intermediate structure to the non-graphitising and graphitising carbons.

Sanada et al. (1973) studied the formation of anisotropic textures of different ranks of carbonised coals (carbon = 81.1 to 90.7% daf) over a temperature range of 350° to 500°C and compared the anisotropic textures of the carbonised products with the findings of Kipling and Shooter (1966). They conclude that the heterogeneity of the original coal components results in the formation of different types of texture, e.g. mosaic, fibrous and leaflet.

Marsh et al. (1973, a, b) examined critically the factors influencing the formation of liquid crystals in coal carbonised under pressure, demonstrating that the small size of the mosaic in prime coking coal (carbon = 89.1%) is due to heterogeneity of the constituent molecules and to their physico-chemical properties. This was confirmed by mixing anthracene and diphenyl and carbonising the mixture under pressure. A small mosaic (2 nm) was produced in comparison with a large mosaic (10 nm) produced by only anthracene. Non-coalescence of liquid crystals in coal was attributed to (i) the presence of heterogeneous non-fusible material, (ii) obstruction of coalescence by accommodation of the residual compounds, which do not participate in the formation of liquid crystals, on the surface of crystals, (iii) loss of viscosity of the plastic mass due to the higher molecular weight of the liquid crystals in coal, which is higher than coal-tar pitch, and (iv) prevention of coalescence by the dilution of the molecules composing the liquid crystals due to an isolation mechanism. The coalescence of liquid crystals in high-rank coals (carbon = 90.2 and 91.5% daf) takes place because of higher aromaticity and the more homogeneous structure produced during coalification and also because of increase in the surface area of non-fusible constituents.

Later Marsh et al. (1973, c) investigated the formation of liquid crystals in a mixture of aromatic and oxygen-group compounds, comparing the results with the coalification series. Growth of the mosaic was enhanced by the presence of oxygen groups. It was concluded that the development of a large mesophase in prime coking coal was due to changes brought about during coalification; e.g. the content of oxygen decreases and its chemical structure becomes more attached to aromatic or cyclic structures. Carbonisation of some oxygen-containing heterocyclic compounds results in production of isotropic carbon, but the co-carbonisation of some materials produces an anisotropic carbon.

The above results demonstrate the influence of various factors on the formation of mosaic structures in cokes with different systems of carbonisation, e.g. atmospheric pressure or at higher pressure. The development of liquid crystals in carbonaceous material, e.g. vitrinite, depends on three main factors, (a) the purity of the constituent molecules (b) the oxygen content, and (c) the ability to fluidise during carbonisation. The formation of different types of texture produced in the carbonised residues of different vitrinites is certainly also directly related to the rank of the starting material. In general, low-rank coal (carbon = 81%) remains isotropic, whereas the caking and coking coals develop a different type of mosaic texture with rising temperatures. Conversion of the isotropic plastic vitrinite to an anisotropic mosaic is supposedly direct for British vitrinites under normal conditions of carbonisation, but under extreme carbonisation conditions, such as pressurised carbonisation, a mesophase develops, the units fuse to one another but do not coalesce. The spherical bodies in Australian coals, found by Taylor (1961) have not been reported from any British carbonised coals. If, as Marsh (1973, d) demonstrates, the mesophase can develop under pressure and keep its individuality, then under any extreme carbonisation conditions, such as a very fast rate of heating, carbonised vitrinite would be expected to behave differently, e.g. it might produce a spherical mesophase at a fast rate of heating. Vitrinites of low-rank and bituminous-rank are believed to behave optically as uniaxial negative materials and remain so ? during their carbonisation.

The findings of Honda *et al.* (1971) show that coal-tar pitch and substances which contain more homogeneous aromatic material than vitrinite during early stages of carbonisation, produce mesophase which behaves optically as a uniaxial positive material. Therefore, it is possible that vitrinite of high-rank coal which, according to Marsh (1973), has more homogeneous aromatic structure than lower-rank vitrinite, behaves optically as a uniaxial positive in the early stages of carbonisation. Furthermore, Goodarzi (1971) and Goodarzi and Murchison (1972) anticipated an optically biaxial structure in the bulk carbonised residua of the coking range vitrinites. Oxidation hinders the development of mosaic structure and extensive oxidation results in complete loss of mosaic formation.

6. OPTICAL PROPERTIES AND THE MOLECULAR STRUCTURE OF CARBONISED VITRINITES

(a) Introduction

Although the optical properties of vitrinites of different rank have been investigated, much less effort has been made to correlate the changes in optical properties to the modifications of molecular structure during the carbonisation process. However, Abramski and Mackowsky (1952); Bond *et al.* (1958); Mackowsky (1961); Brown and Taylor (1961); Davis (1965); de Vries *et al.* (1968); Marshall and Murchison (1971) and Goodarzi and Murchison (1972) relate the changes in the optical constants of vitrinite during carbonisation to the deformation and changes of the molecular structure.

Abramski and Mackowsky (1952) maintain that carbonisation and coalification are similar processes and that condensation and re-arrangement of crystallites can be recognised by anisotropy. However, Bond *et al.* (1958) observe that the size of aromatic cluster in carbonised vitrinites are similar to uncarbonised vitrinite of the same carbon content. Mackowsky (1961) noticed an increase in reflectivity at the time of the softening of coal, stating that since there is no increase in reflectivity of carbonised coal in the early stages of carbonisation, then the reflectivity can only be a function of the condensation of the aromatic hydrocarbons and of the size of the aromatic lamellae. Later, Brown and Taylor (1961) state that optical anisotropy is related to the sub-microscopic ordering and is an expression of the degree of the graphitisation.

Finally, Davis (1965), relating the aromaticity of vitrinite carbonised up to 600°C to their reflectivity shows there was little change in reflectivity at low temperature, e.g. 300°C, but that reflectivity increases rapidly with further rise of temperature. The reflectivity increase was accompanied by a substantial rise in aromaticity, although Davis believes that the aromaticity of carbonised vitrinites is higher than a normal vitrinite of the same carbon content. He assumes, however, that the reflectivity of carbonised vitrinite at low temperature is not only a function of its aromaticity, but is also controlled by the manner in which hydrogen is involved in structure. Davis further showed that the ring index (R/C) increases slowly at first with rise of temperature or reflectivity and then more rapidly with rise of temperature above 400°C.

The above studies show that reflectivity is not only a function of aromaticity, but also that the size of aromatic lamellae is an important factor in the increase of the reflectivity of carbonised vitrinites. Since there is little or no change in the size of the aromatic lamellae at temperatures as low as 300°C, it can be assumed that the reflectivity can only substantially increase at about the decomposition temperature. De Vries _et al._ (1968) state that the gradual increase of the reflectivity of vitrinites of different rank during carbonisation is due to the condensation of aromatic carbon caused by degasification. The increase in anisotropy is due to an orientation of the crystallites during the plastic stage. The condensation of the aromatic carbon is more intense in softening vitrinite than non-softening vitrinite, which is reflected in the behaviour of their reflectivity. The former achieves a higher level of reflectivity during the carbonisation than the latter.

The following investigations (Marshall and Murchison 1971); Goodarzi 1971; Goodarzi and Murchison 1972, a and b 1973) have a particular bearing on the work of this thesis and are now discussed in some detail.

Marshall and Murchison (1971) studied the dispersion of the optical properties of three vitrinites (carbon = 83.1, 88.6 and 93.3% daf) and related the changes in the level of their refractive and absorptive indices to the changes in their molecular structure. The refractive indices of the vitrinites increase with rise of carbonisation temperature up to 600°C and then decrease on further heating to 750°C. This initial increase and then decrease of the refractive indices was related to the results of independent X-ray studies, namely molecular improvement and deterioration during carbonisation, such as better stacking order, increase in the diameter of the aromatic lamellae and loosening of the crystallite packing. Rise in the absorptive indices of the three vitrinites, which goes on continuously with rise of temperature was related to the electronic absorption within the aromatic lamellae and to the size of the aromatic lamellae. The differences between the absorptive indices of the three vitrinites diminish with carbonisation temperature and at 750°C they develop similar levels of absorption. The anisotropy of the carbonised vitrinites also increases with temperature of carbonisation and this enhancement of the anisotropy by carbonisation was suggested as being an indication of the degree of the ordering of the molecules and was closely related to the rank of the starting materials. Coking coal vitrinite, which had a rather low initial anisotropy, developed a better structural ordering at a more rapid rate during the carbonisation than did anthracite, which had a stronger anisotropy in untreated samples. It was inferred that the anisotropy would rise with increase of the carbonisation temperature beyond 750°C. Marshall and Murchison stated that further detailed study was needed to follow more closely the changes in optical properties of vitrinites of different rank, particularly using smaller temperature intervals.

Goodarzi and Murchison (1972, a) published the results of a detailed study on three vitrinites (carbon = 82.5, 88.0 and 93.1% daf) carbonised at temperatures up to 950°C. The optical behaviour of the carbonised vitrinites was related the the different phases of the carbonisation process and also to molecular changes produced by thermal treatment and independent X-ray diffraction studies (not by those authors).

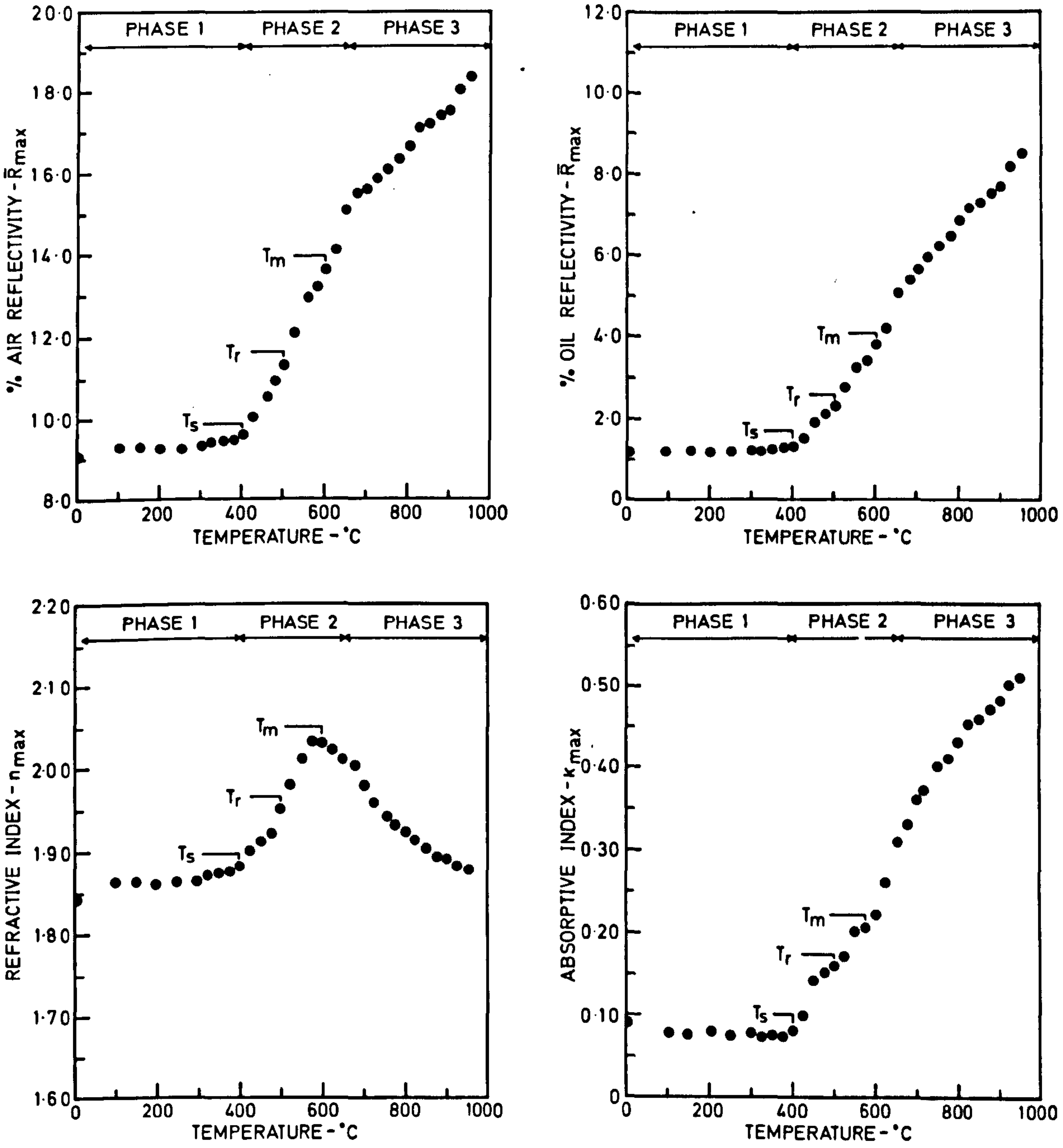
(a) Reflectivity (Figs. 13a and b)

The reflectivity of the two bituminous-rank vitrinites show little change during Phase 1. This slight change of reflectivity was attributed to changes in aromatic molecular structure, e.g. partial dehydroxylation, decarboxylation and destruction of some carbon-bonded CH_3 groups. Anthracitic vitrinite was not affected at this stage. Phase 2 began at approximately 400°C, and was marked by the onset of plasticity (Ts), ending at about 650°C. This phase also contains the onset of resolidification (Tr).(Fig 17). The rapid increase of reflectivity during this stage was related to progressive distillation of non-aromatic carbon, to the development of polycondensed aromatic lamellae and also to better ordering of aromatic layers in the crystallites. The rise of reflectivity of the anthracitic vitrinite at about 500°C was presumed to be due to the incipient growth of aromatic lamellae. Phase 3 ranged between 650°C and 1000°C; in this phase, the carbonised residues of the three vitrinites became optically more similar as growth of the lamellae continued due to dehydrogenation.

(b) Bireflectance (Fig. 12)

Early loss of the optical anisotropy of two bituminous-rank vitrinites was related to the complete disordering of the molecular structure at the onset of plasticity, a feature observed also by Davis (1965). The rapid increase of bireflectance of all three vitrinites in Phase 3 was attributed to a rapid increase

Fig 17 From Goodarzi and Murchison (1972)



Variation of the optical properties of a carbonized vitrinite (carbon = 88·0% d.a.f.) with temperature at 546nm

T_s - Onset of plasticity
T_r - Onset of resolidification
T_m - Onset of molecular reorganization
in the solid

in the degree of ordering of the lamellar structure.

(c) Refractive Index (Fig. 13c)

The behaviour of the refractive-index curves of the three vitrinites with temperature was related mainly to changes taking place in the crystallite stack heights (L_c) and also to the packing of the lamellae within the crystallites. Reversal of curves representing both refractive indices and crystallite heights began at similar temperatures. The reversal of the curve trend of refractive-index was suggested as being due to a reduction of crystallite height, probably because of disordering of the layer planes on degasification and also because of improvement of the packing of lamellae and increase of the interlayer spacing. The vitrinites could be divided into graphitising or non-graphitising, because of the contrast between the curve of refractive index for the coking coal vitrinite and those of the low-rank or anthracitic vitrinites.

The above studies clearly demonstrate the possibility of obtaining information about the changing molecular structures of carbonised residues by studying their optical properties, an alternative method to study of the structures by X-ray diffraction methods, especially in carbonised residues produced below 1000°C. One point should be emphasised; the results obtained by both these methods (X-ray diffraction and optical) are bulk studies of the substance.

The optical properties employed can be divided into three groups according to the nature of the information required.

(i) Refractive Index: the most sensitive optical constant to modification of the crystallite heights (L_c) and to the packing of layers within the crystallites.

(ii) Absorptive Index: good indicator of the crystallite diameters (L_a). Since in general there is a similarity between the behaviour of the reflectivity and absorptive-index curves, it can be assumed that the trends of reflectivity can also indicate changes in the size of crystallite diameters.

(iii) Bireflectance: the most informative of the optical properties on the degree of ordering of the structural units (or the orientation of the crystallites).

7. X-RAY DIFFRACTION STUDIES OF CARBONISED AND GRAPHITISED VITRINITES

(a) Introduction

A number of X-ray diffraction studies have been conducted at temperatures up to a temperature of 3000°C with the object of elucidating structural changes in vitrinites of different rank during the carbonisation or graphitisation processes. In these studies, the diffraction bands which form during the heat treatment of vitrinites are compared with the diffraction bands of graphite, which is normally used as a standard in X-ray diffraction studies of carbonaceous materials. Three parameters, termed 'L_a', 'L_c' and 'd' spacing are also much used.

What are '(L_a)', '(L_c)' and the 'd' spacing? 'Crystallinity' in carbons consists of a number of aromatic lamellae stacked parallel to one another. '(L_a)' refers to the 'crystallite' diameter, '(L_c)' to the 'crystallite' height and the 'd' spacing (interlayer spacing) is the distance between the aromatic layers which are stacked parallel to one another in the crystallites.

The crystalline structure of hexagonal graphite consists of layer planes of carbon stacked parallel to each other with a C – C distance of 1.41 Å and an interlayer spacing of 3.35 Å with unit-cell dimensions of 2.46 Å at room temperature. The layers stack parallel to each other in a sequence ABABA... to produce a hexagonal unit cell (Fig.18). A rhombohedral form of graphite also exists but with layer planes in the sequence

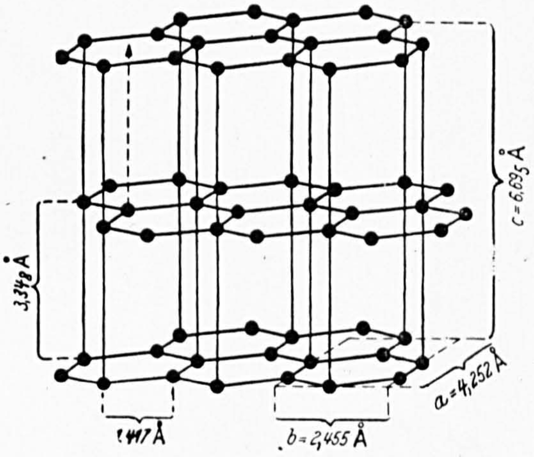


Fig 18 The crystalline structure of rhombohedral graphite (from Dahme and Mackowsky 1949, after Hoffman 1947)

ABCABCA..(see Dhame and Mackowsky 1949 and Rutland 1968).

X-ray diffraction studies are discussed in this section, because it is intended to use a qualitative interpretation of diffraction bands of vitrinites of different rank at high temperatures as supporting evidence for structural changes of coal macerals during carbonisation which is apparent in the trends of their optical behaviour. Marshall and Murchison (1972); Goodarzi and Murchison (1972) and Goodarzi and Murchison (1973) have already used independent X-ray diffraction studies by other workers as supporting evidence for optical studies.

The X-ray diffraction investigations of heat-treated vitrinites will be discussed in two parts:

(i) low-temperature (or carbonisation) up to about 1000°C, and

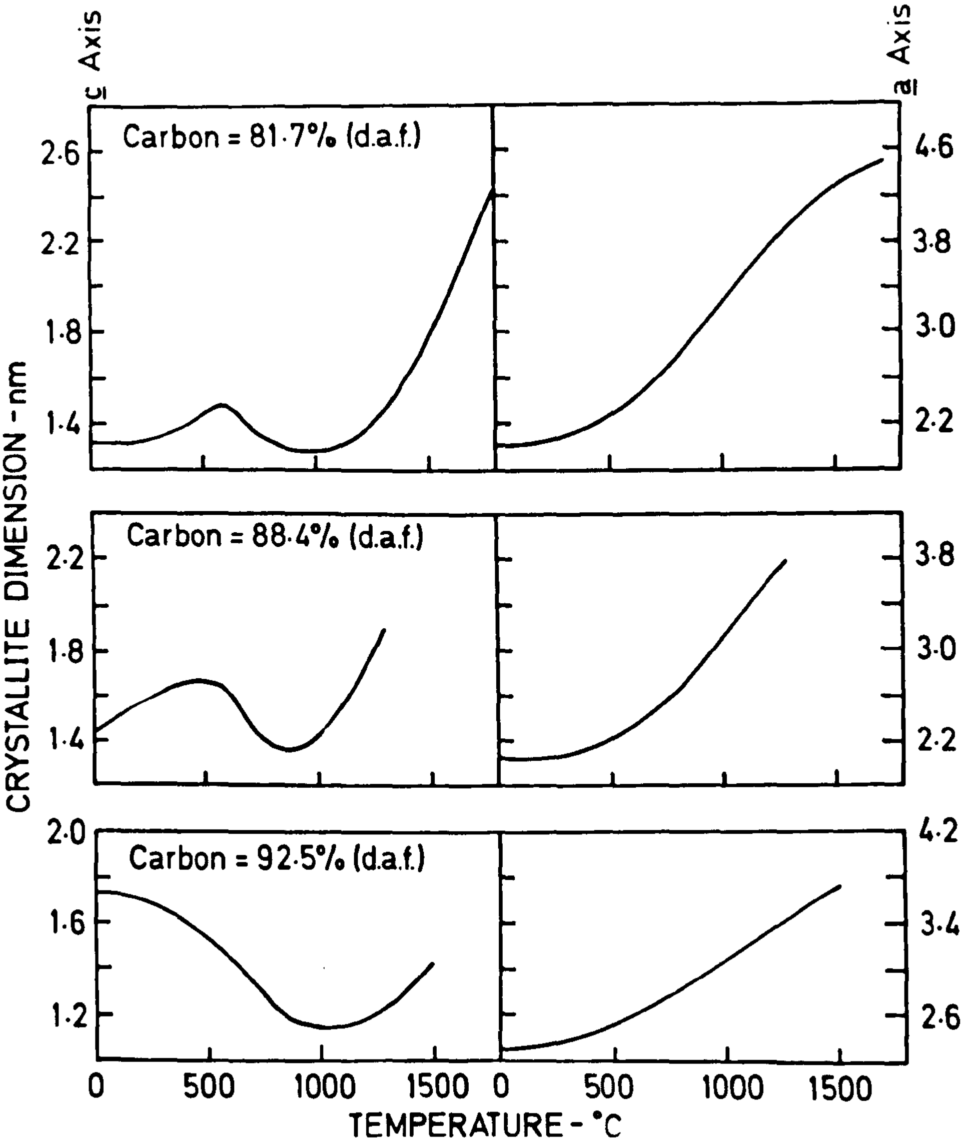
(ii) high-temperature (or graphitisation) between 1000°C and approximately 3000°C.

(b) Low-temperature X-ray diffraction studies

Investigation of the X-ray diffraction patterns of carbonised vitrinites in the temperature range up to about 1000°C have been carried out by a number of workers. Blayden et al. (1944) made a detailed study of the X-ray scattering of carbonised residues of a series of coals (carbon = 81.0 to 94.0% daf) calculating the crystallite heights (L_c) and the crystallite diameters (L_a) of the carbonised products (Fig 19). The (L_c) of carbonised bituminous-rank coal increases with rise of temperature to a maximum at about 500°C. A decrease of crystallite height between 500° and 900°C was attributed to a deterioration of the layer planes caused by devolatilisation. The (L_a) of the carbonised residues of the same coal increased only slowly up to 500°C and then increased more rapidly with further rise of temperature. The (L_a) of carbonised anthracite increased continuously with rise of temperature beyond 500°C, but the (L_c) of the carbonised anthracite fell with rise of temperature up to 1000°C.

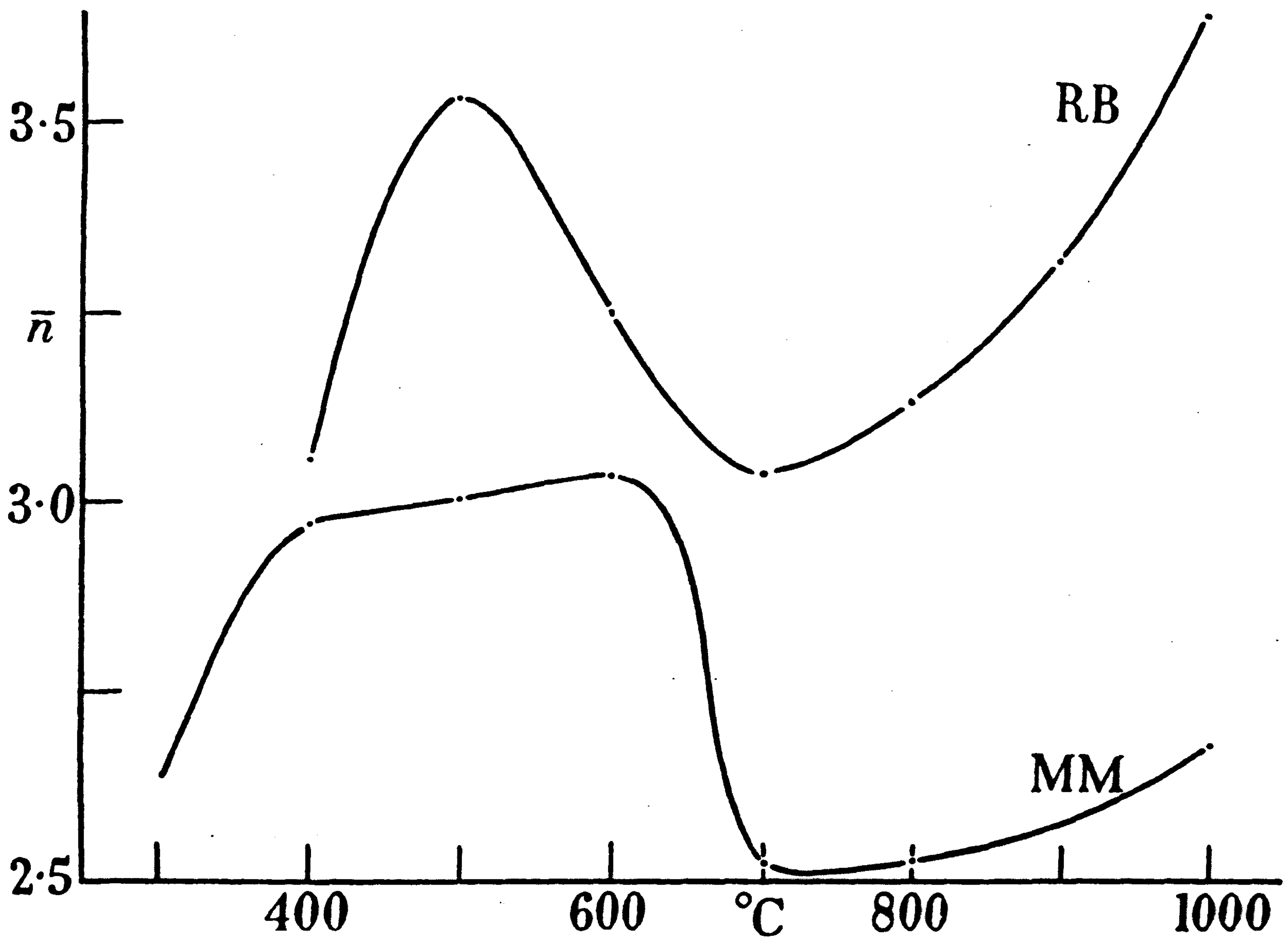
Diamond and Hirsch (1958) and Diamond (1960) also investigated by X-ray diffraction methods the structural changes in different vitrinites (carbon = 80.5 up to 94.1% daf) carbonised in the temperature range between 300° and 1000°C in general confirming the results of Blayden et al. Study of the (11) and (20) bands (scattering at high angles) showed that up to 300°C the molecular size remained similar to that of the parent coal. Growth of the layers developed between 500° and 600°C and was more rapid for anthracitic vitrinites. The variation of the average layer diameter with carbonisation was similar to that demonstrated by Blayden et al. (1944), but the absolute values were approximately half that of the other values. However, up to 500°C a large number of $-OH$ and $-CH_2-$ groups (amorphous material) were lost as volatile matter, allowing the layers to pack better. Replacement of $-CH_2-$ groups by C - C bonds began

Fig 19 after Goodarzi and Murchison 1972



Variation of crystallite diameter (La) and crystallite height (Lc) with temperature in low-rank bituminous coal (carbon=81·7% d.a.f.) high-rank bituminous coal (carbon=88·4% d.a.f.) and anthracite (carbon=92·5% d.a.f.) (redrawn after H.E. Blayden, J. Gibson and H.L. Riley)

Fig 20 The variation of number of layers per parallel group with temperature of (RB) vitrinite (carbon = 89% daf) and (MM) vitrinite (carbon = 84.3% daf) (After Diamond 1960)


3·5
$\bar{n}$
3·0
2·5
400
600
°C
800
1000
RB
MM

between 500° and 600°C, resulting in growth of layers which was then followed by removal of aromatic hydrogen at higher temperatures with further aromatic-layer growth by coalescence. The growth of layers in anthracitic vitrinite was greater, because of better original orientation of the layers parallel to the bedding planes. The average layer diameter after 600°C increased linearly up to 1000°C with rise of temperature.

Diamond and Hirsch (1958) emphasised that the average perfect molecules were very small and did not consist of large numbers of condensed aromatic rings. These small perfect layers were cross-linked to one another extensively, but imperfectly, and this resulted in large, buckled, imperfect sheets. Study of the (002) band (scattering at low angles) produced data about the packing of the layers during carbonisation which was qualitatively similar to the results of Blayden _et al._ (1944). The crystallites in coal consist of 2, 3 and 4 layer groups which are poorly packed. Packing of these layers improved with increase of temperature between 400° and 500°C, possibly due to removal of -OH groups and aliphatic materials, but with progressive increase of temperature, the packing of the layers deteriorated because the formation of larger layers caused a reduction in crystallite height by driving the layers out of the stacks sideways, and changes of orientation or cross-linking of the layers producing buckling. This deterioration reached a maximum at about 700°C, after which the packing of the layers improved again, because of the alignment of large molecules parallel to each other (Fig.20). The 'd' spacing decreased with rise of temperature to a minimum between 500° and 600°C, possibly due to removal of -OH hydroxyl and $-CH_2-$ ether groups. The 'd' spacing increased after 600°C because of cross-linking of the layers to one another. Scattering at very low angles indicated formation of large pores of 100 Å diameter.

The foregoing investigations indicate that carbonisation up to 300°C does not modify the molecular structure of vitrinites, but further increase of temperature above 300°C results in degasification of volatile groups (amorphous material) and the growth of layer diameters, which in low-rank vitrinites commences at about 300°C, in caking and coking coal vitrinites between 500° and 600°C. The increase in layer diameter is greater for anthracite. The crystallite height (L_c) also starts to increase at about 400°C, rising with increase of temperature to a maximum between about 500° to 600°C and then decreasing with further increase in carbonisation temperature until it finally rises again at about 700°C.

(c) High-temperature X-ray Diffraction Studies

Many studies have been carried out on the stages of graphitisation (above 1000°C) of vitrinites. (see for example Blayden et al. 1944; Franklin 1951; Ouchi 1955; Warren 1956 and Loebner 1956). Among them the work of Franklin (1951) is particularly important. According to Blayden et al. (1944), the crystallite diameter (L_a) and crystallite height (L_c) of vitrinites of different rank increase continuously with rise of temperature above 1000°C up to about 2200°C (Fig 19). However, this study of the molecular structure of carbonised residues of coals is one of the earliest results obtained by X-ray diffraction studies and while acceptable qualitatively it is not so quantitatively (see Hirsch 1954).

Franklin (1951) studied the structure of coals of different ranks at temperatures between 1000° and 3000°C. The coals were divided into two groups:

(i) non-graphitising, which do not graphitise, even at temperatures of 3000°C, and

(ii) graphitising, which develop a partial three-dimensional graphitic structure.

There are also those non-graphitising coals, such as anthracites, which at temperatures between 1700° and 3000°C produce graphitic carbon and also caking coals which produce an intermediate structure between graphitising and non-graphitising coals (Fig 21).

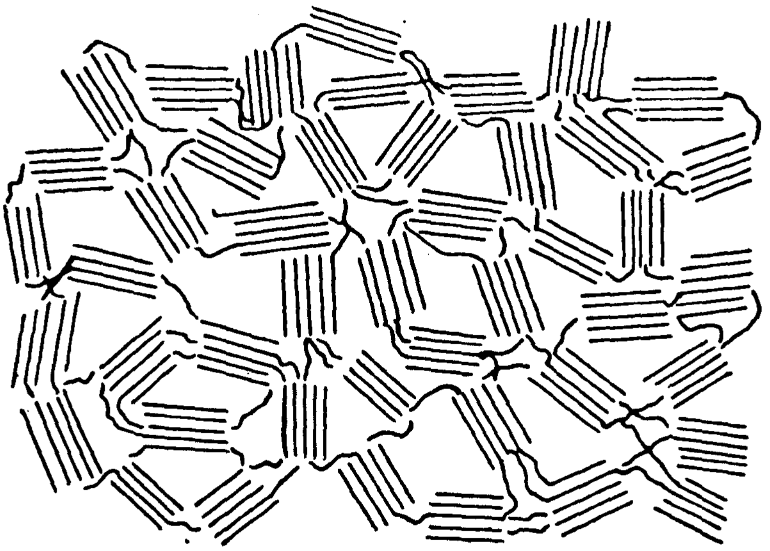
(i) Non-graphitising carbons

Low-rank coals (carbon = 83% daf, in Franklin's study) are non-graphitising due to low hydrogen and high oxygen contents. The oxygen content intensifies the degree of cross-linking between the neighbouring crystallites. However, this rigid

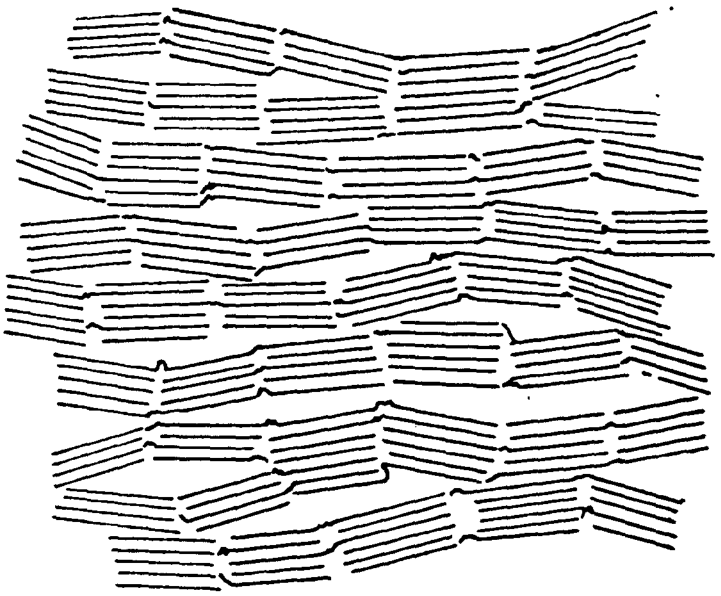
Fig 21 Molecular structure of carbonised carbons

(a) non-graphitising carbon
(b) graphitising carbon
(c) low-temperature anthracitic residue

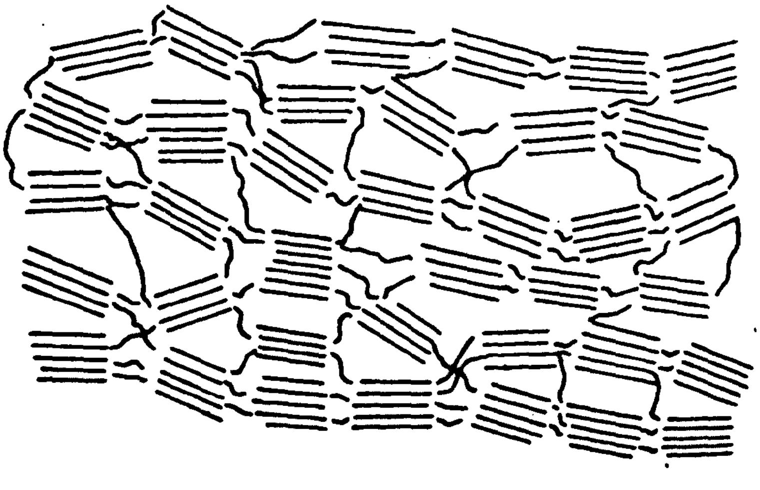
(from van Krevlen 1961, after Franklin 1951)



a



b



c

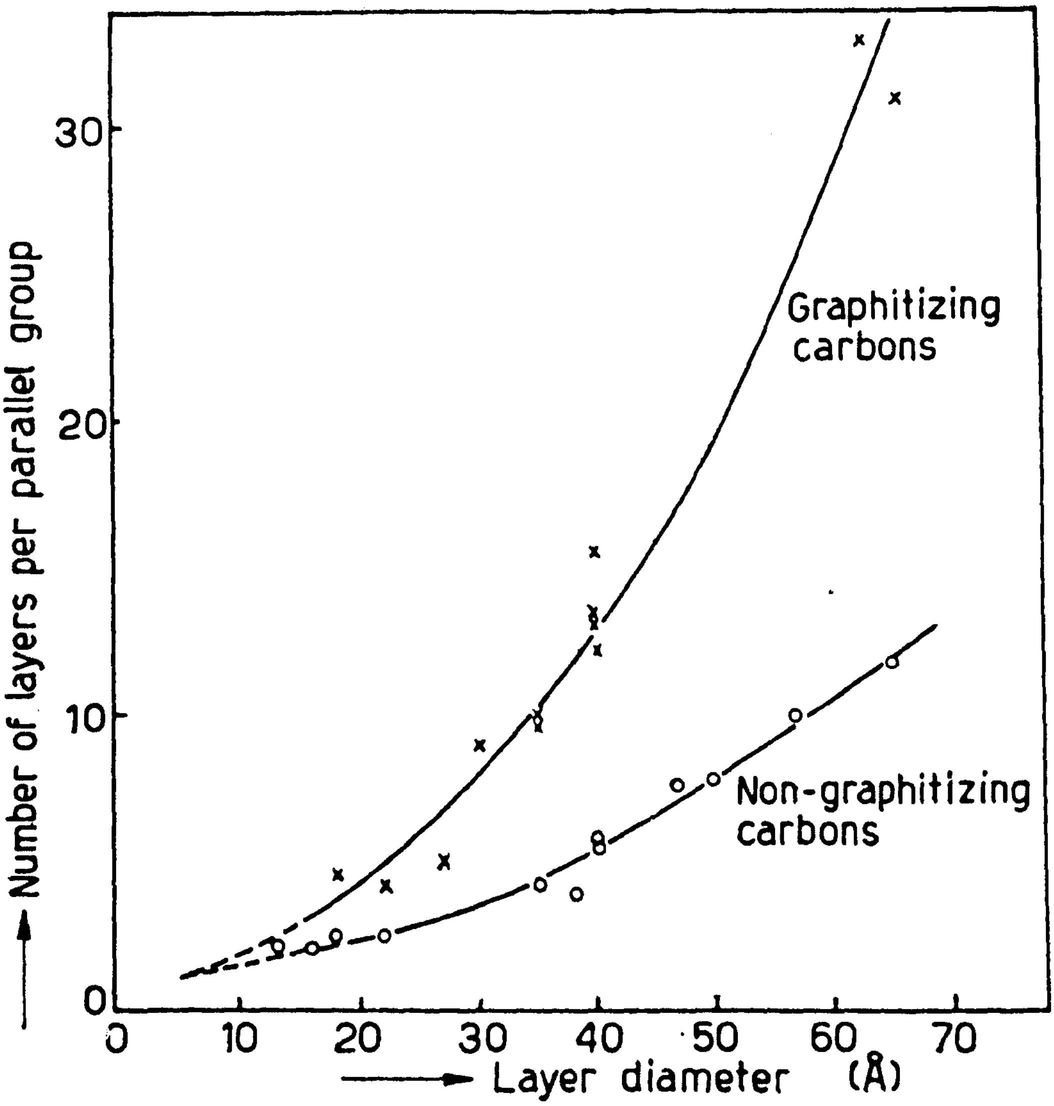
cross-linked system and large number of finely structured pores prevent two layers or groups of layers rotating in respect of their basal sections to form a parallel group of layers. However, at high temperatures, because of localised pressure and due to a strong system of cross-linking, the non-graphitising carbons produce a slight but consistent amount of graphitic structure, which results in partial destruction of the cross-linking (Fig 22).

(ii) Graphitising Carbons

A. Coking coal (carbon = 89.7% daf) is non-porous and has a compact mass. The cross-linking between aromatic lamellae is here very weak and the lamellae remain mobile in the early stages of carbonisation. The existence of a degree of preferred orientation of layer planes parallel to one another results in better ordering of the aromatic layers on heating to higher temperatures (Fig 23).

B. Anthracite anthracitic coals (carbon = approximately 93 and 94% daf) have a non-graphitic character up to 1700°C, again because of their abundant finely structured pores and even on carbonisation up to 2000°C, there is no change of structure. However, the transformation from non-graphitising to graphitising takes place on heating from 2000°C to 2500°C, producing a highly graphitising carbon due to the initial ordering of the starting material. The strong cross-linkage between the lamellae can resist temperatures up to 1000°C, after

Fig 22 Variation of number of layers per parallel group with layer diameter for graphitising and non-graphitising carbon (from van Krevelen 1961, after Franklin 1951)


Graphitizing carbons
Non-graphitizing carbons
Number of layers per parallel group
Layer diameter (Å)
0
10
20
30
0
10
20
30
40
50
60
70

which the cross-linking is destroyed slowly. When the cross-linking is destroyed, the random but perfectly orientated lamellae start to change their position by unification to form orientated crystallites with disappearance of pores (Fig 23).

(iii) Intermediate Carbons

Caking coal has an intermediate character of finely structured porosity between the graphitising and non-graphitising coals. Heating to 3000°C produces a level of graphitisation which can be obtained at about 1700°C from coking coal (Figs 23 and 24). Franklin concluded that to produce a graphitised carbon at high temperature, the starting material must be non-porous and/or suitably orientated. The mean number of layers in the parallel groups (M), or the number of stacks of c-axis layers or (L_c) and layer diameter (L_a) in graphitising vitrinite is much higher than non-graphitising vitrinites.

The above studies show different levels of molecular organisation reached by different ranks of vitrinites during graphitisation. Caking coals also develops a level of molecular organisation which is intermediate between non-graphitising and graphitising coal, and anthracite vitrinite changes from non-graphitising to a highly graphitising substance. The studies also explain that the rigid cross-linking of the layers formed in carbonised residues of vitrinite below 500°C are responsible for the non-graphitising behaviour of these vitrinites at higher temperatures. The layer diameter of the intermediate carbon

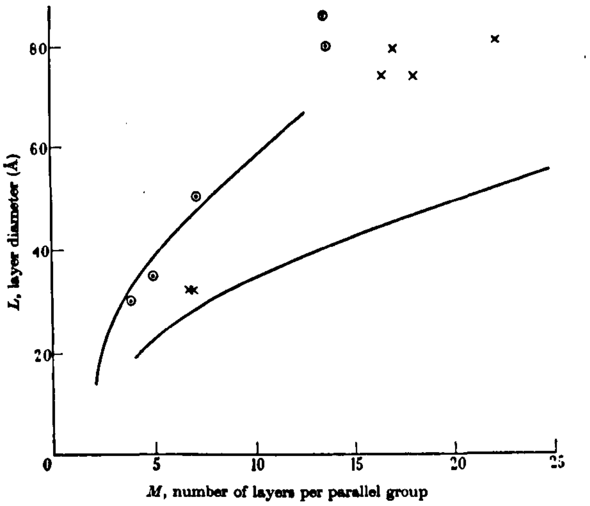


Fig 23 Relationship between the number of layers per parallel group and layer diameter for

⊙ anthracite

× intermediate carbon

(after Franklin 1951).

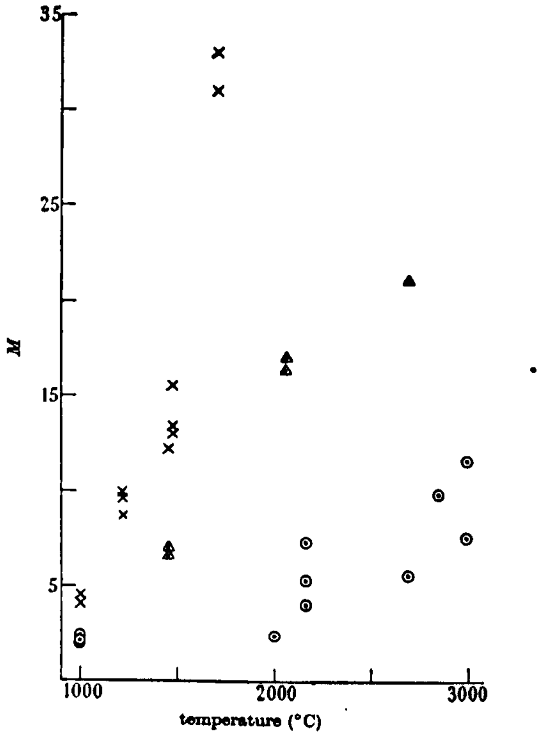


Fig 24 Variation with temperature of layers per parallel group (M) for carbons from:

× graphitising
△ intermediate
⊙ non-graphitising

(after Franklin 1951)

(such as caking coal) lies between the value of layer diameter for graphitic and non-graphitic coal.

Ouchi (1955) later investigated the molecular changes in carbons heat-treated up to 2000°C. The crystallite height increased continuously after 1000°C, whereas the crystallite diameter, after an initial increase with heat-treatment temperature, decreased to a minimum between 1200°C and 1400°C and then rose with further increase of temperature. The decrease of (L_a) in this region is related to the rupturing of the three-dimensional bonding of molecular structure in this region. A minimum of (L_a) had not been reported previously, probably because of the large temperature interval used by other investigators. Warren (1956) also studied the changes in (L_a) and (L_c) of carbon blacks heat-treated between 800° and 2800°C. The (La) and (L_c) of the carbon blacks start to increase slowly up to 1000°C and then sharply with further increase of temperature up to 2800°C (Fig 25). The sharp increase in (L_a) and (L_c) after 1000°C is related to rapid devolatilisation of hydrogen. The orientation of layers remains random even at 2800°C, when the layer diameter reaches about 65 Å, but when, in some carbon blacks, the (L_a) reaches about 100 Å, then graphitisation commences with the two nearest layers appearing to take on a graphitic relationship. Warren's results agree with the earlier findings of Franklin (1951) about two stages of graphitisation of hard carbons.

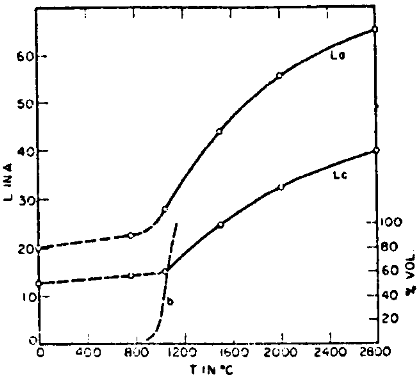


Fig 25 Variation with temperature of crystallite diameter (L_a), crystallite height (L_c) and per cent by volume of hydrogen in volatile matter for carbon black (after Warren 1956).

Loebner (1956) studied the X-ray diffraction of hard and soft carbons up to 2800°C, stating that the molecular changes brought about by heat-treatment of soft carbon differs considerably from the hard carbons. His results are essentially similar to the earlier findings of Franklin (1951).

It appears that the rate of growth of layer diameter (L_a) and the crystallite height (L_c) is dependent upon the physical and chemical structure of the starting materials (see below).

(i) graphitising coal: containing much hydrogen and little oxygen and possessing a compact molecular structure,

(ii) non-graphitising coal: with little hydrogen or much oxygen and a porous structure,

(iii) intermediate coal: with a physical and chemical structure between that of the above two coals, and

(iv) anthracite: graphitic according to its chemical structure but because of its physical properties behaving as a non-graphitic substance at low temperatures, but with increase of temperature providing the thermal energy required to break down its non-graphitic structure, altering to graphitic carbon.

A high proportion of 'amorphous' material is lost in low-temperature carbonisation up to about 1000°C.

SUMMARY

The overall molecular changes caused by carbonisation and graphitisation of vitrinites of different rank are as vollows:-

(a) Crystallite height (L_c)

The (L_c) increases with rise of temperature up to 500°C. Further increase of temperature up to about 700°C results in decrease of the crystallite height, due to various factors, including increase of layer diameter (see Diamond and Hirsch 1958; Diamond 1960). The (L_c) increases continuously after about 700°C with further rise of temperature up to 3000°C. The number of layers per crystallite is about 12 for non-graphitic carbons, about 18 for intermediate and approximately 33 for graphitic carbons (Fig 23).

(b) Layer diameter (L_a)

The growth of the layer diameter starts between 500°C and 600°C by coalescence of neighbouring layers. The rate of growth of layers is linear up to 1000°C and is greater for anthracite. Above 1000°C the growth of layers is greater for graphitising coal than non-graphitising coal (Fig 22). The layer diameter of the graphitising carbons is about 70 Å for graphitising (coking coal) at about 1460°C and 80 Å in anthracite (at about 2290°C) and 80 Å for caking coal.

PART II EXPERIMENTAL

Contents Page

1. REFLECTIVITY EQUIPMENT

(a) Reflectivity Apparatus (Plate 1)

The reflectivity photometer used in this project was constructed in the Organic Geochemistry Unit. The main parts of the measuring equipment comprise a Leitz 'Ortholux' reflected-light microscope, an auxilliary magnification system based upon a design by Gabler et al. (1960), an E.M.I. 6094B eleven-stage photomultiplier, with a spectral response extending from 200 nm to 800 nm and a peak response of approximately 500 nm, a D.C. Amplifier and a Phillips PM8220 pen recorder giving 10Mv full-scale deflection. A detailed description of similar reflectivity equipment (Fig 26) was given by Jones et al. (1968) and the equipment has been used in a number of research studies in this Unit. A Schott IL interference filter giving approximately monochromatic light at 546 nm and with peak transmission of 30% was used for reflectivity measurement. Two Leitz polarising objectives (x50 air and x60 oil) were used for measurements on field areas whose diameter could be varied from 2 to 35 microns in air and 1.5 to 30.0 microns in oil Illumination was provided by a 12 v. 60w tungsten filament lamp. The microscope stage could be rotated evenly by hand during measuremeht.

(b) Standards

Five optical glass standards, a diamond wedge and two

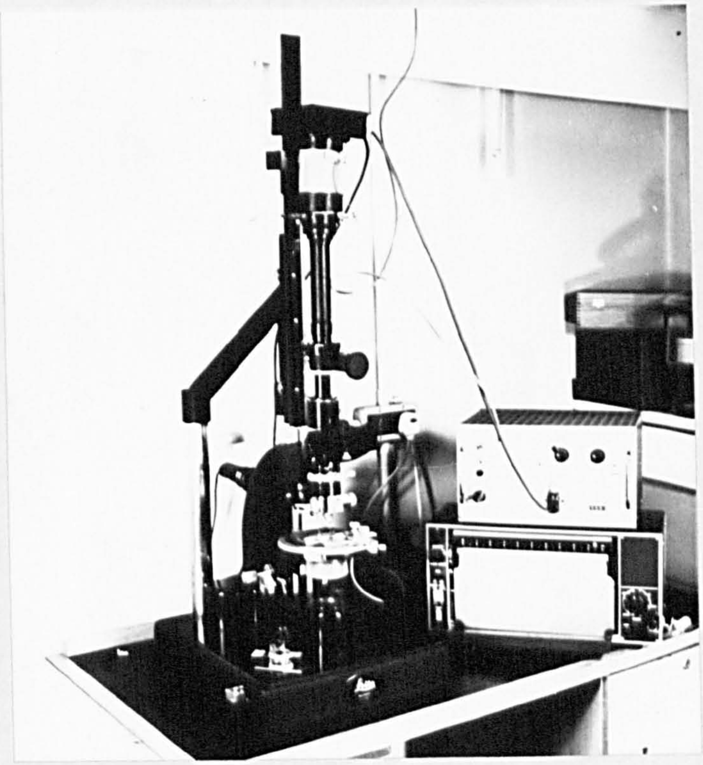
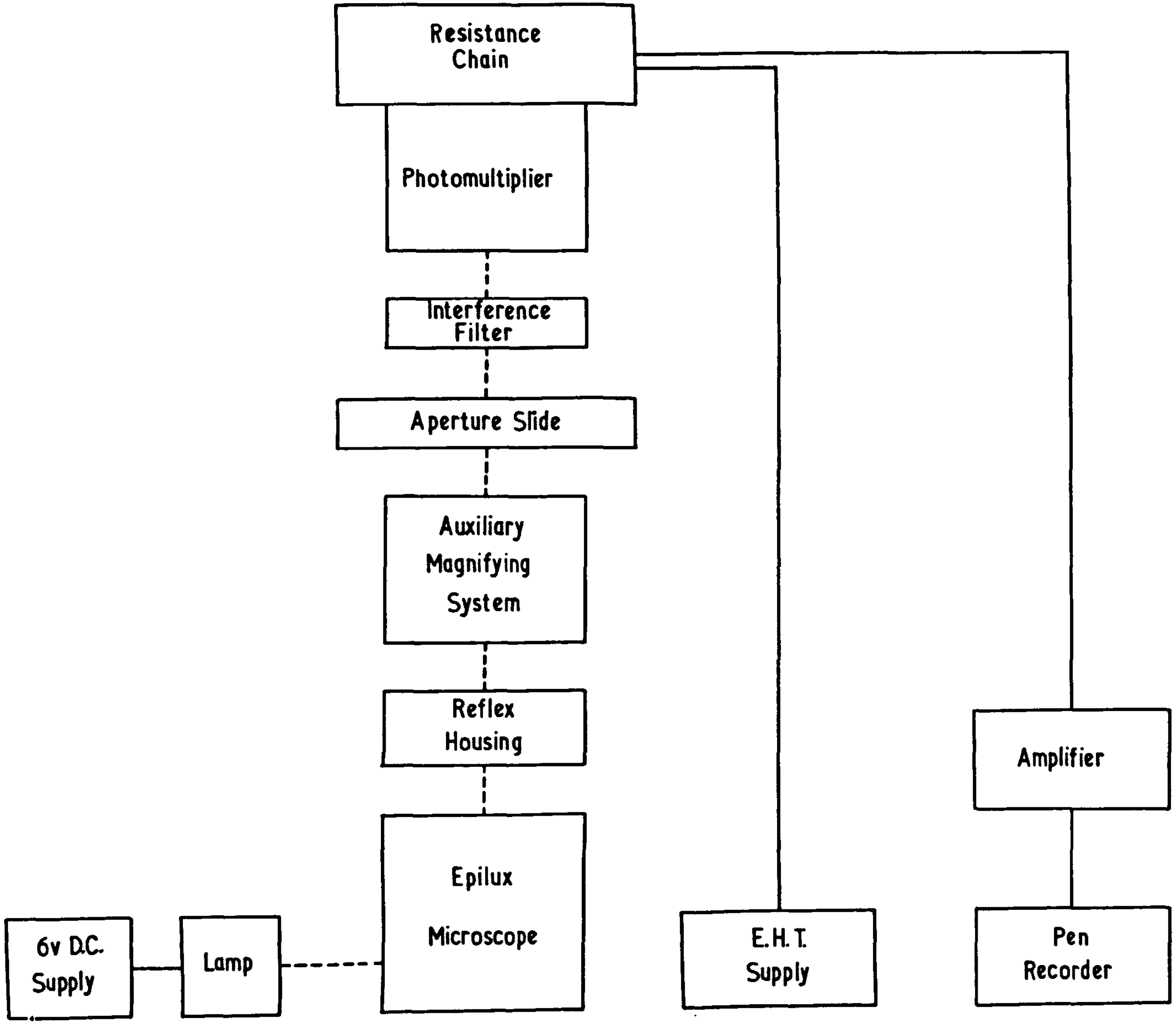


Plate 1 Reflectance equipment: Leitz 'Ortholux' reflected-light microscope, intermediate magnification system and photomultiplier Tube.

Fig 26 Diagram of microscope and photometer (after Jones *et al.* 1968).


Resistance Chain
Photomultiplier
Interference Filter
Aperture Slide
Auxiliary Magnifying System
Reflex Housing
Epilux Microscope
6v D.C. Supply
Lamp
E.H.T. Supply
Amplifier
Pen Recorder

basal plates of silicon carbide were used as standards.

(i) Glass Standards

The optical glasses were manufactured by Schott Limitd and were used for reflectivity measurement of substances with reflectivity levels of less than 2% in oil (Table 2). The optical glasses were isotropic and highly polished, but they could tarnish rapidly in air. If the standards are kept under oil, and also under cover to protect them from the direct contact with air, they can be used for as long as three weeks without further polishing - providing that the oil is regularly changed.

TABLE 2. OPTICAL DATA FOR GLASS STANDARDS AT 546 nm.

Standard	*Refractive Index	$\%R_{air}$	$\%R_{oil}$
A	1.9277	1.429	10.041
A1	1.9286	0.696	10.054
B	1.7292	1.435	8.045
B2	1.7921	0.697	8.048
C	1.7350	0.454	7.221

* Quoted to this accuracy by Schott Ltd.

(ii) Diamond Standard

The diamond standard was employed against unknowns with reflectivities higher than 12% in air or 2% in oil. A diamond wedge, mounted on a 'Bakelite' resin block provided a suitable standard because of its properties. The wedge is extremely hard so it cannot be scratched; it does not require polishing; it is isotropic and also has a strain-free surface. The reflectivity in air and oil of diamond was calculated using the Fresnel equation with values for the refractive index of diamond quoted in Dana's Textbook of Mineralogy (1892) (Table 3).

TABLE 3 OPTICAL DATA FOR DIAMOND STANDARD

Wavelength	Refractive Index	$\%R_{air}$	$\%R_{oil}$
546	2.4236	17.29	5.307

(iii) Silicon-Carbide

Basal sections of two silicon-carbide crystals mounted in 'Bakelite' were used as standards. The crystals had high hardness, were isotropic and had strain-free surfaces. The reflectivity of silicon carbide was determined by measuring reflectivities in air and oil against diamond (Table 4).

Silicon carbide has the disadvantage of being an absorbing material, so reflectivity cannot be determined directly from its refractive indices.

TABLE 4 OPTICAL DATA FOR SILICON CARBIDE PLATES

Wavelength nm 546	$\%R_{air}$	$\%R_{oil}$
Standard 1	20.32	7.33
Standard 2	20.32	7.23

The silicon carbides were used mainly for matching against the diamond standard.

(c) Immersion Oil

Low viscosity Zeiss immersion oil (no = 515) was used as an immersion medium. The oil had a refractive index of 1.516 at 546 nm and at 24°C.

(d) Specimen holder for Standards

The diamond and silicon carbide standards were levelled in a specimen holder designed by Mr. E. Scott of the Organic Geochemistry Unit. A perfect levelled surface for measurement was achieved by this method.

(e) Mounting Press

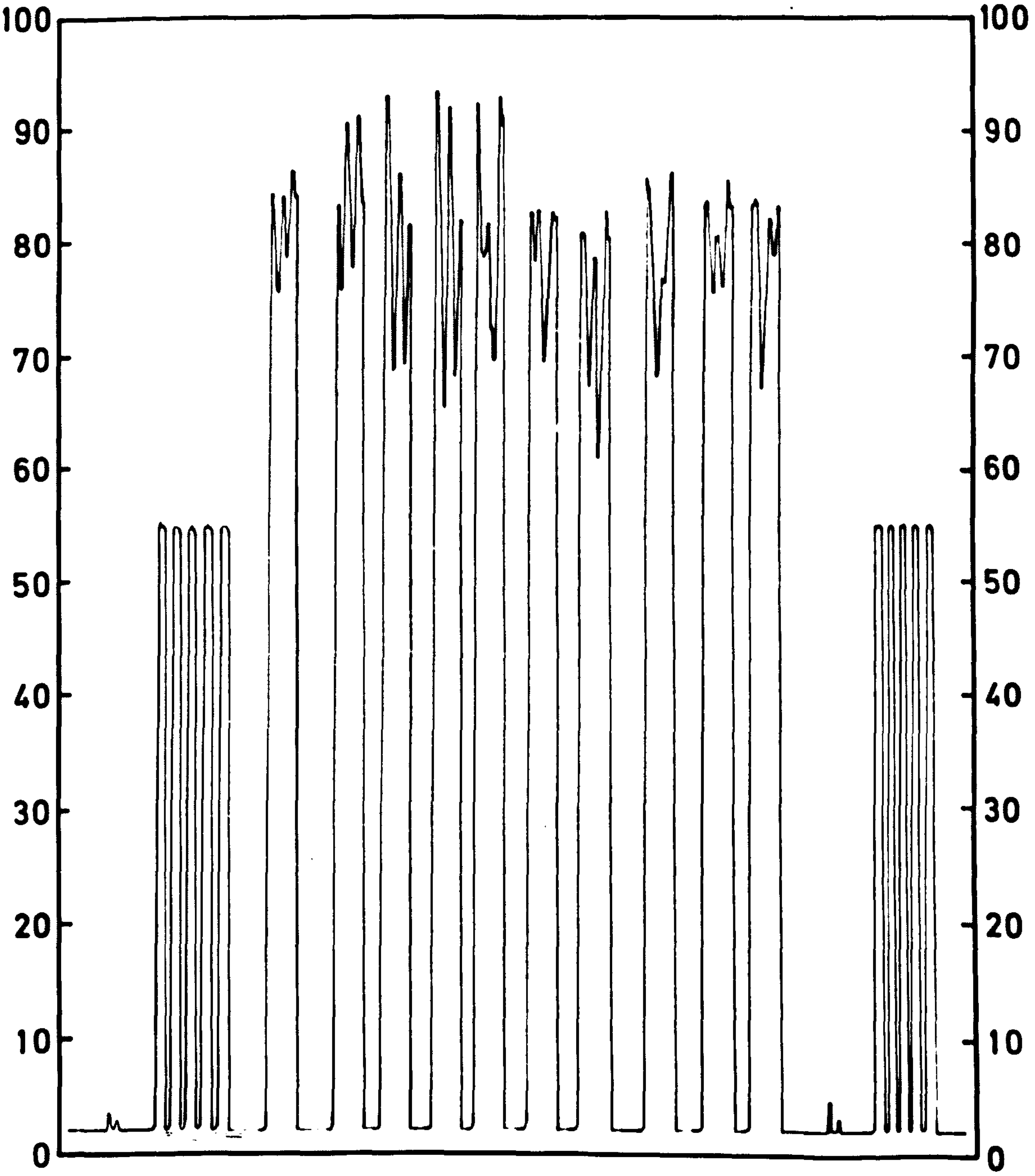
The glass standards and the specimens were mounted on glass slides using plasticene. The jaws of the mounting press were checked periodically for alignment.

2. THE METHOD OF THE REFLECTIVITY MEASUREMENT

The reflectivity of unknowns were determined directly from the trace of individual points of measurement displayed on the chart of the pen recorder by comparison with the traces on the chart produced by two standards of known reflectivity. The standards for any set of the measurements were selected so that one was higher and the other lower than the unknown material. In the case of highly reflecting materials ($\%R_{oil}$ 2.0), only the diamond standard was used, but before any measurement on an unknown, it was matched against a silicon-carbide standard. If any 'drift' was observed during the course of measurement, the diamond was once again matched against silicon carbide.

Reflectivity measurements upon an unknown were carried out in blocks of ten with five readings on alternate standards (Fig 27). In this manner, any 'drift' which might occur within the photometer during the course of the measurements, due to electrical or mechanical instability, can be detected. The stage of the microscope was rotated at each measuring point on the unknown to detect any possible anisotropy. If the unknown is anisotropic, it exhibits two maximum and two minimum values within a 360° revolution of the microscope stage. Commonly a total of fifty individual measurements of reflectivity for unknowns were made, but in some samples, to find fifty satisfactory measurable individual particles was

Fig 27 Typical recorder trace for carbonised vitrinite.



Typical recorder-chart presentation of measurements on ten different particles of a biaxial absorbing substance compared against diamond as a standard $\left[R_{oil}(546\text{nm}) = 5{\cdot}307\%\right]$

impossible - attempts were then made to keep the number of the measurements as high as possible, but only thirty individual measurements on such samples may be possible.

The mean maximum reflectivity of carbonised coal samples was calculated by averaging the two maximum readings (at each 180°) for each individual point, after which the mean of the total points measured was computed. During measurements on fresh macerals and their carbonised products up to temperatures of 450°C, the field diameter was kept at 16.0 microns in air and 14.0 microns in oil, but it was reduced to 8.0 microns in air and 6.0 microns in oil when the reflectivity measurements were carried out on carbonised residues displaying mosaic structures. Minimum reflectivity measurements were carried out on carbonised residues displaying mosaic structures. The minimum reflectivity was determined by selecting the two individual points in each set of ten measurements on the unknown which exhibited the largest bireflectance. The average value of these two individual points was accepted as the minimum reflectivity values. Vitrinite A (see Brown *et al.* 1964) was mostly measured in fresh specimens. Only one reflectivity measurement was carried out on each particle to remove any effect of type variation within the sample.

3. ORIGIN OF COAL SAMPLES

Ten different ranks of British coals were used in the present studies, the coals ranging from low-rank bituminous to anthracitic. The low-rank and caking coals (Table 5, Nos. 1 to 6) were received as large lumps and were supplied by the National Coal Board; the coking coal (Table 5, Nos 7 and 8) were collected personally and the anthracites (Table 6) were available in polythene bags filled with oxygen-free nitrogen from a collection in the Organic Geochemistry Unit. The ultimate analyses (dry ash free or dry mineral matter free bases) for these coals (vitrinite and sporinite) were all carried out by the National Coal Board analytical laboratories (Tables 5 and 6); the different bases for analysis are of little concern in the outcome of the work since the coals were originally low in ash.

TABLE 5. CHEMICAL ANALYSES OF VITRINITE SAMPLES

		PER CENT DRY ASH FREE			
Seam	Locality	C	N	S	N + O
Shallow	Lea Hall Colliery: Staffordshire	77.0	5.2	0.76	16.3
High Hazel	Warsop Colliery: Derbyshire	79.6	5.4	1.0	14.0
High Hazel	Whitwell Colliery: Yorkshire	82.3	5.0	1.1	11.6
Clown Bright	Shireoak Colliery: Yorkshire	80.0	5.30	1.2	13.5
Parkgate	Houghton Main Colliery: Yorks	85.4	5.3	1.0	8.3
Silkstone	Cortonwood Colliery: Yorkshire	86.6	5.5	1.0	6.9
Unnamed	Whitonstall Opencast Site; Northumberland	87.9	5.30	1.1	5.7
Betteshanger	Kent No.6: Kent	90.0	4.80	1.5	3.7

TABLE 6 CHEMICAL ANALYSES OF COAL SAMPLES

		PER CENT DRY MINERAL MATTER FREE					
Seam	Locality	C	H	S	N	O & errors	Volatile matter
Red Vein	Abernant Colliery: So. Wales	93.5	3.4	0.7	1.3	1.1	6.2
Pumpquart	Pentramawr Colliery So. Wales	94.2	3.0	0.9	1.1	0.8	4.8

TABLE 7 CHEMICAL ANALYSES OF SPORINITE SAMPLES

		PER CENT DRY ASH FREE			
Seam		C	H	S	O + N
High Hazel	Warsop Colliery Derbyshire	83.0	7.4	1.3	8.3
Silkstone	Cortonwood Colliery Yorkshire	87.1	6.40	1.3	6.1

4. SEPARATION AND PURITY OF VITRINITE AND SPORINITE CONCENTRATES

Vitrinite and sporinite concentrates were prepared for the carbonisation experiments as follows:-

(a) Vitrinite

The coal samples were first broken into small lumps of about 0.5 kg. and then the vitrinite bands were handpicked and concentrated into pure vitrinite samples. Brown et al. (1964) have shown that handpicked vitrinite (termed 'Vitrinite A') has a higher reflectivity and a more homogeneous appearance than the remainder of the vitrinite ('Vitrinite B') in the seam. Vitrinite A usually occurs in layers of nearly 100% purity and may have a coherent botanical structure. Vitrinite A was chosen as representative of the different rank levels in this research programme.

Handpicking of pure vitrinite was rather more difficult from the caking and coking vitrinites, due to the thinness of the vitrinite bands. Particulate blocks of handpicked vitrinites, ground to pass through -72BS sieve size were made. After polishing, the proportion of the different maceral groups and mineral matter in the samples were determined under the microscope using a Swift point-counter consisting of a counting mechanism linked to an electrically operated mechanical stage. Details of this technique are given by Glagolev (1934) and Saleh (1968). A total of about 500 points on each sample is sufficient to estimate

TABLE 8. PETROGRAPHIC ANALYSES OF COAL SAMPLES

No.	Seam	Locality	PER CENT BY VOLUME Vitrinite	Exinite	Inertinite	Mineral matter.
1.	Clown Bright	Shireoak Colliery: Yorkshire	95.0	2.0	2.0	-
2.*	High Hazel	Warsop Colliery: Derbyshire	91.0	4.0	4.0	1.0
3.	High Hazel	Whitwell Colliery: Yorkshire	96.0	2.0	2.0	-
4.	Shallow	Lea Hall Colliery: Staffordshire	94.0	3.0	3.0	-
5.	Parkgate	Houghton Main Colliery: Yorkshire	89.0	6.0	5.5	0.5
6.*	Silkstone	Cortonwood Colliery: Yorkshire	94.5	1.0	4.5	0.3
7.	Unnamed	Whitonstall:** Northumberland	92.0	5.0.	3.0	-
8.	Betteshanger	Kent No. 6: Colliery, Kent.	90.0	6.0	4.0	-
9.	Red Vein	Abernant Colliery: S. Wales	93.0	-	6.0	1.0
10.	Pumpquart	Pentremawr: Colliery, S.Wales.	94.0	-	6.0	-

** opencast site
* after J. Allan 1975

the percentage of the constituents to a sufficiently accurate level. The concentration of the three maceral groups and the mineral matter in coals are shown in Table 8.

(b) Sporinite

Two sporinites and their corresponding vitrinites were supplied by Mr. J. Allan of the Organic Geochemistry Unit. The sporinite samples were concentrated using a zinc-chloride density separation method (see J.Allan 1975). They were then ground to pass - 240 BS sieve size for the Warsop sporinite and - 240 to + 400 BS sieve size for the Silkstone sporinite. The two corresponding vitrinites were ground to pass through - 100 BS sieve. The concentrations of the three maceral groups in the concentrate are shown in Table 9. It is desirable to have a high initial concentration of sporinite, but preparation of pure sporinite concentrates is very difficult and usually the sporinite concentrate is comprised chiefly of sporinite and also other exinite macerals, rather than pure sporinite.

TABLE 9. PETROGRAPHIC ANALYSES OF SPORINITE SAMPLES (AFTER J. ALLAN 1975)

		PER CENT BY VOLUME		
Seam	Locality	Vitrinite	Sporinite	Inertinite
High Hazel	Warsop Colliery: Derbyshire	0.2	94.6	5.2
Silk-stone	Cortonwood Colliery: Yorkshire	1.0	89.7	9.3

5. GRINDING AND POLISHING OF SAMPLES AND STANDARDS

(a) Coals and Cokes

Particulate blocks were made from fresh and carbonised macerals, using small pre-cast 'Bakelite' resin discs of about 2.5 cms diameter and 1 cm thickness. A hole of 1 cm diameter and 3 mm depth was drilled in the top surface of each disc and the ground particles of macerals or their carbonised residues were placed in this depression before mixing with 'Bakelite' resin containing the appropriate percentage of accelerator and catalyst for rapid setting. The surfaces of the samples were ground on a diamond lap to produce a flat, finely scratched surface. The grinding was continued on silicon-carbide paper (grade 400) and then the sample was rotated 90° and polishing was continued on 'micro-cut' grinding paper (grade 600). Water was used for lubrication and both grinding papers were backed by glass plates, when a smooth matt surface was produced. Wet polishing was carried out on 'Selvyt' cloth-covered laps, using three different grades of alumina ($^5/20$, $^3/50$ and 'gamma'). With carbonised residues, further impregnation of the surface with 'Bakelite' was occasionally necessary due to the presence of cracks and voids which could accommodate some of the earlier polishing media and so reduce the possibility of obtaining a satisfactory polished surface at the final stage. Commonly the cracks and vacuoles could be seen after polishing to the 600 grade stage.

Fresh macerals and also specimens carbonised or oxidised up to 600°C were polished using slow rotating laps, but for samples prepared above 600°C, fast rotating laps were used, because it was found that for these samples the fast rotating laps produced better polished surfaces with reduced relief. Lengthy polishing, as well as strong hand pressures, with 5/20 and 3/50 grades was needed for the carbonised residues produced above 1000°C due to their hardness. Light hand pressure was maintained during the final stages of polishing. All specimens were rinsed in water and left in an ultrasonic cleaner for two minutes after polishing with each grade of alumina. The samples were finally rinsed in water and left for three minutes in ultrasonic cleaner before drying with tissue. Great care was taken on cleaning and drying, since improper washing could lead to the deposition of some of the polishing powder on the surface and cause a reduction of the reflectivity value.

(b) Polishing of the standards

Flat wax laps were used for polishing the glass standards. The laps were scratched with two sets of the lines perpendicular to one another to form a rectangular pattern of grooves to accommodate the polishing powder. A dilute soap solution was used for lubrication. The temperature of the lap was kept as low as possible to prevent any smearing of wax onto the surface of the standards, because of frictional heat generated during polishing.

The polishing was carried out with 5/20 and 3/50 and finally with 'gamma' aluminas and a strong hand pressure was applied during polishing. After final polishing, the standards were rinsed in water and cleaned with 'Acetone' to remove any smeared wax from the surface of the standards; then the standards were buffed on dry clean 'Selvyt' cloths. Commonly, if a standard was tarnished, firstly it was polished with 'gamma' and then, if the desired polish was not obtained, the polishing was carried out with a coarser grade of polishing powder.

6. CARBONISATION EQUIPMENT

Introduction

The coal macerals were carbonised in four tube furnaces, a pressurised carbonisation apparatus and a high-temperature graphite furnace. Depending on the nature of the experiment, different combinations of furnace and temperature controls were used (Table 10).

(a) Low-temperature tube furnaces (< 1000°C)

The tube furnaces were wound with 'Kanthal' wire, the temperatures of the 'hot zones' of the furnace being controlled by two thermocouples, one from each end of each furnace. The ends of the furnaces were sealed by rubber bungs, each of which was pierced to allow insertion of either a gas inlet or outlet and one of the thermocouples. The thermocouples were inserted separately into silica sheaths of appropriate length to reach the hot zones of the furnaces. One was connected to a 'Fostronic' chart recorder by a length of compensating cable to allow a check on temperature variation during experiments. The other thermocouple was connected to a temperature control unit. The two ends of the furnaces were cooled by a current of cool water.

Oxygen-free nitrogen was flushed through the furnaces during the course of carbonisation. All joints were painted with soap solution at the beginning of each experiment to detect

TABLE 10

THE CARBONISATION AND HIGH TEMPERATURE EQUIPMENT

Type of Furnace	Nature of Experiment	Type of Container	Gas Flush	Types of Temperature Controllers & Indicators	Type of Thermocouple	Width of Uniform Hot Zone	Temperature Range
Tube	Carbonisation	silica boats 4.5 cm length	nitrogen-free oxygen	CNS Instrument 'Sirect' Mark II proportional temperature controller	two platinum/ platinum 13% rhodium	6 cm	25° to 1000°C
Tube	Carbonisation	silica boats 4.5 cm length	nitrogen-free oxygen	'Eurotherm' temperature controller units consisting of (i) An 'Eurotherm' Programmer JA 06' set point ramp generator (ii) Eurotherm proportional temperature controller type 0.17 (iii) Eurotherm 'Thyristor' unit Type 0.31 for protection against excessive voltage	two platinum/ platinum 13% rhodium	7 cm	25° to 1000°C
Tube	Carbonisation	silica boats 4.5 cm length	nitrogen-free oxygen	Eurotherm horizontal temperature controller Type 0.72	two platinum/ platinum 13% rhodium	5 cm	350°C
Tube	Carbonisation	silica boats 4.5 cm length	nitrogen-free oxygen	Ether 'Transitrol' temperature controller	a platinum/platinum 13% rhodium & a chromal-alumel	6 cm	150°C
'Bomb' Pressurised Apparatus	Carbonisation under hydraulic pressure	sealed gold tube	none	CNS instrument 'Sirect' Mk I proportional temperature controller	two platinum/ platinum 13% rhodium	-	350° to 600°C
High Temperature graphite furnace	High-temperature heating	nuclear grade graphite boats 2.5 to 5 cm length	argon	Cambridge 'disappearing filament' pyrometer	none	10 cm at 2000°C 5 cm at 2900°C	1000° to 2400°C

any leaks of gas. The gas leaving the furnace was bubbled through a flow-meter to ensure even flow through the furnace.

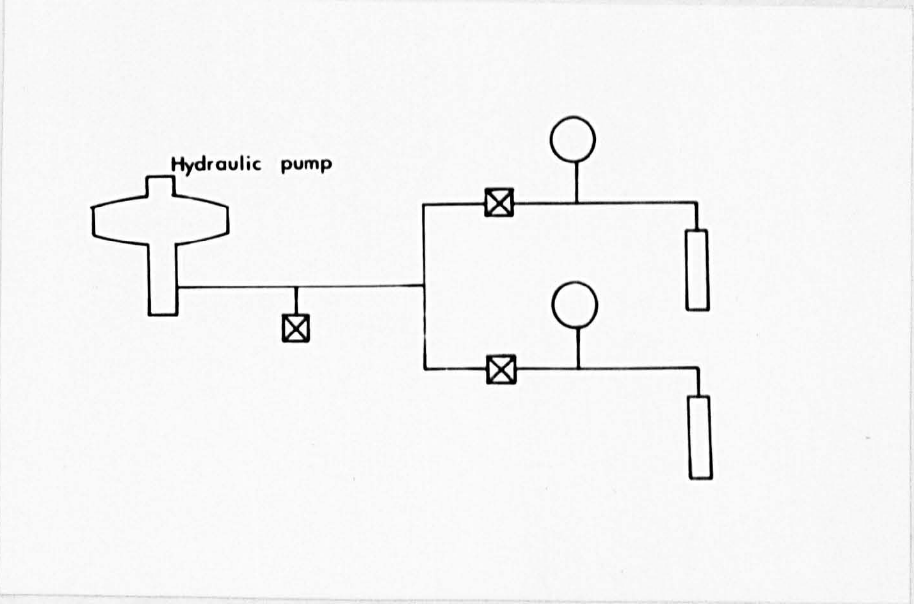
(b) Pressurised carbonisation apparatus (Figs 28 a and b)

This apparatus provided a maximum hydraulic pressured 4Kbar, at a temperature level of up to 600°C. An air compressor (Fig 28a) indirectly pressurises the hydraulic system by pressurising the hydraulic fluid, which transmits the pressure to a 'Stellite bomb' (Fig 28b) capable of withstanding pressure of 60000 psi. A full description of this apparatus was given by Marsh *et al.* (1970) and Melvin (1974).

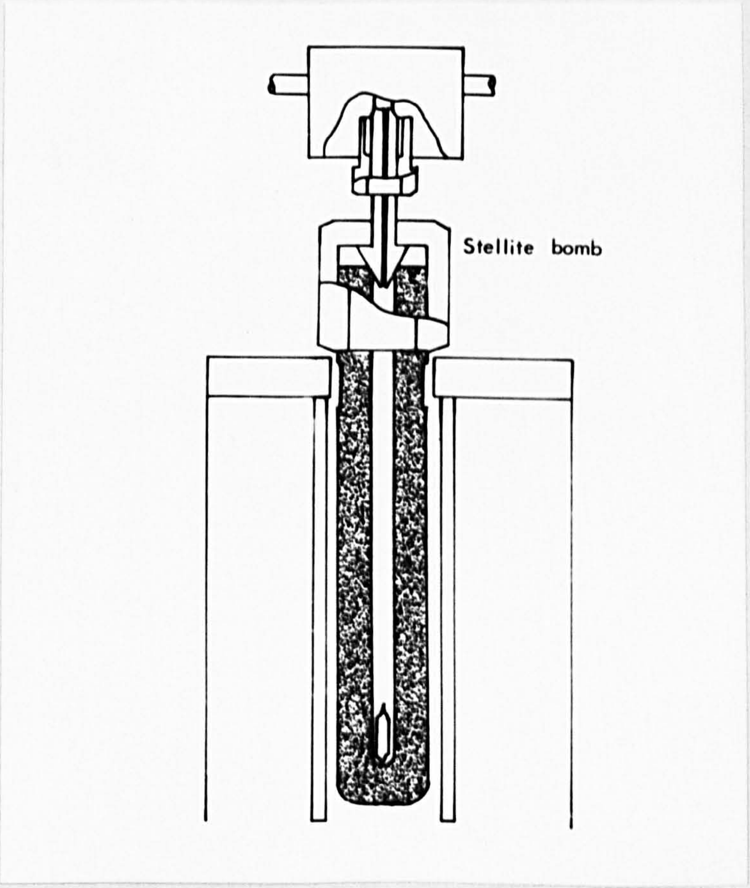
(c) High-temperature graphite furnace (Fig 29)

This furnace was used for the temperature range above 1000°C up to 2400°C and was described in detail by Marsh and Wynne-Jones (1965). Further detailed information relating to the above equipment can be found in Table 10.

Fig 28 Apparatus for carbonisation under pressure (after Melvin 1974)

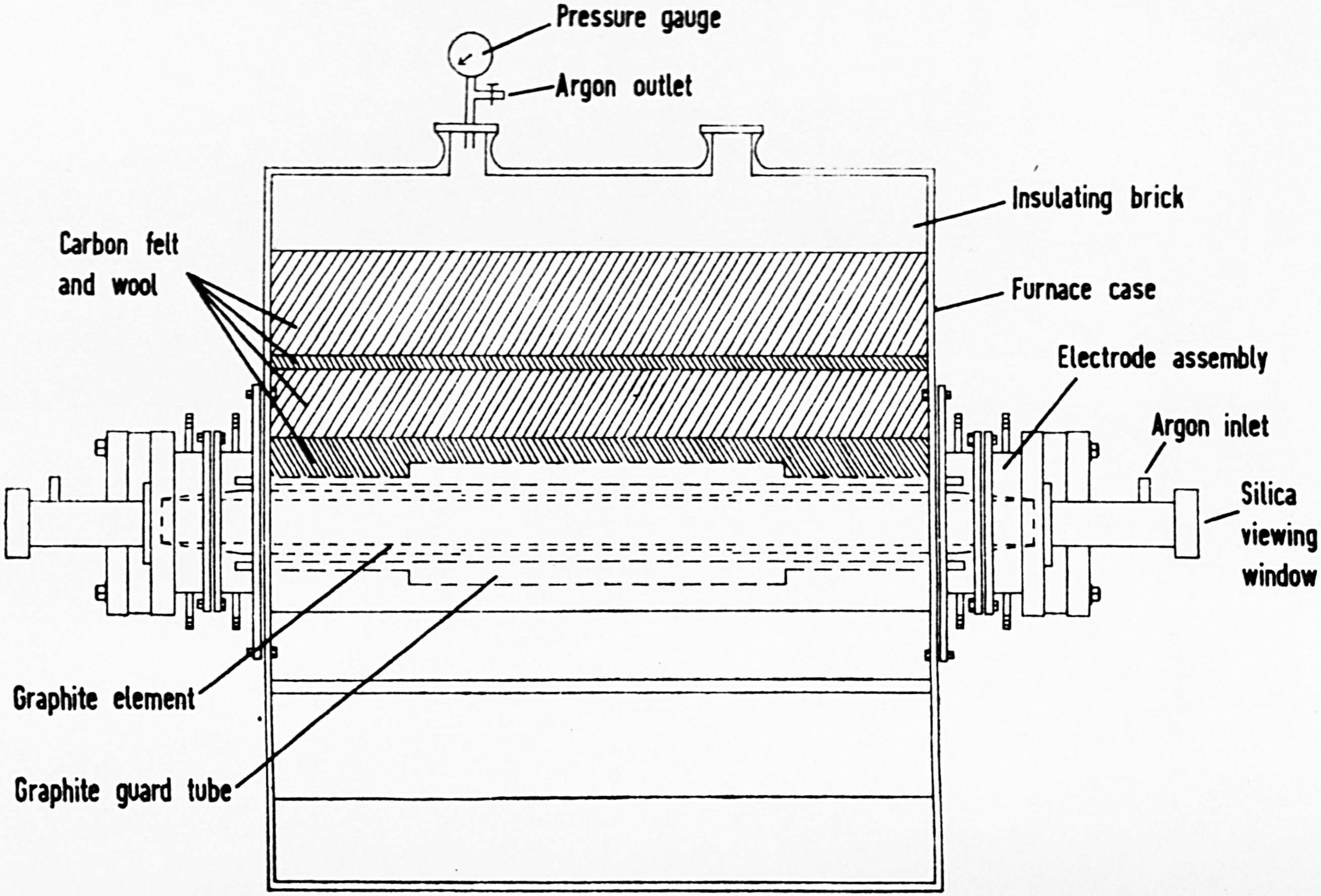


(a) whole system



(b) satellite 'bomb'

Fig 29 High-temperature graphite furnace (after Marsh and Wynne-Jones 1965).


Pressure gauge
Argon outlet
Insulating brick
Carbon felt and wool
Furnace case
Electrode assembly
Argon inlet
Silica viewing window
Graphite element
Graphite guard tube

7. STORAGE AND INSERTION OF SAMPLES INTO FURNACES

Introduction

The ground samples were dried overnight at room temperature in a dessicator flushed with oxygen-free nitrogen prior to the start of each experiment. Samples used in high-temperature carbonisations (i.e. $> 1000^\circ C$) were first carbonised at $900^\circ C$ for one hour and were then kept in bottles flushed with oxygen-free nitrogen so they did not need drying prior to the start of high-temperature treatment.

(a) Low-temperature tube furnace

The samples were inserted ½ hour before the start of the experiments and the furnace was flushed with oxygen-free nitrogen to remove the oxygen in the system. The boats were half-filled with ground samples to allow some space for swelling which occurred during carbonisation of some samples. They were then placed on a firebrick or a metallic container with a semi-circular section. After the appropriate soak period, the temperature of the furnaces was allowed to drop to room temperature (about $25^\circ C$). The samples were removed and stored in sealed bottles, which were flushed with oxygen-free nitrogen.

(b) Pressurised carbonisation apparatus

This apparatus was operated by members of staff of the Northern Coke Research School of Chemistry Laboratories. The samples were sealed in gold tubes, which were placed at the bottom of the vessel ('bomb') (Fig 28b). The bomb was then filled with distilled water as a transmitting medium and connected to the hydraulic compressor (Fig 28a) before the bomb was lowered into the furnace. Rapid quenching in cold water was carried out at the end of each carbonisation (for further information see page253).

(c) High-temperature graphite furnace

One hour 'waiting' time was allowed prior to the start of carbonisation when the furnace was flushed through with argon. The boats were directly inserted into the uniform hot zone. Removal of the samples was similar to the low-temperature tube furnaces.

8. EXPERIMENTAL FACTORS INFLUENCING THE CARBONISATIONS

Introduction

It is desirable to expose all samples to the same conditions during each experiment. In the present research programme a wide range of temperature levels, rates of heating, soak periods and pressure levels were employed (Table 11). To obtain accurate and uniform results, the different samples in each experiment, when appropriate, were carbonised together, so that the residues at that particular level of heat treatment suffered the same conditions. The degree of control of the various experimental factors varied, however, with the type of furnace and temperature-controlling equipment.

(a) Tube Furnaces

The temperatures were controlled to an accuracy of about ± 5°C within a uniform hot zone which varied, depending on the furnace, from 5 - 7 cm. The rate of heating was controlled to an accuracy of ± 2°C/min at the fastest rate of heating used (60°C/min), but the control on the rate of heating increased as the rate fell. 'Soak periods' were controlled exactly.

(b) Pressurised carbonisation apparatus

The accuracy of control of the temperature levels of this equipment to about 10°C with a control on the rate of heating

TABLE 11. THE EXPERIMENTAL CONDITION EMPLOYED IN PRESENT RESEARCH PROGRAMME

Nature of experiment	Temperature (°C)	Rate of heating °C/min.	Temperature interval	Soak period: time
Influence of rate of heating during carbonisation	400–950°C	± 1°C ± 10°C ± 60°C	50°C 400–550°C 25°C 550–700°C 50°C 700–950°C	1 hr.
Heating below decomposition phase, for different periods of time.	150°C and 350°C	none	none	between 1 & 32 wks.
Carbonisation of sporinite alone and sporinite and vitrinite mixtures	300–950°C	± 5°C	50°C 300–450°C 25°C 450–700°C 50°C 700–950°C	1 hr.
Influence of pressure during carbonisation	350–600°C	± 4.5°C	50°C	1 hr.
High temperature treatment	1000–2400°C	± 10°C	50°C–1000–1400° 100°C–1400–1600° 200°C–1600–1800° 400°C 2000–2400°	1 min.

about ± 0.7°C/min (see Part VI later for details: note there is a 20°C gradient through the gold tubes from top to bottom). The soak period was approximately one hour. A wide range of pressure levels was used in the present study, lying between about 3000 psi to 45000 psi. The level of pressure could be controlled to an accuracy of ± 1000 psi at highest pressure level.

(c) High-temperature graphite furnace

The temperature could be controlled to an accuracy of about ± 10°C within the hot zone, but the accuracy of temperature measurement could be much less accurate than ± 10°C because of the use of a visual pyrometer. The accuracy of the rate of heating was about ± 2°C/min and a rate of approximately 10°C/min was used, although the rate was higher than 10°C/min up to 1200°C and then decreased with rise of temperature. A precise soak period of 1 minute was used throughout this series of experiments.

9. PHOTOGRAPHY

(a) Optical photomicrography

Optical photomicrographs were taken with an 'ASAHI' camera mounted on a Zeiss 'Standard Universal' reflected-light microscope (Plate 2). With a built-in magnification of x1.25 and using Zeiss x16 or x40 'Antiflex' oil immersion objectives with a x10 ocular to give an overall magnification of either x174 or x184 onto the film, images were recorded on 'Pan F' film. The photomicrographs were taken either in plane-polarised light or with crossed polars.

(b) Electron micrography

A 'Stereoscan' (Foster-Cambridge Instruments Ltd) scanning electron microscope was used. For this purpose, a small amount of sample, a 1mm cube (approximately) of a relief-polished, or unpolished, sample was mounted on a flat mushroom-shaped specimen holder. To promote electrical conductivity, gold-palladium alloy shadowing was carried out under high vacuum. (full details of the technique emplöyed are given by Boult and Brabazon 1968).

Plate 2 Photomicrography equipment. Zeiss and Standard Universal microscope and 'Asahi' camera.

10. X-RAY EQUIPMENT AND METHOD

(a) Equipment

X-ray powder photographs were obtained using cuK α radiation produced by a Phillips X-ray generator with a camera radius of 6 cm. To obtain sharper diffraction bands, small collimeters were used throughout the experiments.

(b) Method

The specimens were ground to pass through a 240 BSS sieve and poured into a 0.3 mm silica-glass capillary. The glass capillary was then placed in the camera and carefully centred after loading the film. The camera was mounted on the X-ray generator. The cuKα radiation was produced at 40 KV and 20 MA. A nickel filter was placed immediately in front of the slit to absorb the Kβ radiation. Films were exposed for 2 hours and then developed. The diffraction bands were indexed and compared qualitatively with those of graphite.

11. DETERMINATION OF THE OPTICAL PARAMETERS OF OPAQUE MATERIALS

(a) Reflectivity

Specular reflectivity is the percentage of incident light which is reflected from the surface of an optically flat polished surface. The reflectivity of a transparent substance is dependent on the refractive index of the surrounding medium, the wavelength at which the reflectivity measurement is carried out and the condition of the surface of the substance.

The percentage reflectivity of a material with negligible or no absorption, such as diamond or glass, can be calculated from the Fresnel equation.

$$R = \frac{(n - n_m)^2}{(n + n_m)^2} \qquad \text{............ (1)}$$

where

R is the percentage reflectivity of the substance at normal incidence,

n is the refractive index of the substance, and

n_m is the refractive index of the surrounding medium

The above equation is modified for an absorbing material when the following equation (Beers) is used:

$$R = \frac{(n - n_m)^2 + n^2k^2}{(n + n_m)^2 + n^2k^2} \qquad \ldots\ldots\ldots\ldots\ (2)$$

where

k is the absorptive index,

the absorption coefficient K is sometimes used in above equation, where K = nk.

(b) Refractive Index

Refractive indices may be calculated by applying Beers equation (2) after measuring the reflectivity in two media, (e.g. air and immersion oil), using the equation in the following transposed form:

$$n = \frac{\frac{1}{2}(n^2_{oil} - n^2_{air})}{n_{oil}\frac{1 + R_o}{1 + R_o} - n_{air}\frac{1 + R_a}{1 - R_a}} \qquad \ldots\ldots\ldots\ldots(3)$$

where

n is the refractive index of the substance

n_{air} is refractive index of air

n_{oil} is the refractive index of the immersion oil

R_a is the reflectivity of substance in air, and

R_o is the reflectivity of substance in oil.

(c) Absorptive Index

The absorptive index (k) can be calculated from the following equation:

$$k = \frac{R_a (n + 1)^2 - (n - 1)^2}{n^2 (1 - R_a)} \quad \ldots\ldots\ldots\ldots (4)$$

(d) Bireflectance

The bireflectance of a substance is calculated from the difference between the true maximum and true minimum reflectivities.

$$\text{Bireflectance} = (\%R_{max} - \%R_{min}) \ldots\ldots\ldots\ldots (5)$$

12. FACTORS INFLUENCING THE ACCURACY OF THE REFLECTIVITY MEASUREMENT

The improvement in techniques of reflectivity measurement has greatly enhanced the accuracy of such determinations. Many investigations have been carried out to detect the sources of error in reflectivity determinations and in the derived optical constants, but some of these lacked systematic study and only considered a few of the factors involved.

Dahme and Mackowsky (1950) and (1951); Wege (1954); Jones (1961); Murchison and Boult (1961); von Gehlen and Piller (1964); Harrison (1965); Galopin and Henry (1972); Juckes (1973); Melvin (1974) and Cook and Murchison (1975) studied the errors in reflectivity measurement and their correction. With careful adjustment of the reflectivity equipment and the correct polishing techniques, the fundamental sources of error can be reduced and a reproducibility of less than 1% can be achieved. Accurate reflectivity measurement is dependent on the elimination of many sources of error. Some of these sources of error arise within the reflectivity equipment and are termed internal sources of error; some are due to inaccuracies caused by the surfaces of specimens and standards and the operators. These are termed external sources of error. All the possible sources of error are summarised below, although many have been considered by previous workers in this Unit.

(A) Internal sources of error

These errors are as follows:-

(i) errors due to misuse of standards,
(ii) levelling errors,
(iii) focusing errors,
(iv) errors due to the conditions of the microscope system, and
(v) errors due to change in properties of the immersion oil.

(i) Errors due to misuse of standards

It is desirable to employ standards whose reflectivities lie as close as possible to the unknown sample so as to reduce the errors due to the drift, secondary glare and variation of the properties of the immersion oil (see later). Naturally glass standards would not be used against diamond or silicon carbide, because of errors that would arise from their much different levels of reflectivity.

(ii) Levelling Errors

The standards and the specimen must be correctly aligned perpendicular to the optic axis of the microscope, because inaccurate results will be obtained due to the tilt away from the optic axis. Wege (1954) and Galopin and Henry (1972) have clearly demonstrated that erroneous reflectivity values can be obtained because of inaccurate levelling.

(iii) Focusing Errors

Improper focusing leads to incorrect reflectivity values and care must be taken to ensure correct similar focusing on standards and unknowns. Dahme and Mackowsky (1950); Wego (1954); Jones (1961) and Galopin and Henry (1972 recognise the errors that arise due to focusing. However, accurate focusing is rather difficult on standards, particularly, with reflectivity measurements under oil on glasses, but this difficulty can be overcome by focusing on a mark or scratches on the surface of the standards. There is no problem when making measurement on coal constituents, due to their more heterogonous nature.

(iv) Errors due to the Condition of the Microscope System.

A reproducible result can only be obtained if the optical conditions of microscope are stable, e.g. the lamp and photomultiplier are stable and also the photomultiplier is linear in its response. However, within this group, there are other sources of error due to:

(a) instability of the electrical system,
(b) drift,
(c) 'warm-up' time of the microscope,
(d) microscope stage,
(e) 'glare' effect

(a) Instability of the electrical system

The Electrical stability decreases when operating the photomultiplier using the very small apertures and high voltages, e.g. above 1400v. Use of the photomultiplier in this condition results in excessive electrical noise and continuous fluctuation of the signal received by the photomultiplier. The signal noise within the system can be eliminated by decreasing the voltage across the photomultiplier and increasing the aperture size. However, after establishing electrical stability within the equipment, if any further modifications are needed during the course of the measurement, e.g. due to a sudden increase in the level of the reflectivity of the unknown, then this problem can be overcome only by adjustment of the light intensity.

(b) Drift

Instrumental drift can be observed by alteration of the level of the standard reading on charts during reflectivity measurements; normally the drift is linear between standards. However, the reflectivity measurements must be stopped if the drift is irregular or changes direction. The greater the drift, the more frequent must be the measurements on the standard. Melvin

(1974) states that the drift effect increases with rise of temperature.

(c) 'Warm-up' time of the Microscope

The reflectivity equipment, after switching on, must be allowed 20 mins 'warm-up' period to reach equilibrium, due to the electrical components in the circuits of the apparatus. Determination of reflectivity during this period would lead to inaccurate results.

(d) Microscope Stage

If the stage of the microscope is not properly centred to the optic axis of the microscope, then in measurements of anisotropy it produces inevitable errors due to movement of the particle away from the point on which measurements are being made. Uneven movement of the stage on rotation results in an increase or decrease of reflectivity due to increase and decrease of the distance between objective and stage (see Melvin 1974).

(e) 'Glare' Effect

Glare or back-reflectance is the amount of stray light within the optical system reflected from surfaces of various components. This error can simply be eliminated by measuring the amount of this light and subtracting it from the total reading. However, there is another more complex type of glare ('secondary glare') which is due to light reflected by specimen being reflected down again by the objective front lens. Piller (1967) recognises this source of error. The magnitude of secondary glare effect is related to the microscope objective and level of specimen reflectivity, but is relatively unimportant in lower reflecting materials.

(v) Errors due to change in properties of immersion oil

The refractive index of the oil has a direct influence on the reflectivity of an unknown material. The refractive index of immersion oil decreases with increase of temperature, which results in an increase of the reflectivity of the specimen. Jukes (1973) reported on changes in the refractive index of immersion oil with temperature, concluding that errors arising from the variation of the refractive index of the oil in the temperature range of about 25° up to 35°C is negligible. The same author also pointed out a variation in the properties of the immersion oil due to contamination or deterioration with age. To eliminate this source of error, the immersion oil should be changed daily.

(B) External sources of Error

In making routine reflectivity measurements, external sources of error are also a limiting factor. These sources of error are as follows:-

(i) errors due to the operator,
(ii) polishing errors,
(iii) errors in chart reading,
(iv) errors due to the moisture content of specimens (coal macerals), and
(v) errors in the number of measurements.

(i) Errors due to the operator

The results of a series of experiments conducted by the British Coke Research Association (1972) at different laboratories to determine the reproducibility of the reflectivity of a series of coal within and between the laboratories are shown (Table 12). It is evident from this Table that the average maximum oil reflectivity values determined by different laboratories for the same coals produce a difference in results. The discrepancy of the results is probably a combination of the different levels of accuracy and the varying quantity of the areas to which the reflectivity measurements were made, e.g. the reflectivity values given by the University of Newcastle upon Tyne for all three coals are higher than those from other laboratories, in this case, probably due to making the reflectivity measurements only on Vitrinite A which would normally result. in a higher reflectivity value.

TABLE 12 REPRODUCIBILITY OF THE REFLECTIVITY WITHIN AND BETWEEN THE LABORATORIES (AFTER B.C.R.A. REPORT, 1972)

Laboratory No.	a.Low-rank* %R_{oil}	b.Medium-rank* %R_{oil}	c.High-rank* %R_{oil}
1 operators A	0.855	1.251	1.432
B	0.876	1.157	1.459
2	0.86	1.14	1.530
3	0.887	1.235	1.537
4	0.888	1.2265	1.524
5 Operators A	0.89	1.19	1.48
B	0.89	1.20	1.47
6	0.897	1.197	1.517
7	0.901	1.199	1.518
8	0.902	1.184	1.476
9	0.905	1.213	1.500
10	0.909	1.89	1.447
11	0.94	1.20	1.52
University of Newcastle	0.95	1.29	1.57
Spread of results	0.095	0.165	0.14
%R_{oil} (absolute)	10.5%	13.6%	9.33%

* The reflectivity was quoted to this accuracy by the laboratories.

(ii) Polishing Errors

An accurate reflectivity measurement depends on the quality of the polished surfaces of the standards and unknowns.

(a) Standards

Commonly a tarnished glass standard will give a reflectivity value lower than its true value, but occasionally matching of the two glass standards cannot be achieved with accuracy because of undetected errors, such as tarnishing of the two standards in proportion to their reflectivities; this rarely happens because of the frequent use of the standards, but if the standards are kept unused under oil immersion for relatively long periods of time (say 1 month), then it is better to repolish before use.

(b) Specimens

The nature of the polished surfaces of the unknown specimens are of great importance in reflectivity measurements, in particular when the detection of small reflectivity differences is required. The results of Wego (1954) and Murchison and Boult (1961) suggest that lengthy polishing leads to deterioration of the polished surfaces, so care must be taken to avoid unnecessary polishing on 'gamma' alumina. Improper washing and drying also leaves some of the polishing powder on the surfaces and also the polished surfaces can be smeared with soap (used as lubricating agent during polishing), resulting in incorrect reflectivity values.

(iii) Errors in Chart Reading

The chart of the pen recorder is divided into 100 divisions and the length of the trace on the chart from zero is proportional to the intensity of the light. However, it is important to read the chart accurately, because an inaccurate reading results in an erroneous reflectivity value.

(iv) Errors due to the moisture content of the specimen (Coal macerals)

An influence of moisture content on the reflectivity of vitrinites, particularly low-rank and anthracitic vitrinites was reported by Harrison (1965). The reflectivity decreased with rise of moisture content and the same author suggested a standard 15-hour drying period for wet-polished specimens before making reflectivity measurements. The more recent results of Murchison (private communication) show that the moisture also causes a decrease of reflectivity in vitrinite of coking rank. Again, to eliminate this source of error, specimens were dried for 15 hours as was suggested by Harrison (1965).

(v) Error from the number of measurements

The accuracy of the reflectivity value of the unknowns is a function of the number of determinations.

In routine reflectivity measurement, the errors encountered are normally due to polishing and to the mounting of the standards and specimens, and to some extent, focusing.

13. ACCURACY AND PRECISION OF REFLECTIVITY AND DERIVED PARAMETER ON HOMOGENEOUS SURFACES

If both internal and external sources of error are eliminated, or reduced as far as possible, then accurate and reproducible reflectivity results can be obtained. According to von Gehlen and Piller (1964), the errors in reflectivity measurements range from 1 to 5%, the amount of error increasing as the reflectivity of the unknown falls. The error in the reflectivity of low-reflecting materials can be as great as 10%. The errors normally quoted for a series of experiments are the reproducibilities for a particular apparatus and they do not include all the fundamental errors arising from the specimen and apparatus. The fundamental errors have to be calculated if the reflectivity values are to be used to calculate its optical constants. More recently Galopin and Henry (1972) have supported the above view, stating that a distinction must be made between the fundamental errors occurring in the whole measuring procedure and the accurate reproducibility of reflectivity measurement with equipment. The errors in the values of the optical constants derived from reflectivity measurements are high, even if all precautions are taken to reduce as far as possible the errors in reflectivity measurement. The errors in the values of refractive and absorptive index will be the higher the lower are the reflectivities; absorptive index in particular, can show imaginary values in low-absorbing material even when the reflectivity measurements are made with high accuracy.

14. ACCURACY AND PRECISION OF OPTICAL PROPERTIES OF COALS AND COKES

The accuracy in reflectivity measurement on vitrinites increases with rising reflectivity (see, for example, Jones 1961). More recently Cook and Murchison (1975) support the above statement and they have also shown that the refractive and absorptive indices are more liable to incorrect values the lower is the level of the reflectivity of the vitrinite. The largest errors in refractive and absorptive index will arise when the reflectivity in air is higher and that in oil lower by some percentage. In general, the effect on absorptive index is greater than that on refractive index.

Vitrinites in the coking range develop a heterogeneous mosaic structure during the carbonisation, whereas vitrinites of lower rank and anthracitic rank keep their relatively homogeneous structure. Thus the accuracy of the reflectivities and the derived optical constants for low rank and anthracitic vitrinites should be relatively higher than measurements on mosaics from coking coal vitrinites. The mosaic structure with its heterogeneous nature adds further complexity to the problem of eliminating errors. It is very difficult, if not impossible, to measure reflectivities on individual mosaic units, even with modern reflectivity equipment and restricted field areas. Consequently, unlike low-rank vitrinite, each individual reflectivity measurement on a mosaic structure involves a number of the individual mosaic units and each of these mosaic units normally behaves optically differently at low temperatures, i.e. one may show a minimum reflectivity, whereas another (in the same field area) exhibits maximum reflectivity. Thus, a reflectivity measurement on a mosaic structure is a 'bulk' measurement, estimating the light intensity of the whole field. Goodarzi and Murchison (1972) acknowledge the above problem, but contend that the method is satisfactory having obtained meaningful results in the trends of optical properties, which correlate well with trends of independently derived parameters. With increase of temperature, the mosaic units behave optically more similarly, i.e. there is aggregation of several units (in the same field area) producing a larger area with homogeneous optical behaviour.

In the present research programme, the accuracy of reflectivity measurement on homogeneous surfaces is about ± 1%, but may well be lower in measurements on mosaics.

15. THE OPTICAL CHARACTER OF VITRINITES AND THEIR CARBONISED RESIDUES

Vitrinite in coal is widely believed to behave optically in a similar manner to uniaxial negative substance with its maximum reflectivity in the section parallel to the bedding and the true minimum reflectivity in the section perpendicular to the bedding. Optically anisotropic crystals are either uniaxial or biaxial. The uniaxial indicatrix has a single optic axis and a rotational ellipsoid, the axes in the section perpendicular to the optic axis are equal, i.e. the section perpendicular to the optic axis is isotropic. The other principal section of the ellipsoid is elliptical (anisotropic). If the axes of the circular section are shorter than the optic axis, then the crystal is optically positive; with the reverse condition it is optically negative (Fig 30). In randomly oriented particles of a uniaxial negative crystal, there will be a constant value for maximum reflectivity and a variable value for minimum reflectivity, but a uniaxial positive crystal shows the reverse condition.

The biaxial indicatrix has three axes of unequal length and two optic axes. The sections perpendicular to these two optic axes are circular and all other sections are elliptical. The two optic axes are equally inclined to the horizontal and the angle between the optic axis is termed the '2v angle'. The biaxial crystal likewise may be optically positive or negative

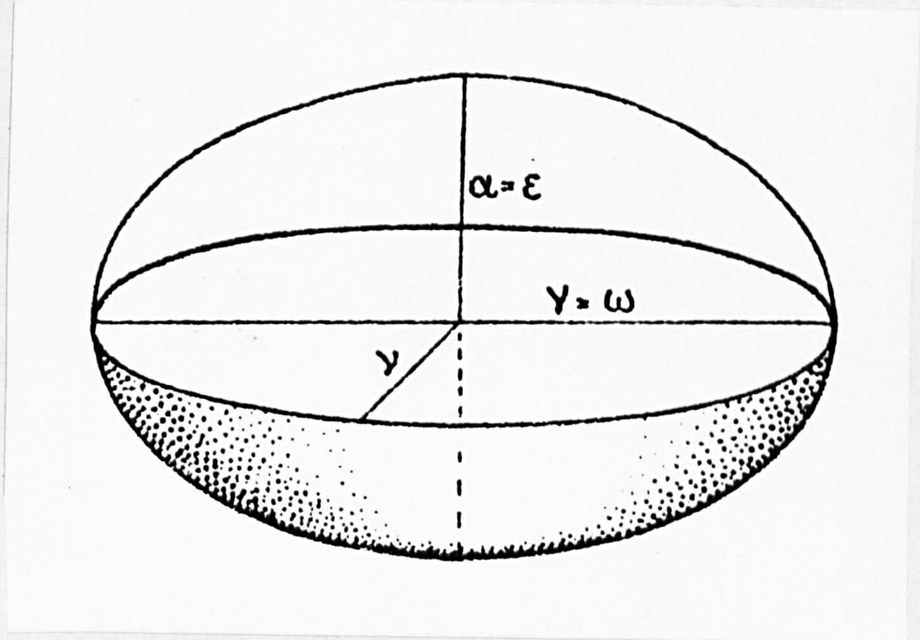


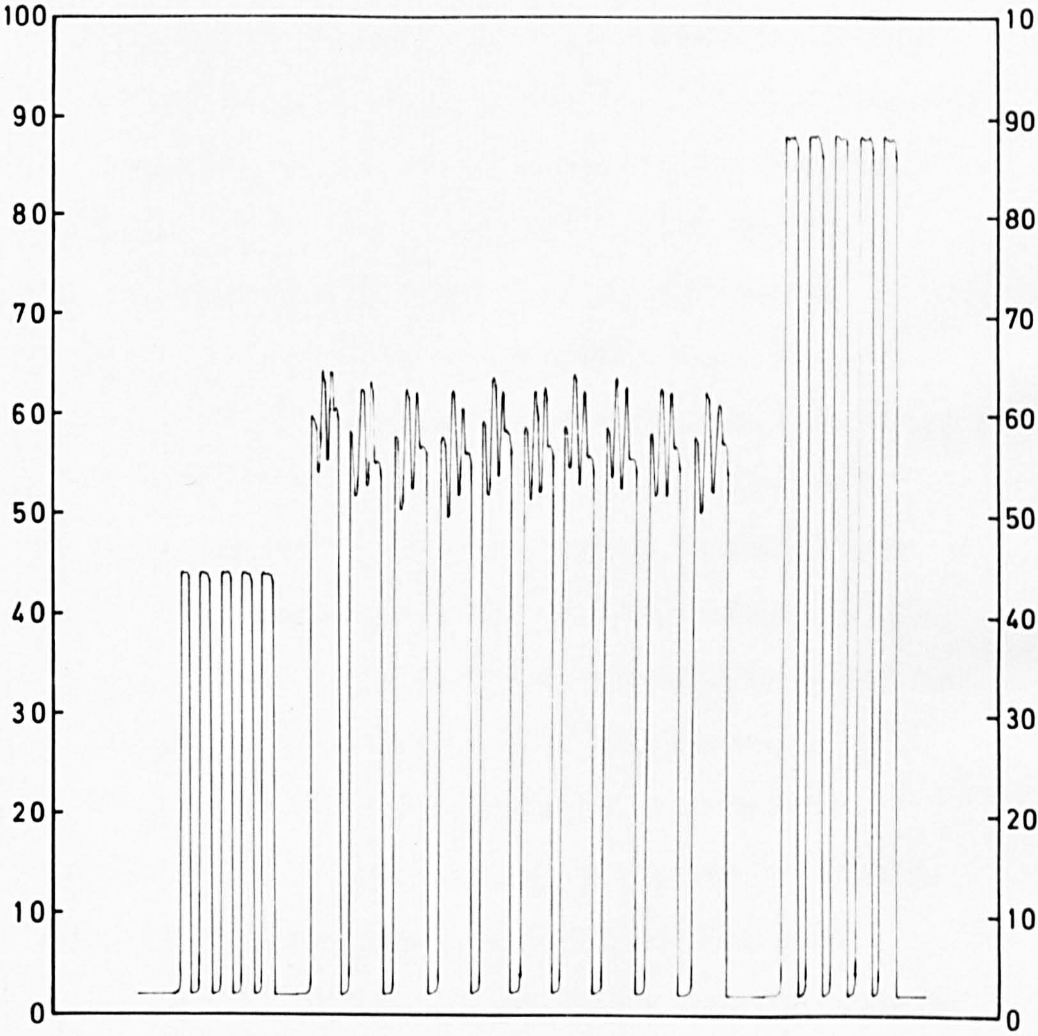
Fig 30 Uniaxial negative indicatrix.

depending on whether the 2v angle is cut into equal halves by (α) the major axis or (γ) the minor axis. In the randomly oriented particles with a biaxial indicatrix, both maximum and minimum reflectivity values are variable. The above description is an over simplification of the biaxial indicatrix in the case of absorbing substances. With absorbing materials, the absorptive indices also must be considered and in fact the material will possess four optic axes.

Vitrinite particles in particulate blocks always exhibit the maximum reflectivity, but the true minimum is only exhibited in particles cut perpendicular to the circular section of the indicatrix. Otherwise they only show the maximum and not the true minimum reflectivity. Since the particles lie randomly, the majority show a minimum lying somewhere between the maximum and the true minimum (Fig 31); probably only a few particles will show a value close to the true minimum.

Cook et al. (1972) suggest a biaxial behaviour in a meta-anthracitic vitrinite (carbon = 93.8% daf). The reflectivity showed different values for both maximum and minimum reflectivity in sections parallel and perpendicular to bedding. Later, Cook et al. (1972) examined a range of anthracitic vitrinites and were able to confirm their earlier findings. The biaxial behaviour of anthracitic vitrinite was related to strain within the molecular groups, lateral stress and remnant botanical-form anisotropy.

Fig 31 Typical recorder trace for fresh vitrinite



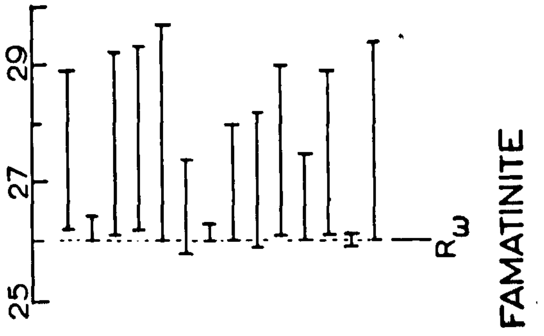
Typical recorder-chart presentation of measurements on ten different points of a uniaxial absorbing substance with some inherent variation compared against two glasses as standards $\left[R_{oil}(546\text{nm}) = 0{\cdot}6953\%\ \text{and}\ 1{\cdot}4293\%\right]$

Goodarzi and Murchison (1972) anticipated an optically biaxial structured behaviour for mosaics produced during carbonisation of coking-range vitrinites (Fig 27). Melvin (1974) argued that the mosaic produced by natural metmorphism of coal is optically uniaxial. A biaxial 'crystal' contains two circular sections, which are isotropic and a uniaxial crystal contains only one such section. Also a biaxial 'crystal' shows only maximum anisotropy when it has been sectioned perpendicular to the intermediate axis, whereas in a uniaxial crystal, a section containing the optic axial plane exhibits maximum anisotropic value. Thus, if a mosaic is optically biaxial, it should show about twice as much isotropic behaviour than with uniaxial particles and a high anisotropy should be obtained less frequently during the reflectivity measurement, which does not appear to be the case. However, the same author believes that there is extreme difficulty in obtaining an isotropic section in a mosaic, because even a minute deviation from the circular ellipsoid leads to observable anisotropy. Melvin states that the variation in the maximum and minimum values of reflectivity of mosaics is not due to biaxial behaviour, because the variation of maximum and minimum reflectivity are independent of each other in biaxial crystals, whereas in uniaxial crystals, an increase in minimum reflectivity is accompanied by decrease in maximum reflectivity.

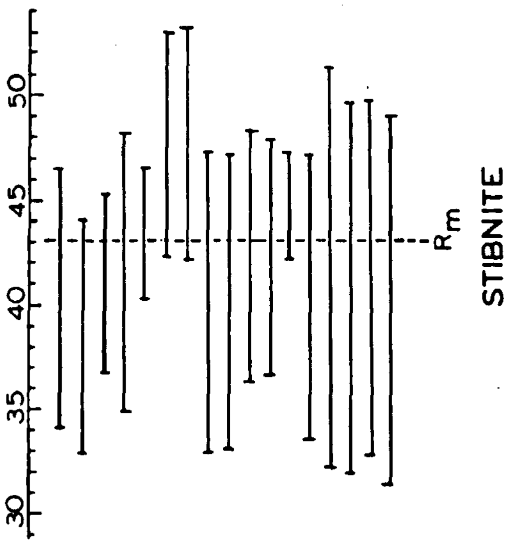
Melvin did not definitely state whether coke mosaics would behave as biaxial or uniaxial materials. Cameron (1961) measured the reflectivity of randomly-oriented particles of some anisotropic minerals at 549 nm and successfully demonstrated that it is possible to recognise by reflectivity measurement the optical symmetry of uniaxial and biaxial minerals and even to determine their optical sign. Figs 32a and b demonstrate the method which Cameron used to represent his results. It is clear that uniaxial materials have either a constant maximum and variable minimum for negative sign and the reverse situation for positive sign (Fig 32a). Fig 32b shows the results of the biaxial crystal. It is evident that neither the maximum values nor the minimum values stay constant.

It seems clear from the above results that fresh vitrinites in coals up to anthracitic rank behave optically as a uniaxial negative material and that anthracitic vitrinites may possess lower symmetry, behaving as optically biaxial materials. Mosaics in carbonised vitrinites which Goodarzi and Murchison (1972) suggest behave as biaxial materials are uniaxial negative according to Melvin (1974). Melvin also states that the minimum reflectivity in coke mosaics increases with decrease of the maximum value and also that biaxial crystals only 'randomly' show high anisotropy, but the results of Goodarzi (1971) show that the maximum or minimum reflectivities increase or decrease independently of one another. Towards the end of his argument, even Melvin states that 'a proportion of the individual readings do display a range of maximum and minimum values which would fit a biaxial hypothesis', although he goes on to state that these reflectivity readings can also be attributed to uniaxial behaviour.

Fig 32 Reflectivity of randomly orientated particles (after Cameron 1963)



(a) famatinite, showing uniaxial behaviour



(b) stibnite, showing biaxial behaviour

PART III THE EFFECT OF RATE OF HEATING ON THE OPTICAL PROPERTIES OF VITRINITE.

Contents Page

1 GENERAL INTRODUCTION

The background to certain factors which influence the character of the products of the carbonisation process have been considered earlier (see Section II of this thesis). In the present chapter, a review is first given of previous investigations into the influence which heating rate has generally on the carbonisation process and then the changes which have been observed on morphology, optical properties and molecular structure (through X-ray studies) by variation of heating rate.

The results of current investigation are described and discussed in the following order:-

(a) A summary of the changes in morphology and mesophase with varying heating rate and vitrinite rank and a discussion of the implications of these changes - the detailed descriptions are given in Volume III (Appendix I).

(b) Descriptions of the variations in optical properties (reflectivity, bireflectance, refractive and absorptive index) with rank and varying heating rate.

(c) A discussion of the implications of the changes in the optical properties of the carbonised vitrinites, in the first case considering simply the effect of three different heating rates on single vitrinites.

The second part of the discussion considers the properties of all six vitrinites grouped together for individual heating rates, since further conclusions about the carbonisation process can be drawn from such groupings.

2 REVIEW OF RELATED INVESTIGATIONS

A. Introduction

The rate at which coal is subjected to thermal treatment is one of several important factors in determining the quality of a coke. For example, weakly caking coal can produce a coke if carbonised at a rate of approximately 50°C/min (Berkowitz 1968), but a strongly coking coal will not yield a highly swollen coke, or even a strongly coherent coke, if it is heated at a rate of less than 0.05°C/min. Much research has been undertaken to study the effect of heating rate on the physical and chemical properties of the carbonised products of vitrinites of different rank.

Dulhunty and Harrison (1953) carbonised a series of coals of different ranks (carbon = 69.3, 74.4, 80.6 and 91.6% daf) at temperatures between 450° and 700°C and at heating rates of 4 and 20 mins and 1½, 3½, 6½, 32, 64, 99 and 144 hours, over a temperature rise from 150° to 700°C. They measured volume changes and the degree of coherency. The volume changes for caking and high-rank coking coal (carbon = 86.4 and 91.6% daf) were +230 and +475 respectively at the fastest rate of heating and -36 and -6 for the slowest rate of heating. The semi-cokes formed were very strongly coherent and completely fused at the fastest rate of heating, but at the slowest rate of heating were non-coherent with angular particles in the caking coal and slightly coherent with slightly rounded particles in the coking coal. There was a gradual transition of coherency and strength between the two extreme rates of heating. The effect of rate of heating on the volume change became more evident with progressive increase of rank, varying approximately with the square of the rank and the inverse square of the volume change. The authors concluded that the physical conditions and the rank of coal were the two determining factors on the ultra-fine structure of the carbonised residue (semi-coke), not the rate of heating which merely influences the swelling and shrinking of the coal.

Later van Krevelen et al. (1956) carbonised a low-volatile bituminous coal (V.M. = 18% daf) at temperatures ranging between 400°C and 600°C and at rates of heating between 0.6° and 6.6°C/min, concluding that an increase in the rate of heating causes a displacement of the rate of decomposition curve to a higher level and to a higher temperature. Loss of weight during carbonisation was found to be dependent on the rate of heating (Fig 33). The same authors also examined a medium-volatile bituminous coal (V.M. = 24% daf), using a plastometer and a heating rate between 0.7° and 7.2°C/min at temperatures between 370° to 550°C. They found that with faster rates of heating, plasticity increases and all characteristic temperatures are shifted to higher levels (Fig 34). Brown (1956) supported the above findings and further showed that the 'coking' activity of coal increases and a higher degree of plasticity and a greater rate of decomposition results with an increased rate of heating.

Fig 33 Decomposition (loss of weight) of bituminous coal (vm = 18% daf) carbonised at different heating rates (after van Krevelen *et al.* 1956).

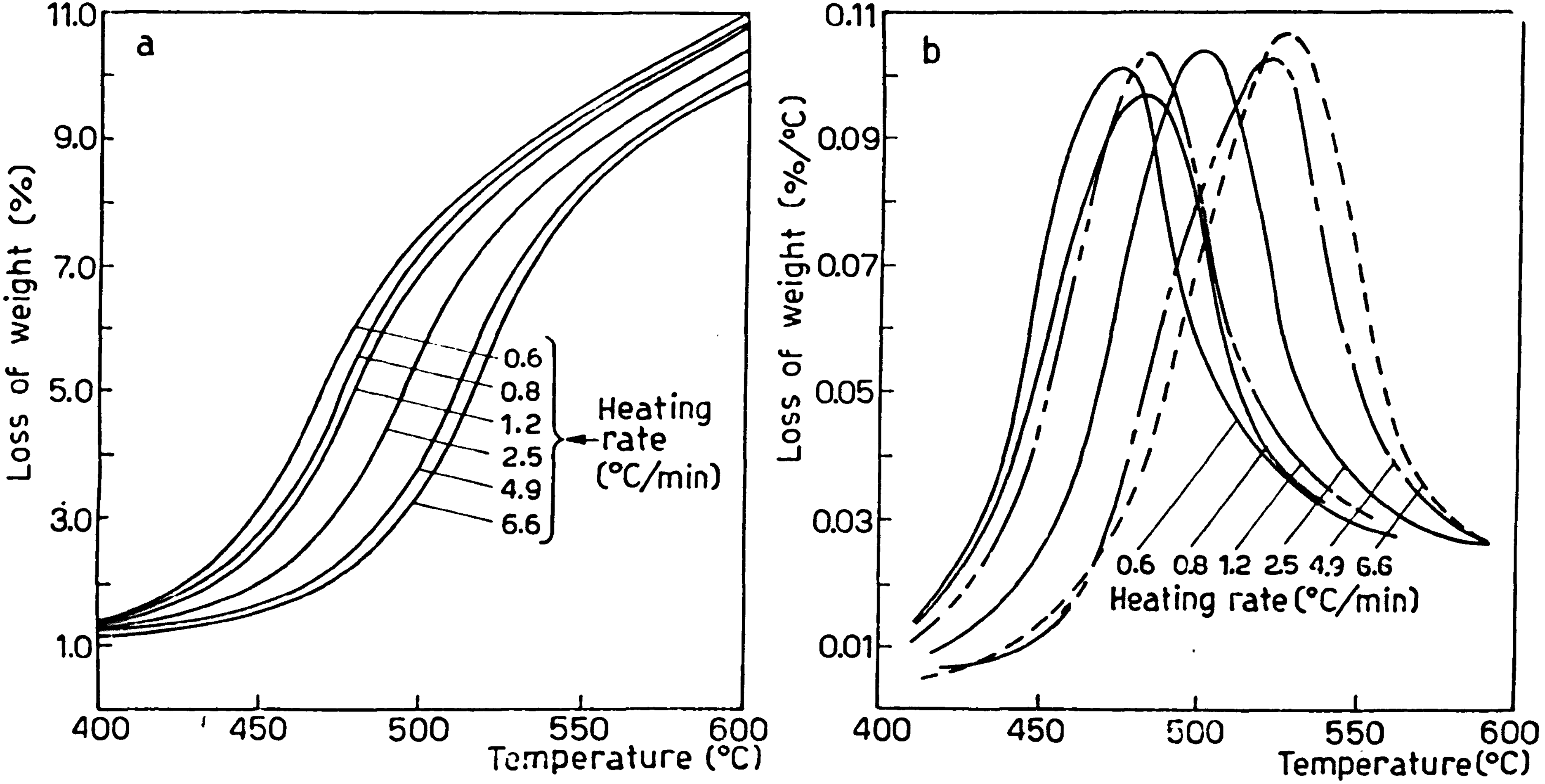

a
Loss of weight (%)
11.0
9.0
7.0
5.0
3.0
1.0
400
450
500
550
600
Temperature (°C)
0.6
0.8
1.2
2.5
4.9
6.6
Heating rate (°C/min)
b
Loss of weight (%/°C)
0.11
0.09
0.07
0.05
0.03
0.01
400
450
500
550
600
Temperature(°C)
0.6
0.8
1.2
2.5
4.9
6.6
Heating rate (°C/min)

Fig 34 Variation of plasticity with heating rates for vitrinite (vm = 24.0% daf) carbonised up to 550°C (after van Krevelen *et al.* 1956).

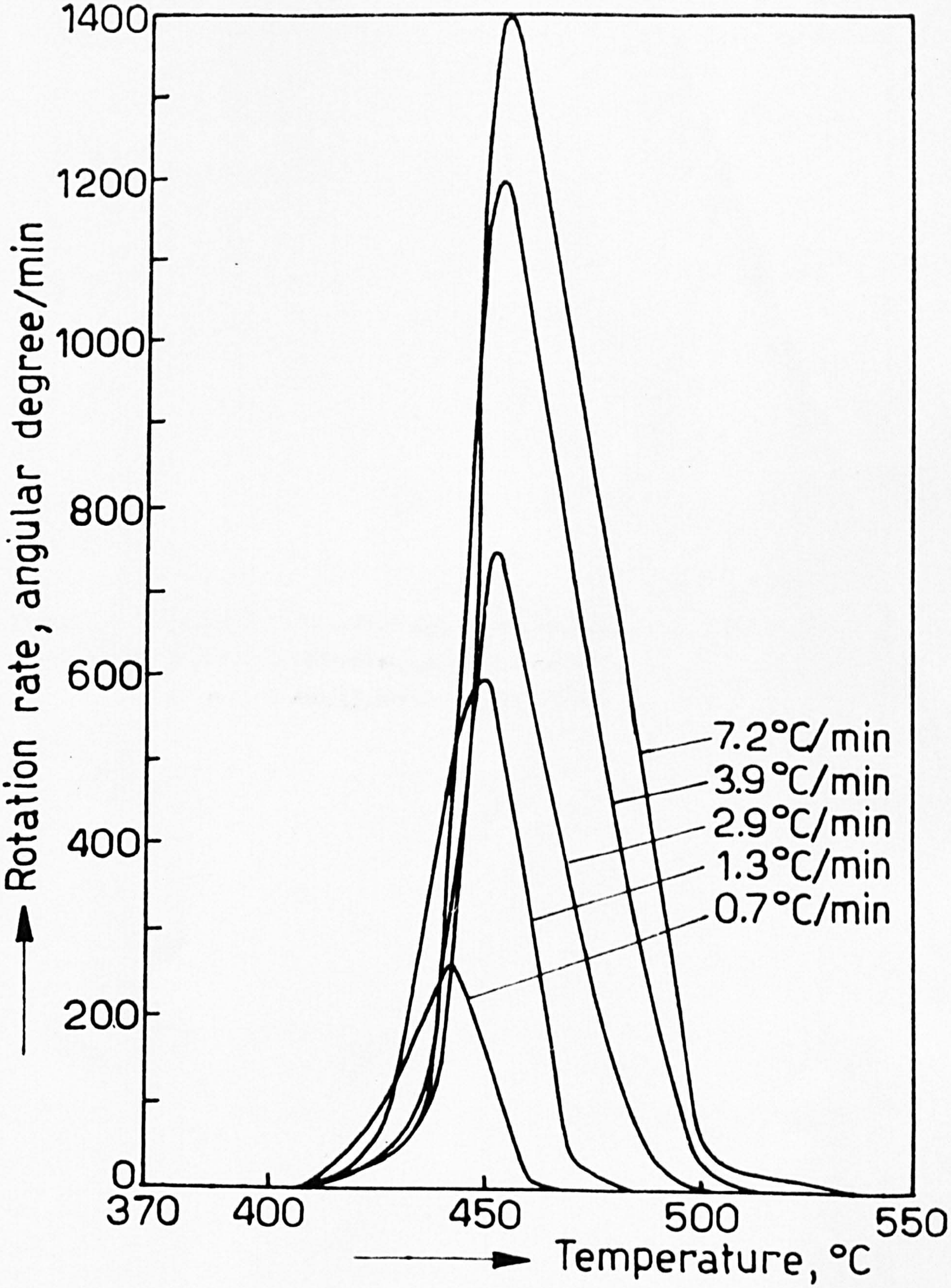
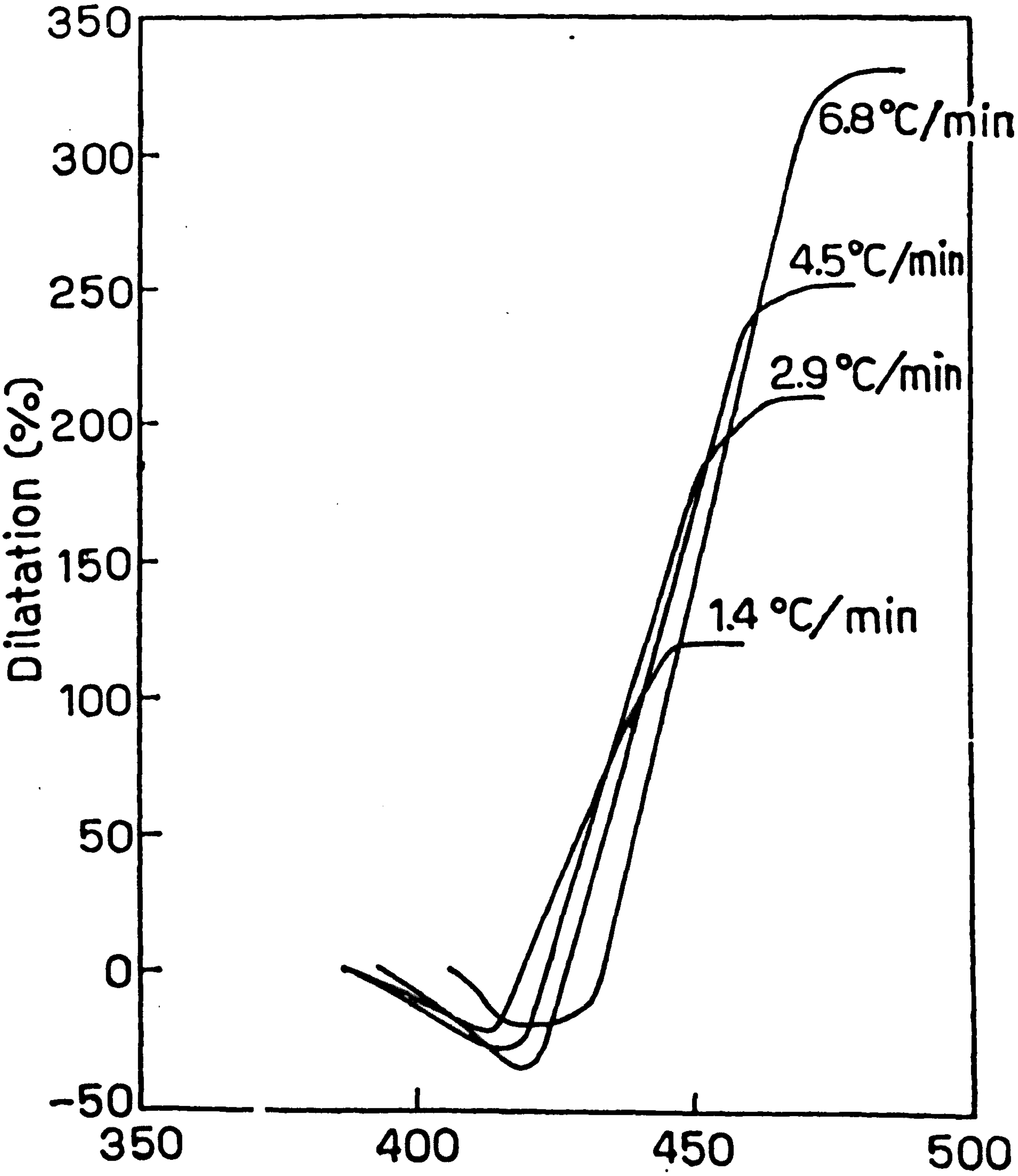

1400
1200
1000
800
600
400
200
0
Rotation rate, angular degree/min
370
400
450
500
550
Temperature, °C
7.2°C/min
3.9°C/min
2.9°C/min
1.3°C/min
0.7°C/min

Fig 35 Variation of dilatation with temperature of a bituminous coal, carbonised at different heating rates (after van Krevelen 1961).


350
300
250
200
150
100
50
0
-50
Dilatation (%)
350
400
450
500
Temperature (°C)
6.8°C/min
4.5°C/min
2.9°C/min
1.4°C/min

Van Krevelen (1961) states that the rate of devolatilisation is largely dependent on the rate of heating and also that the rate of dilatation is higher the faster is the rate of heating (Fig 35). The entire carbonisation process, softening, degasification, swelling and resolidification were shown to be greatly dependent on and related to the heating rate. The results of Brown (1956) and van Krevelen _et al._ (1956) and (1961) are in agreement and they clearly indicate that the rate of heating must influence the structure of the resulting carbonised residue.

In summary, the above studies show that at fast rates of heating the decomposition of coal is delayed; the coal first softens, then decomposes and resolidifies. At slow heating rates, the plastic range is decreased and the coal decomposes at much lower temperatures. Since degasification is a slow process, occurring over a longer period of time, the gaseous materials are released in a stepwise set of reactions. Plasticity can be partially reduced by very slow heating of the coal and it is possible to convert coal to a semi-coke completely without any or little softening during the carbonisation process. This indicates that the primary carbonisation process is suppressed and that resolidification (secondary carbonisation process) is achieved directly.

B. MORPHOLOGY

The morphology of the carbonised residues of coals carbonised at different rates of heating have been studied by optical and electron-scanning microscopical methods by a number of investigators.

(i) Optical Microscopy

Newell and Sinnatt (1924) examined the morphology of fine particles of coal carbonised at a heating rate of about 10°C/min over temperatures ranging from 500° up to 900°C. The carbonised coal particles were examined either by transmitted or reflected light. Up to 575° and 600°C there was no change, apart from rounding and slight swelling of the particles; at approximately 600°C the coal particles formed a hollow spherical shape, termed a 'cenosphere'. Cenospheres consist of fine frames or ribs and 'windows' which are transparent. The size of the cenospheres and the 'windows' enlarges and the 'windows' become more opaque with rise in carbonisation temperature. At about 900°C the ribs and windows can no longer be differentiated.

Mackowsky and Wolff (1966) carbonised a coal (V.M.= 23.9% daf) using different particle sizes (-0.2 to 5mm) up to 600°C at rates of 260°, 3°, and 0.5°C/min and studied the development of degasification vacuoles. At the fastest rate of heating, about 69% of fine particles developed pores, whereas only 38% did so at 3°C/min and 14% at 0.5°C/min. The formation of vacuoles increases with rising heating rate for all particle sizes. A high-rank (V.M. = 10.6% daf), using similar grain sizes to the above coal, was also carbonised up to 600°C at heating rates of 300°C/min and 3°C/min. About 42% of the large particles were converted to coke on heating at the faster rate, but only 10% were coked at 3°C/min. At 300°C/min about 12% of the fine particles were coked, but none of them developed any devolatilisation pores at the slow rate of heating. Mackowsky and Wolfe assume that a non-coking or weakly coking coal can produce a coke at high rates of heating. The results of Mackowsky and Wolff (1966) show that at a fast heating rate the carbonised residues develop larger and more numerous devolatilisation vacuoles than at a slow rate of heating.

Street et al. (1969) carbonised a series of coals of different rank (V.M. = between 6.6 and 45% daf) at heating rates of 105°C/sec up to 700°C with total holding times of about one second. The carbonisation residues were examined by optical and electron microscopy. Coal of 34.5% V.M. after carbonisation at 550°C produces a thin-walled residue, while coals with 28.1 and 21.4% V.M. show typical 'umbrellas' or cenospheres, which consist of a frame or ribs and large windows. Evolution of volatile matter at about 450°C results in the formation of gas bubbles and at approximately 500°C, the ribs, windows and membranes which cover the windows appear to form cenospheres. The results of Newell and Sinnatt (1924) and Street et al. (1969) are similar and indicate that development of 'cenosphere' is typical morphology of vitrinite carbonised at fast rate of heating.

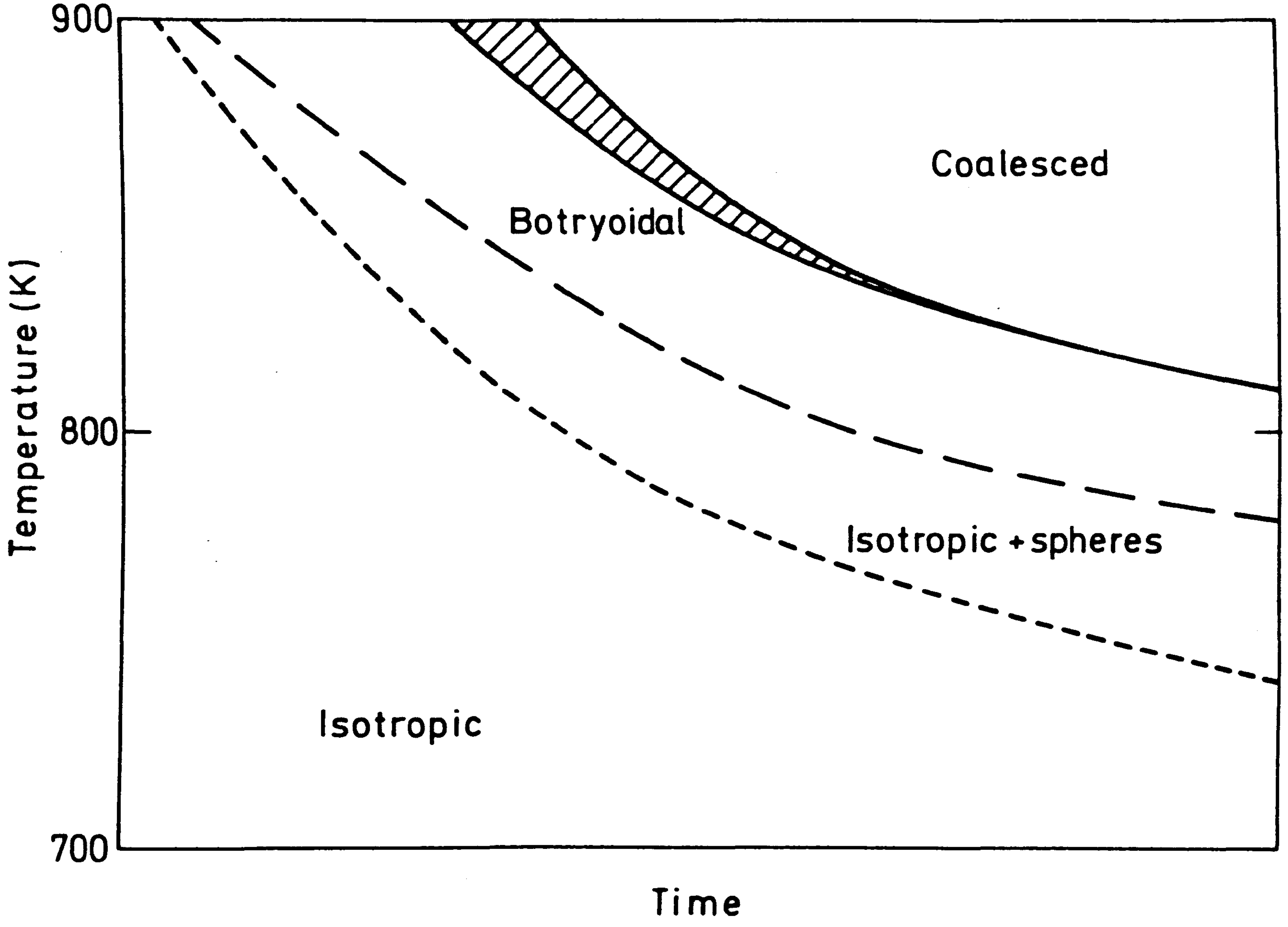
Finally, Goldring (1973) examined the average mosaic size of three cokes carbonised at rates of 3°C and 5°C/min up to 600°C and found that there was no substantial variation in the mosaic size due to the different rates of heating, but he stated that any drastic change in rate of heating can effect the mosaic characteristics.

(ii) Electron Microscopy

McCartney (1971) examined with the electron-scanning microscope cokes produced at heating rates of 3°C/min and about 8000°C/sec at temperatures up to 1160°C from a high-volatile and a medium-volatile, bituminous-rank vitrinite. The medium-volatile vitrinite on heating to 1160°C at the fast rate of heating produced a smooth fused mass with many pores, but the high-volatile bituminous vitrinite in contrast formed a twisted fibrous mass.

Marsh (1973), using optical and electron microscopes, presented schematically the effects of heating rate on the development of mesophase **units** during carbonisation under pressure (Fig 36). At slow rates of heating the mesophase did not develop, but as the rate of heating increased, mesophase first appeared as spheres in an isotropic matrix and then as a 'botryoidal' shape and finally as coalesced mesophase units. This sequence could be restricted by increasing the heating rate, i.e. direct conversion of the isotropic mass to a botryoidal shape.

Fig 36 The conditions of development of spherical mesophase during carbonisation under pressure in relation to temperature and heating time (after Marsh 1973).


900
800
700
Temperature (K)
Time
Coalesced
Botryoidal
Isotropic + spheres
Isotropic

The above studies show that the morphology of carbonised residues is also largely related to the rate of heating. Low-rank coal, which produces angular or subangular particles at a slow rate of heating, develops completely rounded, thin-walled particles at fast rate of heating. The size of the vacuoles is also dependent on rate of heating and they are the larger and more numerous the faster is the rate of heating. The formation of mosaic structure is also a function of the speed of carbonisation. The reaction between the mesophase and the isotropic matrix is more rapid and a larger mesophase will appear at fast rates of heating, which results in the formation of a larger mosaic structure.

C. Optical Properties

Abramski and Mackowsky (1952) stated that the faster is the rate of heating, the larger is the area showing similar optical extinction and the better will be the rearrangement of the 'crystallites', because of the greater level of energy available over a short period of time. Taylor (1957) confirmed the earlier statement of Abramski and Mackowsky.

Brown and Taylor (1961) examined some Antarctic coals to find that one of the naturally metamorphosed coals exhibited a high degree of anisotropy (R_{oil} max = approximately 12.9%; bireflectance = 12.4%). The coal developed a system of vesicles, each less than 100 μm in diameter, a feature not observed in the remainder of the coal samples. The authors attributed the formation of this naturally-coked coal, which was assumed originally to be a low-volatile bituminous coal or a medium-volatile bituminous coal, to either the rapid rate of heating up to about 1000°C or to a lower pressure than the remainder of the coal samples were exposed to.

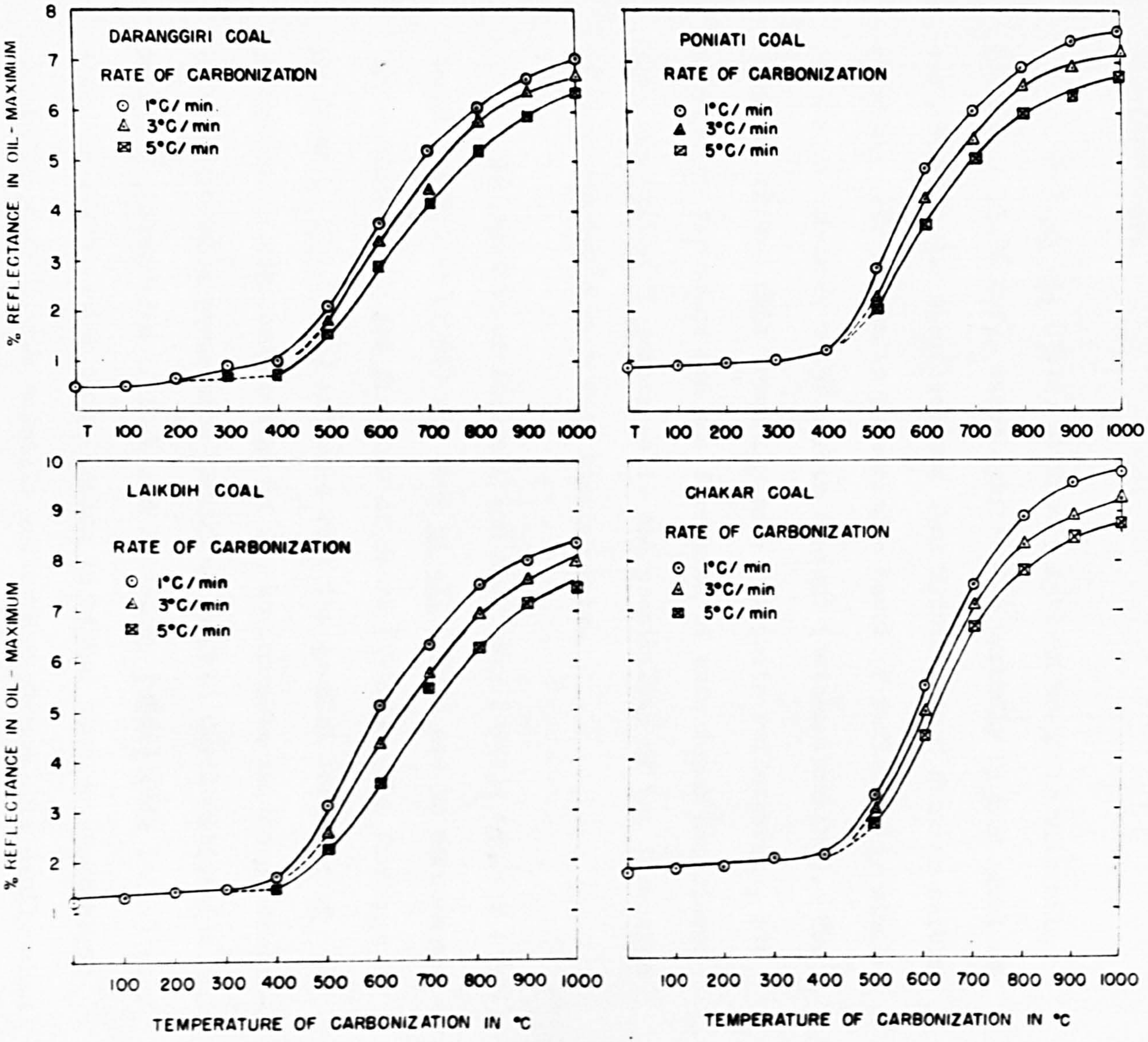
Ghosh (1968) carried out a systematic study of the oil reflectivity and oil bireflectance of a series of coals (carbon = 76.2, 83.5, 86.5 and 91.1% daf) carbonised in the temperature range between 100°C and 1000°C at 100°C intervals using heating rates of 1°C, 3°C and 5°C/min with a one hour 'soak' period. The reflectivity was found to be the higher the lower the rate of heating (Fig 37), while the difference between the reflectivities of the vitrinites carbonised at the different heating rates becomes more evident as the temperature rises. According to Ghosh, the differences appear as low as 300°C for low-rank vitrinite (carbon = 76.2% daf) and at 500°C for the other three coals. The differentiation between the reflectivity curves for the coking coal vitrinite (carbon = 86.5% daf) is greater than that for either the higher or lower-rank vitrinite bituminous coals, which do, however, exhibit greater differences at higher temperatures.

The vitrinite in the coal of 76.5% carbon content was found to be almost isotropic at all three rates of heating up to 1000°C, whereas bituminous-rank vitrinites displayed some degree of anisotropy that was dependent on the rank of the coal, the anisotropy being greater as rank increases. From the graph of the maximum against minimum oil reflectivity, it appeared that

Fig 37 Variation with temperature of oil reflectivity of four vitrinites carbonised at different heating rates (after Ghosh 1968)

Carbon daf

Daranggiri = 76.2%
Poniati = 83.5%
Laikdih = 86.5%
Chakar = 91.1%


DARANGGIRI COAL
RATE OF CARBONIZATION
1°C/ min.
3°C/ min
5°C/ min
PONIATI COAL
RATE OF CARBONIZATION
1°C/ min
3°C/ min
5°C/ min
LAIKDIH COAL
RATE OF CARBONIZATION
1°C/ min
3°C/ min
5°C/ min
CHAKAR COAL
RATE OF CARBONIZATION
1°C/ min
3°C/ min
5°C/ min
% REFLECTANCE IN OIL - MAXIMUM
% REFLECTANCE IN OIL - MAXIMUM
1
2
3
4
5
6
7
8
9
10
T
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE OF CARBONIZATION IN °C
TEMPERATURE OF CARBONIZATION IN °C

the bireflectance not only depends on rank, but also on the rate of heating; the higher is the heating rate, the lower is the oil bireflectance.

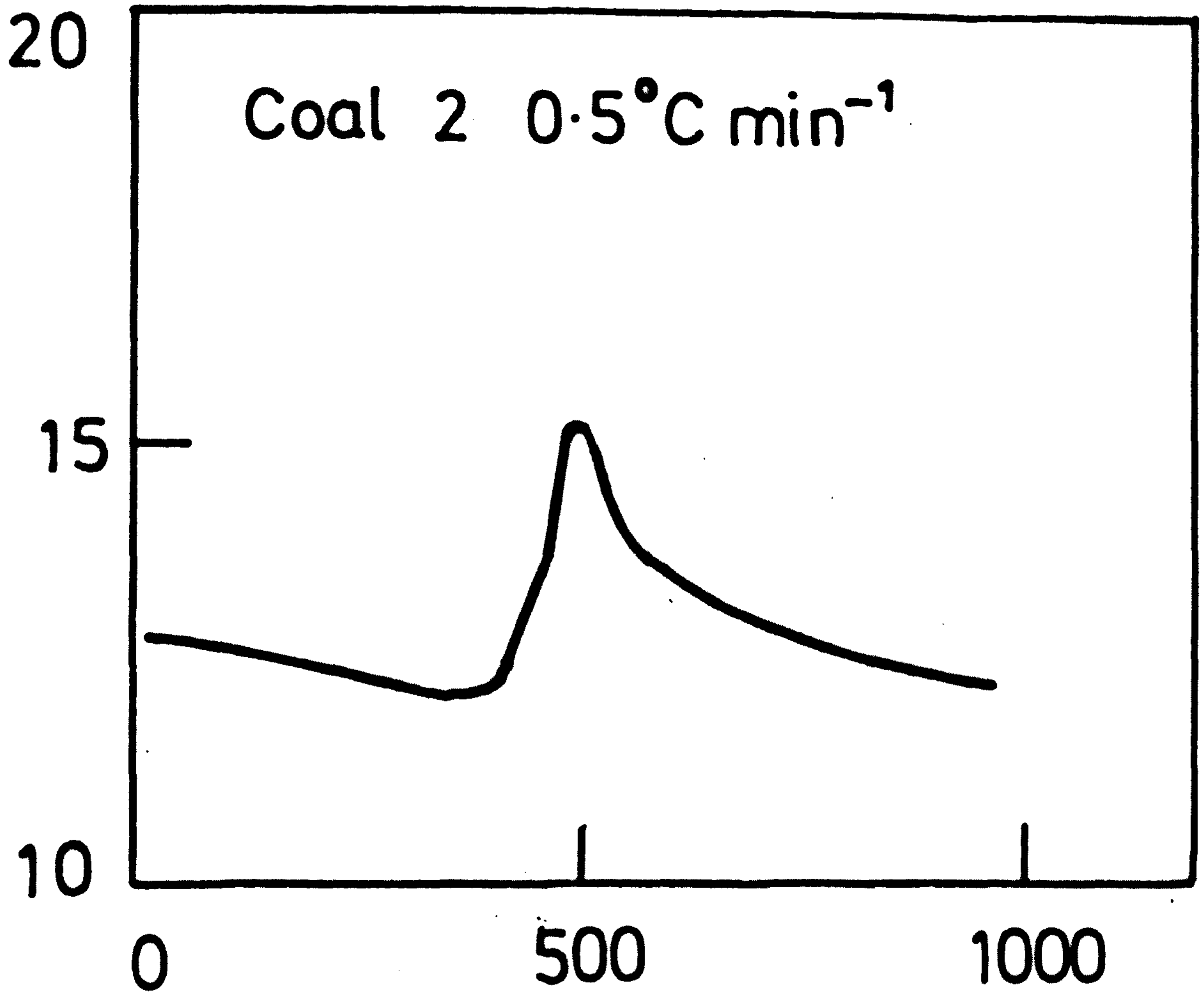
Cook et al. (1972) studied a meta-anthracitic vitrinite (carbon = 93.8% daf), which exhibited a markedly higher level of reflectivity and bireflectance than vitrinites of similar carbon content; the vitrinite possessed a level of reflectivity similar to a coal of about 96.5% carbon content (meta-anthracite). The authors related this unusually high vitrinite reflectivity, its particular structure and the formation of coke found associated with the vitrinite particles to the possibility of the formation of this vitrinite at a fast heating rate.

The results of Abramski and Mackowsky (1951); Taylor (1957); Brown and Taylor (1961) and Cook et al. (1972) are in agreement but contrast with the findings of Ghosh (1968). The findings of de Vries et al. (1968) indicate that the gradual increase of reflectivity with temperature is due to increase in the concentration of aromatic structures caused by gradual devolatilisation and further, the results of Huck and Patteisky (1964) (see later) show that the reflectivity under vacuum is higher than at atmospheric pressure, probably the volatile matter can escape more easily than at atmospheric pressure. It would then seem reasonable that the reflectivity at fast rates of heating would be higher than at slow rates of heating, because of rapid degasification and subsequent concentration of the aromatic structures. Since the trends of the optical properties are a function of molecular modification, so an improvement in structure will affect the optical properties. Thus it may be expected that for the same temperature level, carbonised residues at fast rates of heating will be more aromatic and have a better molecular structure than at slow rates of heating.

D. X-ray diffraction

Changes to the molecular structure of coal during carbonisation with varying rates of heating have been studied by Blayden *et al.* (1944) and Marsh (1971). Blayden *et al.* (1944) studied the effect of rate of heating on the molecular structure of two coals (carbon = 81.73 and 88.4% daf). The coking coal was carbonised up to 700°C at 2°C/min and 5°C/min and the low-rank bituminous coal up to 600°C at 1°C and 5°C/min. The coking coal was more sensitive to rate of heating and the rate of 2°C/min gave a higher value of crystallite height to that of 5°C/min at 500°C. The value for (L_c) at a rate of 2°C/min at temperatures between 450°C and 650°C was higher than the (L_c) of residues carbonised at 5°C/min. The crystallite diameter (L_a) of low-rank bituminous coal showed little variation with rate of heating, whereas the (L_a) of the coking coal at the slow rate had higher values in the temperature range mentioned above. However, the effect of rate of heating on low-rank bituminous coal was the displacement of the maximum value of (L_c) by 100°C, e.g. the maximum (L_c) for 1°C/min was at 500°C whereas for 5°C/min was at 600°C. The crystallite diameter

Fig 38 Variation of (L_c) with temperature for caking-coal vitrinite (carbon = 86.3% daf), carbonised at heating rate of 0.5°C/min (after Marsh 1971).

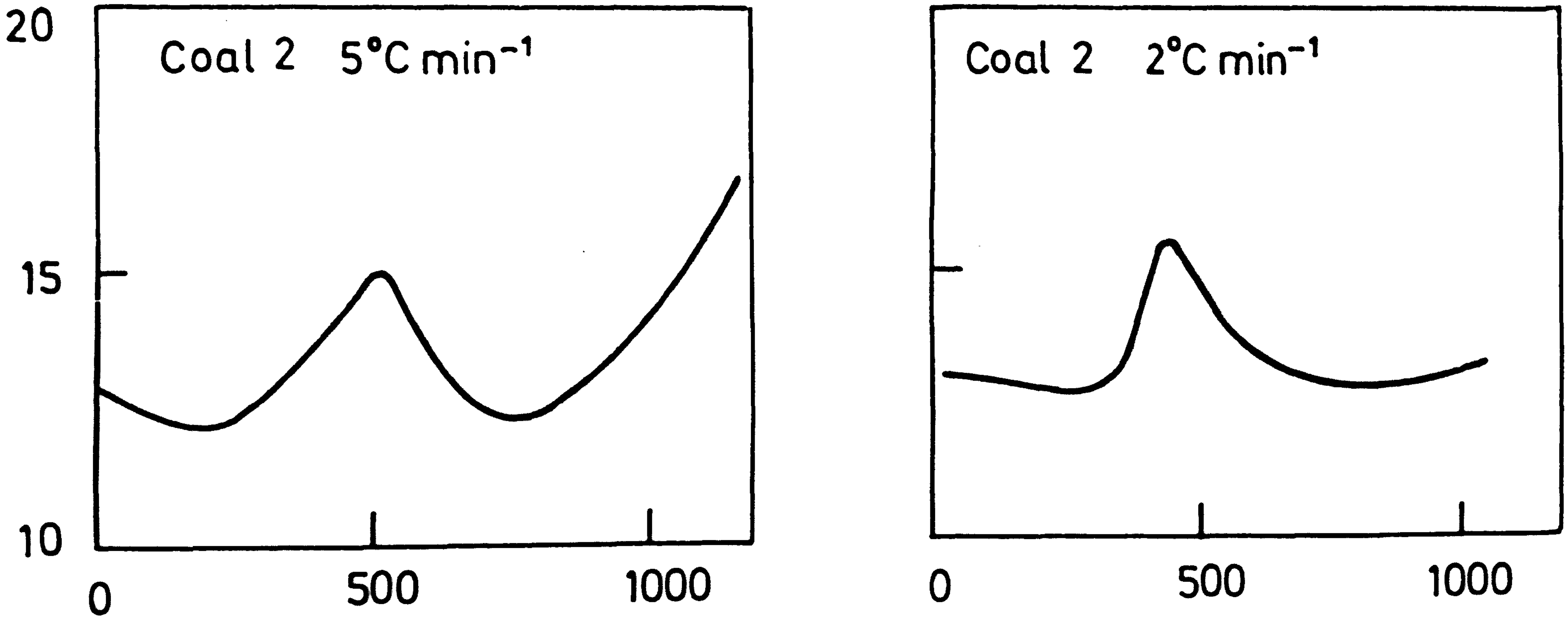


Coal 2 0·5°C min⁻¹
20
15
10
0
500
1000

Fig 39 Variation of (L_c) with temperature for caking-coal vitrinite (carbon = 86.3% daf), carbonised at different heating rates:

(a) 2°C/min
(b) 5°C/min

(after Marsh 1971)


20
15
10
Coal 2 5°C min⁻¹
0
500
1000
Coal 2 2°C min⁻¹
0
500
1000

did not alter with different heating rates. Blayden et al. (1944) concluded that since the movement of the aromatic layers in coking coals was a very slow process, the slow rate of heating would show higher values of (L_c) than would the fast rate of heating; the changes in molecular structure of low-rank bituminous coal are less dependent on time than those in coking coal.

Marsh (1971) studied the X-ray diffraction pattern of a bituminous coal (carbon = 86.3% daf). In the vicinity of igneous dyke, the maximum temperature attained at distance of 0.914 metres from the dyke appeared to be less than 500°C. This coal was carbonised at three different rates of heating (0.5°C, 2°C and 5°C/min) at temperatures up to 1200°C. The 'crystallite' diameter (L_a) was less sensitive to the rate of heating than was the 'crystallite' height (L_c) which showed some variation with the rate of heating (Figs 38 and 39). At the fastest rate of heating the (L_c) was lower with a secondary increase in (L_c) beginning at 750°C; the reverse was true for the slowest heating rate, viz. a higher (L_c) and no secondary increase in (L_c).

E, Summary

In summary, the carbonisation process is extended or suppressed by either increasing or decreasing the heating rate. At a fast rate of heating, plasticity increases, which probably results in the formation of larger mosaic units and larger degasification vacuoles due to the rapid devolatilisation.

The higher levels of reflectivity and bireflectance on rapid heating indicate a better-developed molecular structure. Since the refractive and absorptive index curves are also indicative of molecular modification, then varying behaviour, variation of these parameters.can be expected with varying heating rates.

3. RESULTS, DESCRIPTION

A. Morphology

(i) Introduction

The following summarised morphological features and the detailed description in Appendix I (Vol.III) of the carbonised residues of each of the six vitrinites carbonised at the three heating rates are described and compared with one another at different temperature levels and/or temperature ranges. These temperature levels or ranges were chosen to cover recognised stages in the carbonisation process, viz. softening, resolidification, molecular reorganisation in the solid state, etc (see Fig 7, redrawn after van Krevelen).

(ii) Low-rank bituminous vitrinite (carbon = 80.0% daf)(Plates 6-8)

The size of vacuoles varies, but generally increases with rise of heating rate from about 2.5 um to 50 um. The carbonised residues remain angular and/or become sub-angular at rate of heating of 1°C/min, whereas the residues are generally subangular at heating rate of 10°C/min, and become rounded, developing typical cenosphere appearance at 60°C/min.

(iii) Coking coal vitrinite (carbon = 85.4% daf)(Plates 9 to 17)

The size of vacuoles increases, whereas their number decreases with rise of heating rate; at slow rate of heating the carbonised residues only become coherent after carbonisation to 550°C, whereas at heating rates of 10°C/min and 60°C/min the residues become coherent at about 450°C. At 1°C/min the carbonised products only develop a partial fine-grained mosaic, whereas at 10°C/min the residue develops a fine to medium-grained mosaic texture; at 60°C/min the mosaic units show a fine-grained to flow-type texture; large domains of anisotropic areas are developed at 10°C/min and 60°C/min (Plate 50).

(iv) Low-rank coking vitrinite (carbon = 87.9% daf)(Plates 18-26)

The size of vacuoles generally increases, whereas their number decreases with an increase in heating rate.

The carbonised products at 1°C/min are non-coherent up to 575°C whereas the residues at 10°C/min form a partial coherent semi-coke at 500°C and at 60°C/min a coherent residue is formed even at 450°C.

The mosaic texture at the slowest rate of heating mainly consists of fine-grained and/or medium-grained textures, but at 10°C/min, although the fine-grained and/or medium-grained mosaic textures dominate, flow-type mosaics are present; at 60°C/min the mosaic texture mainly consists of medium-grained to flow-type mosaic. The mosaic textures are even able to coalesce and to form large anisotropic domains (Plate 51), the intensity of anisotropy rising with increase of temperature and rate of heating.

The residues carbonised at 450°C and 500°C at rate of heating of 10°C/min also develop small, spherical bodies (Plate 47).

(v) High-rank coking vitrinite (carbon = 90.0% daf)(Plates 27-35)

At slow heating rate (1°C/min), the carbonised residues remain non-vesicular and/or occasionally develop vacuoles of about 10 um over the whole range of carbonisation temperature; at heating rate of 10°C/min the residues develop vacuoles of about 50 um at about 500°C. At heating rate of 60°C/min, the residues become vesicular and above 450°C, the size of vacuoles increases with rise of rate of heating and temperature.

The carbonised residues are non-coherent and remain non-vesicular and/or occasionally develop vacuoles of about 10 um over the whole range of carbonisation temperature at a heating rate of 1°C/min, whereas the residues at 10°C/min and 60°C/min are coherent once carbonised beyond 450°C. Mosaic textures mainly consist of a granular texture (fine to coarse-grained) for the heating rate of 1°C/min, whereas at 10°C/min and 60°C/min, the mosaic textures are mainly medium-grained to flow-type. Coalescence of mosaic units to form large anisotropic domains is more common at the fast rate of heating and it appears that the faster the rate of heating the better ordered will be the mosaic units (Plates 52 to 54). Botanical structures can be observed at all three rates of heating (Plates 55 to 58), but cell structures are better preserved at the slow rate of heating. At the fast heating rate the cellular structures flow and partially lose their original shape. The residues carbonised at rate of heating of 10°C/min at 500°C develop spherical bodies (Plates 48 and 49).

These spherical bodies show similar optical and morphological behaviour to that of mesophase described by other authors.

(vi) Anthracitic Vitrinites (carbon = 93.5 and 94.2% dmmf) (Plates 36 to 46)

There are few morphological differences between the residues of the anthracitic vitrinites carbonised at different heating rates. There is development of a system of fractures in the residues carbonised at fast rates of heating and a reduction in the numbers of vacuoles after approximately 900°C.

B. OPTICAL PROPERTIES

(i) Introduction

Goodarzi and Murchison (1972) established satisfactory relationships between the behaviour of the optical properties of vitrinites of different ranks carbonised up to 950°C and different stages of the carbonisation process, e.g. temperature of the onset of plasticity (Ts), temperature of the onset of resolidification (Tr) and temperature of the onset of molecular reorganisation in the solid (Tm) (Figs 13 and 17).

In the present study the similar optical data for each vitrinite of different rank carbonised at three different rates of heating are grouped together to display the optical changes occurring during the carbonisation process (Figs 40 – 45). Generalised curves of the individual optical plots for each vitrinite at the three different rates of heating are shown in Figs 46 to 51. The oil bireflectance plots for each vitrinite are shown in Figs 52 to 57.

The six vitrinites of different rank have been initially divided into two groups (see also Tables 5 and 6), a softening and a non-softening.

(a) The non-softening group consists of:-

Low-rank bituminous vitrinite
(carbon = 80.0% daf)
low-rank anthracitic vitrinite
(carbon = 93.5% dmmf)
high-rank anthracitic vitrinite
(carbon = 94.2% dmmf)

(b) The softening group consists of:-

coking coal vitrinite
(carbon = 85.4% daf)
low-rank, coking coal vitrinite
(carbon = 87.9% daf)
high-rank coking coal vitrinite
(carbon = 90.0% daf)

Softening vitrinites include the bituminous-rank vitrinites which soften at the onset of the plastic stage and undergo an extensive molecular reorganisation. These molecular changes begin with temporary loss of optical anisotropy (see for example Taylor 1961 ·, Davis 1965 and Goodarzi and Murchison 1972), due to complete disordering of molecular structure. Because of the coking coal structure (Hirsch 1954), the plasticity developed facilitates a reordering of the structural units due to the mobility of weakly-bonded aromatic lamellae in the plastic state. The degree of ordering of the molecular structure increases with rising carbonisation temperature. Commonly this group of vitrinites produces a graphitised carbon at temperatures required for graphitisation.

Non-softening vitrinites consist of vitrinites which do not become plastic during carbonisation (see for example Davis 1965 and Goodarzi and Murchison 1972), due to their particular molecular structure which consists of aromatic lamellae that are strongly cross-linked by amorphous material (Hirsch 1954). During carbonisation, because of this rigid cross-linkage, the lamellae cannot move freely (Franklin 1951), and so the ordering of the aromatic units which can be brought about by rise of carbonisation temperature is limited

(ii) Reflectivity (Figs 40 to 51a and b)

The reflectivity-temperature curves in air and oil of each vitrinite at a particular rate of heating are described together, because of the similarity between their trends throughout the rank range examined. The reflectivity-temperature curves of the low-rank bituminous vitrinites are plotted on a similar scale as those for the softening vitrinites, because it is possible to bring out the differences between the reflectivity curves; whereas the reflectivity-temperature curves of the anthracitic vitrinites are plotted on a larger scale compared with the softening group and the low-rank bituminous vitrinite, because of the small differences between the reflectivity curves at the different heating rates.

(a) Non-softening Group

1. Low-rank bituminous vitrinites (a and b Figs 40, 46)

The differences between the reflectivity curves at the

Fig 40 Variation with temperature of air and oil reflectivity, refractive index and absorptive index of low-rank bituminous vitrinite (carbon = 80.0% daf), carbonised at three rates of heating.

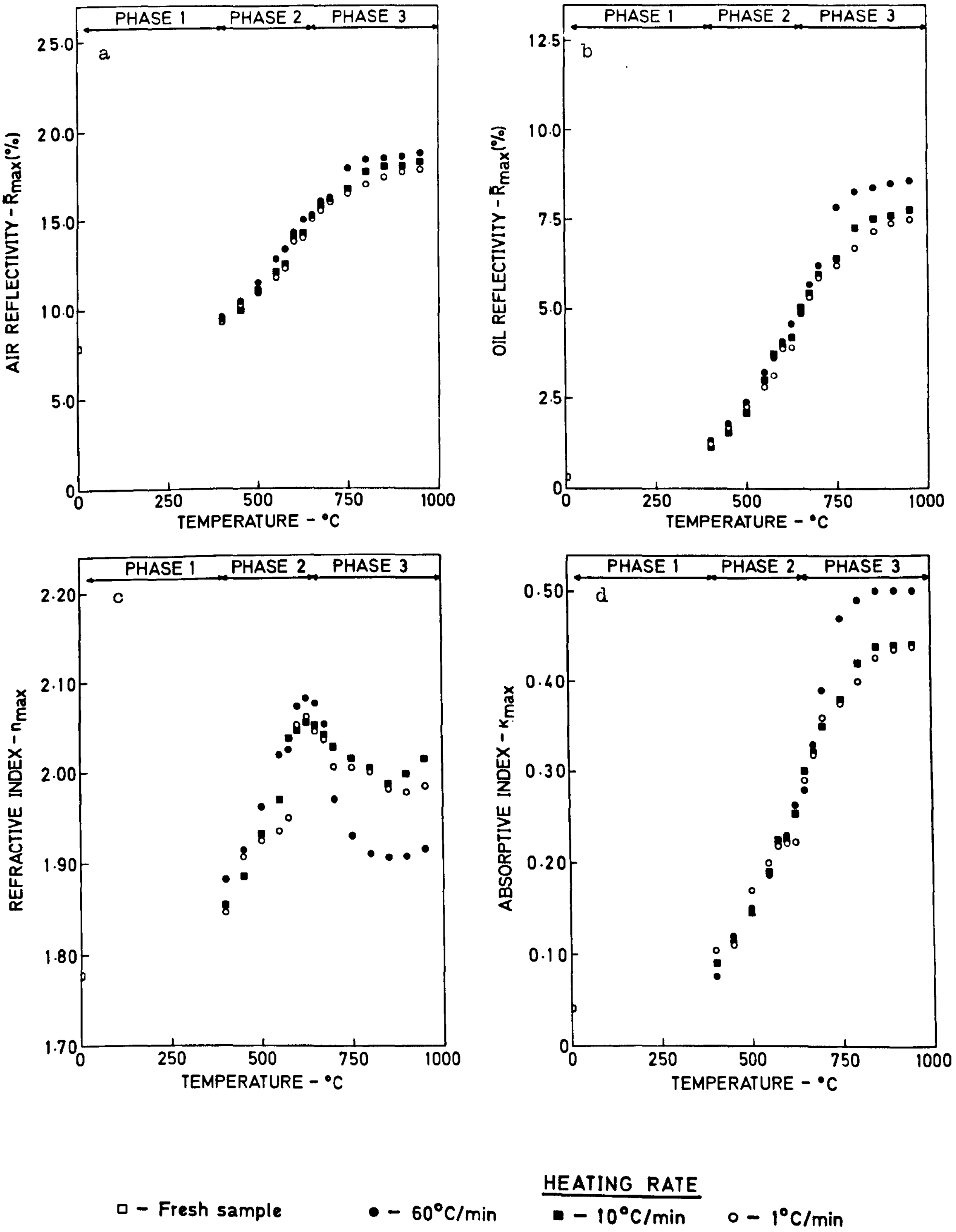

PHASE 1
PHASE 2
PHASE 3
a
b
c
d
AIR REFLECTIVITY - R̄max(%)
OIL REFLECTIVITY - R̄max(%)
REFRACTIVE INDEX - nmax
ABSORPTIVE INDEX - κmax
TEMPERATURE - °C
0
250
500
750
1000
25.0
20.0
15.0
10.0
5.0
12.5
7.5
2.5
2.20
2.10
2.00
1.90
1.80
1.70
0.50
0.40
0.30
0.20
0.10
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

Fig 41 Variation with temperature of air and oil reflectivity, refractive index and absorptive index of low-rank, anthracitic vitrinite (carbon = 93.5% dmmf), carbonised at three rates of heating.

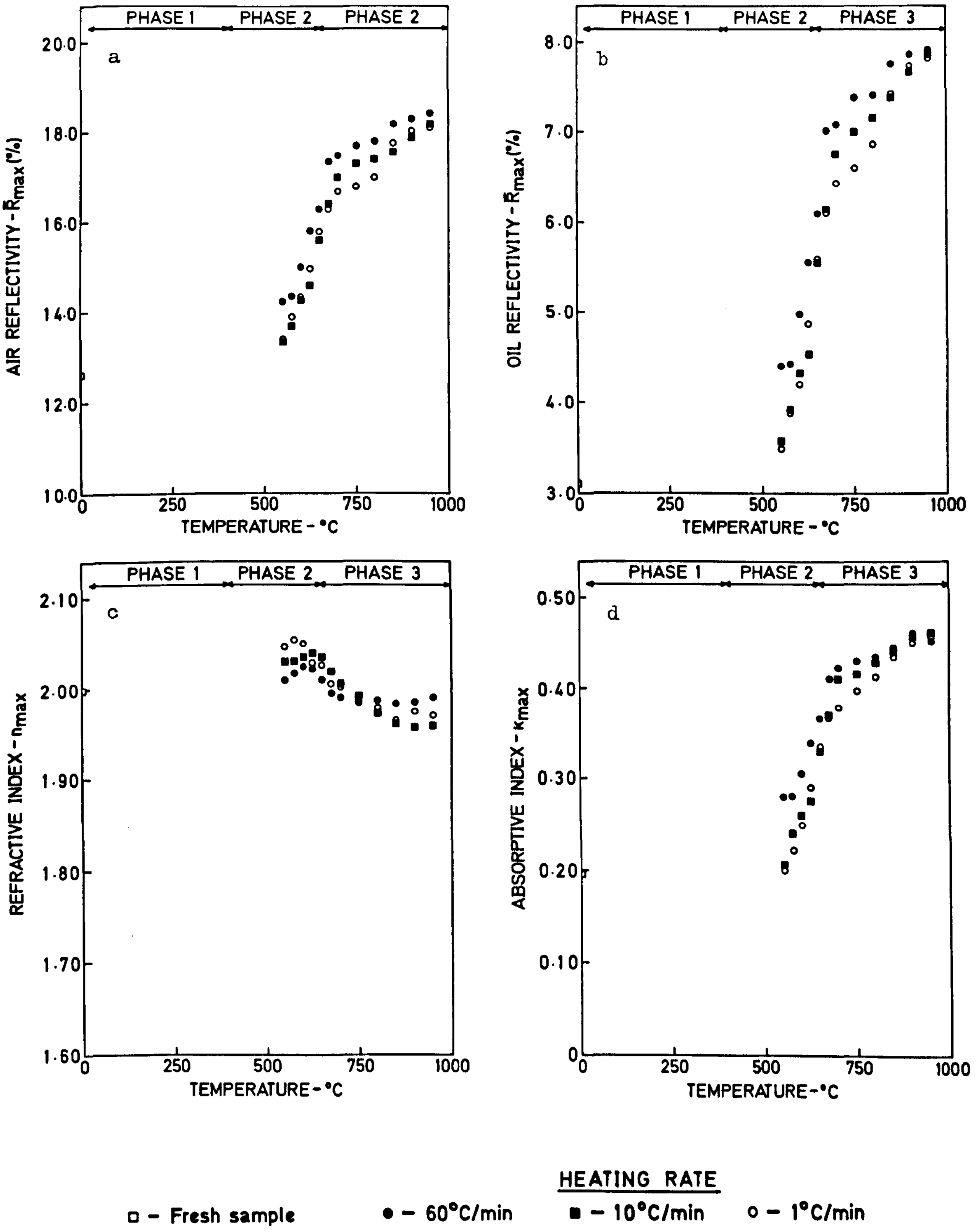

PHASE 1
PHASE 2
PHASE 2
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
20.0
18.0
16.0
14.0
12.0
10.0
0
250
500
750
1000
TEMPERATURE - °C
PHASE 1
PHASE 2
PHASE 3
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
8.0
7.0
6.0
5.0
4.0
3.0
0
250
500
750
1000
TEMPERATURE - °C
PHASE 1
PHASE 2
PHASE 3
c
REFRACTIVE INDEX - n_{max}
2.10
2.00
1.90
1.80
1.70
1.60
0
250
500
750
1000
TEMPERATURE - °C
PHASE 1
PHASE 2
PHASE 3
d
ABSORPTIVE INDEX - κ_{max}
0.50
0.40
0.30
0.20
0.10
0
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

Fig 42 Variation with temperature of air and oil reflectivity, refractive index and absorptive index of high-rank anthracitic vitrinite (carbon = 94.2% dmmf) carbonised at three rates of heating.

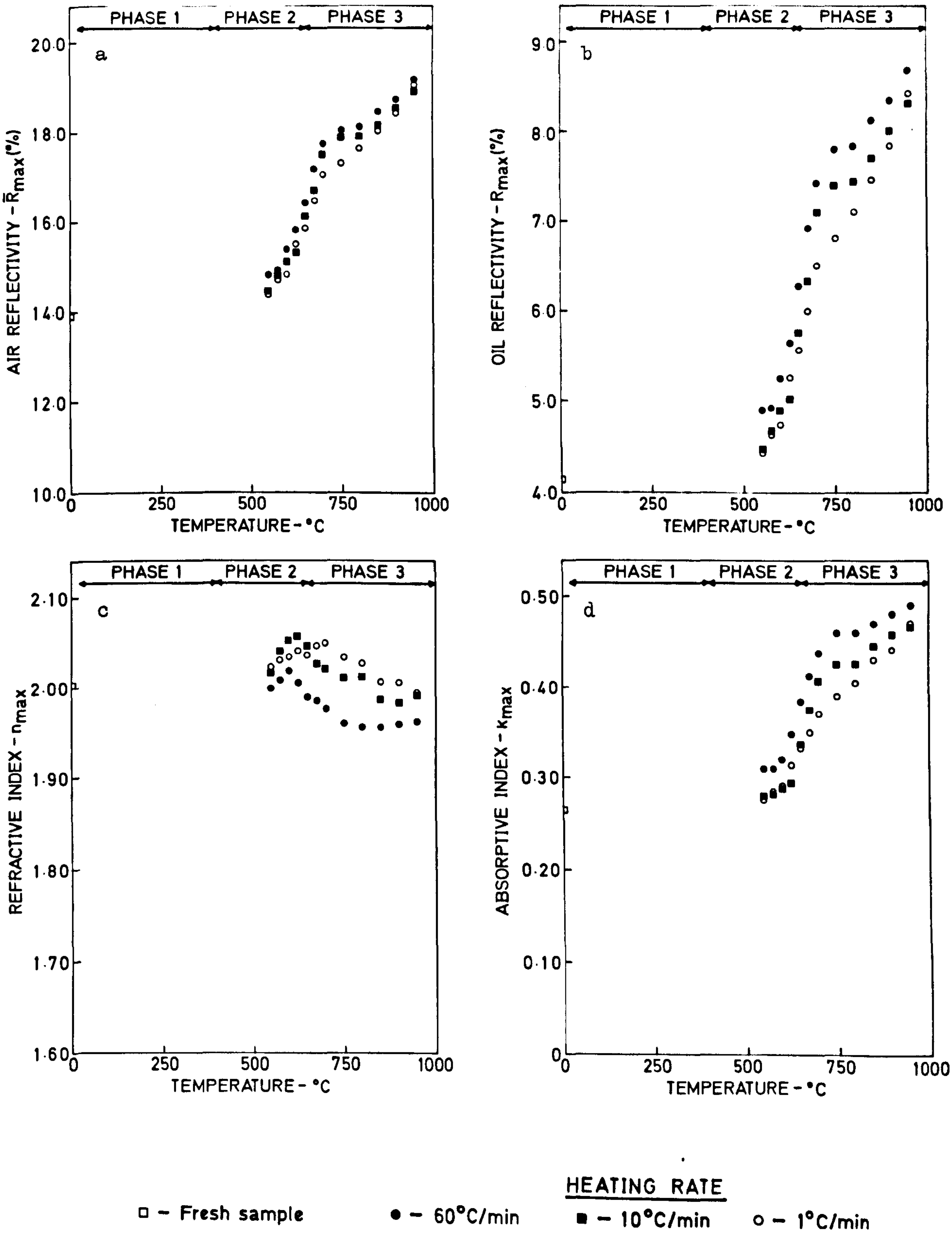

PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$(%)
20.0
18.0
16.0
14.0
12.0
10.0
0
250
500
750
1000
TEMPERATURE - °C
b
OIL REFLECTIVITY - R_{max}(%)
9.0
8.0
7.0
6.0
5.0
4.0
c
REFRACTIVE INDEX - n_{max}
2.10
2.00
1.90
1.80
1.70
1.60
d
ABSORPTIVE INDEX - k_{max}
0.50
0.40
0.30
0.20
0.10
0
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

Fig 43 Variation with temperature of air and oil reflectivity, refractive index and absorptive index of caking-coal vitrinite (carbon = 85.4% daf), carbonised at three rates of heating.

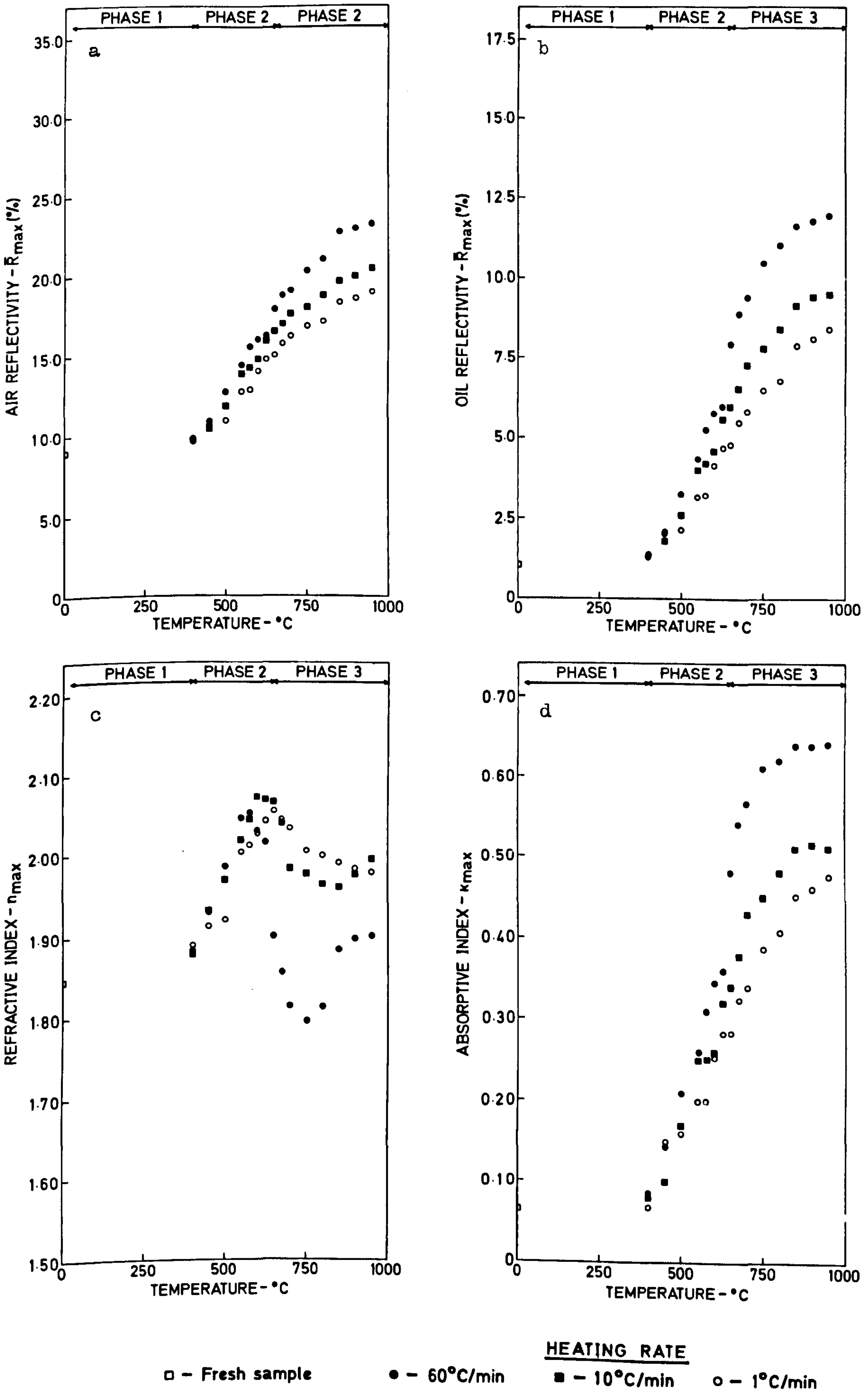

PHASE 1
PHASE 2
PHASE 2
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
TEMPERATURE - °C
0
250
500
750
1000
PHASE 1
PHASE 2
PHASE 3
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0
TEMPERATURE - °C
0
250
500
750
1000
PHASE 1
PHASE 2
PHASE 3
c
REFRACTIVE INDEX - n_{max}
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
TEMPERATURE - °C
0
250
500
750
1000
PHASE 1
PHASE 2
PHASE 3
d
ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
TEMPERATURE - °C
0
250
500
750
1000
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

Fig 44 Variation with temperature of air and oil reflectivity, refractive index and absorptive index of low-rank, coking coal vitrinite (carbon = 87.9% daf), carbonised at three rates of heating.

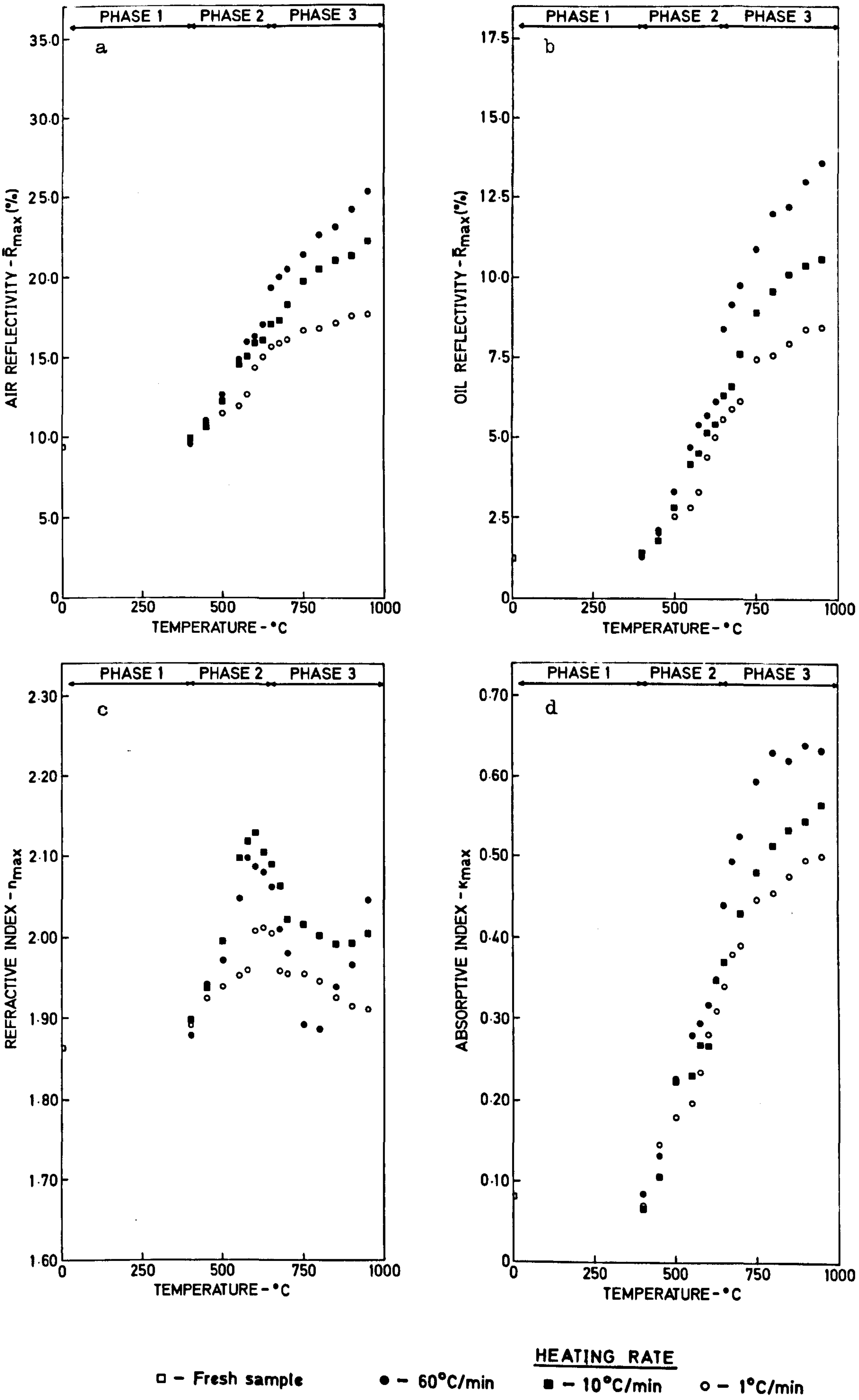
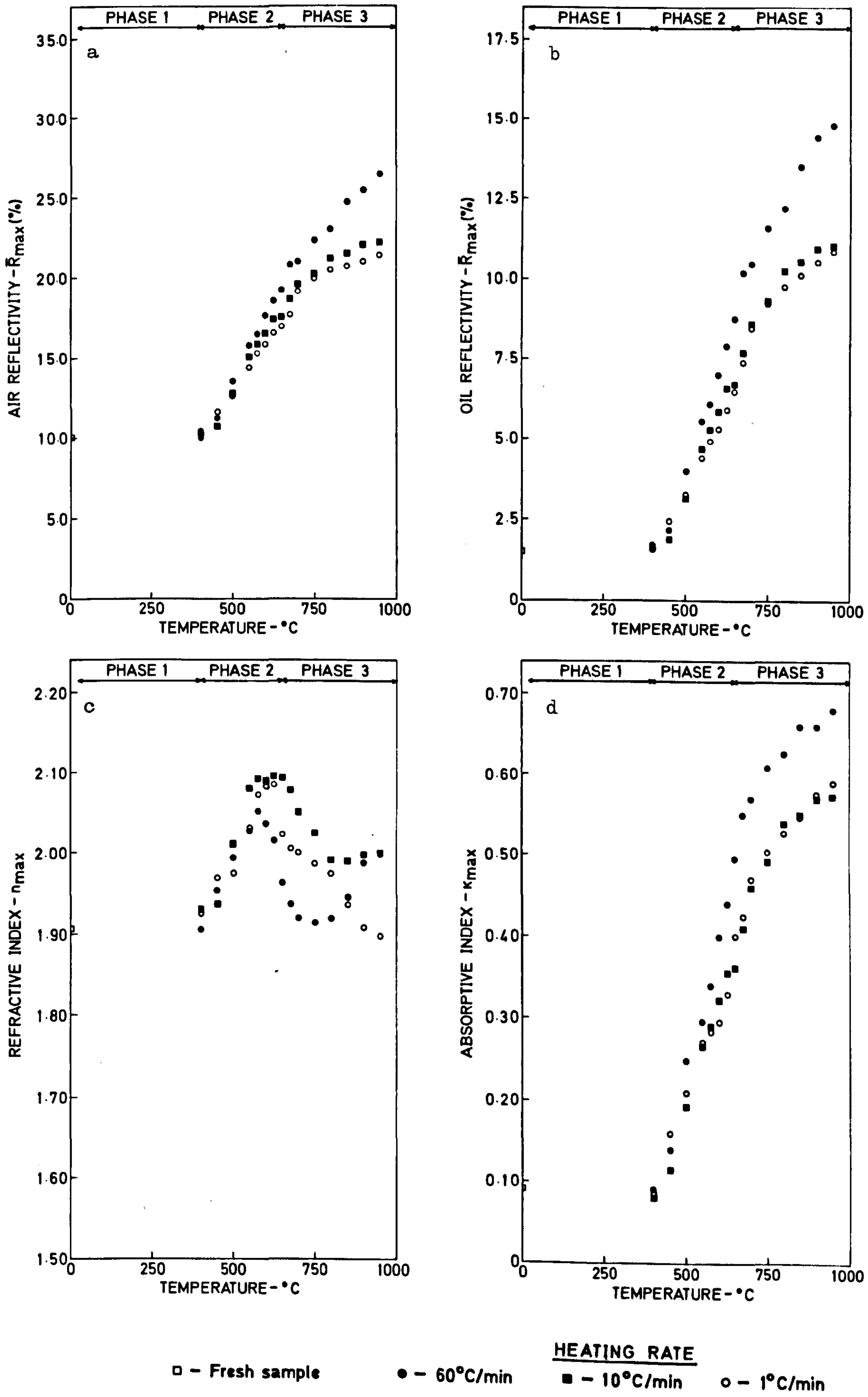

PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
TEMPERATURE - °C
0
250
500
750
1000
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0
c
REFRACTIVE INDEX - n_{max}
2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
d
ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
HEATING RATE
□ – Fresh sample
● – 60°C/min
■ – 10°C/min
○ – 1°C/min

Fig 45 Variation with temperature of air and oil reflectivity, refractive index and absorptive index of high-rank, coking coal vitrinite (carbon = 90.0% daf), carbonised at three rates of heating.


PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
TEMPERATURE - °C
0
250
500
750
1000
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0
c
REFRACTIVE INDEX - n_{max}
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
d
ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

three rates of heating are very small on carbonisation up to 700°C, with the reflectivity curve of 60°C/min following a slightly higher upward trend than those at 10°C and 1°C/min. The reflectivity curves follow a sequential pattern after 700°C, that for the fast rate of heating being highest, the intermediate rate of heating in the middle and the slow rate of heating below up to 950°C.

2. Anthracitic vitrinites (a and b Figs 41, 42, 47, 48)

The behaviour of the two sets of reflectivity curves for the anthracitic vitrinites is very similar. The reflectivity curves at 60°C/min show a higher upward trend than those at 10°C and 1°C/min up to 950°C. However, the reflectivity curves at 10°C and 1°C/min follow similar paths which almost coincide up to 650°C for the high-rank anthracite and 675°C for the low-rank anthracite. The reflectivity curves then separate from one another and follow different upward paths. Finally, the differences between these reflectivity curves diminish once more at about 850°C for the low-rank anthracitic vitrinite and at about 900°C for the high-rank anthracitic vitrinite, after which the reflectivity curves follow similar trends up to 950°C.

(b) Softening Group (a and b Figs 43 to 45, 49 to 51)

The reflectivity curves of this group at all three rates of heating increase slightly up to 400°C and then more rapidly but slowly up to 450°C. The differences between the reflectivity

Fig 46 Generalised curves for variation with temperature of air and oil reflectivity, refractive and absorptive index of low-rank bituminous vitrinite (carbon = 80.0% daf), carbonised at three rates of heating.

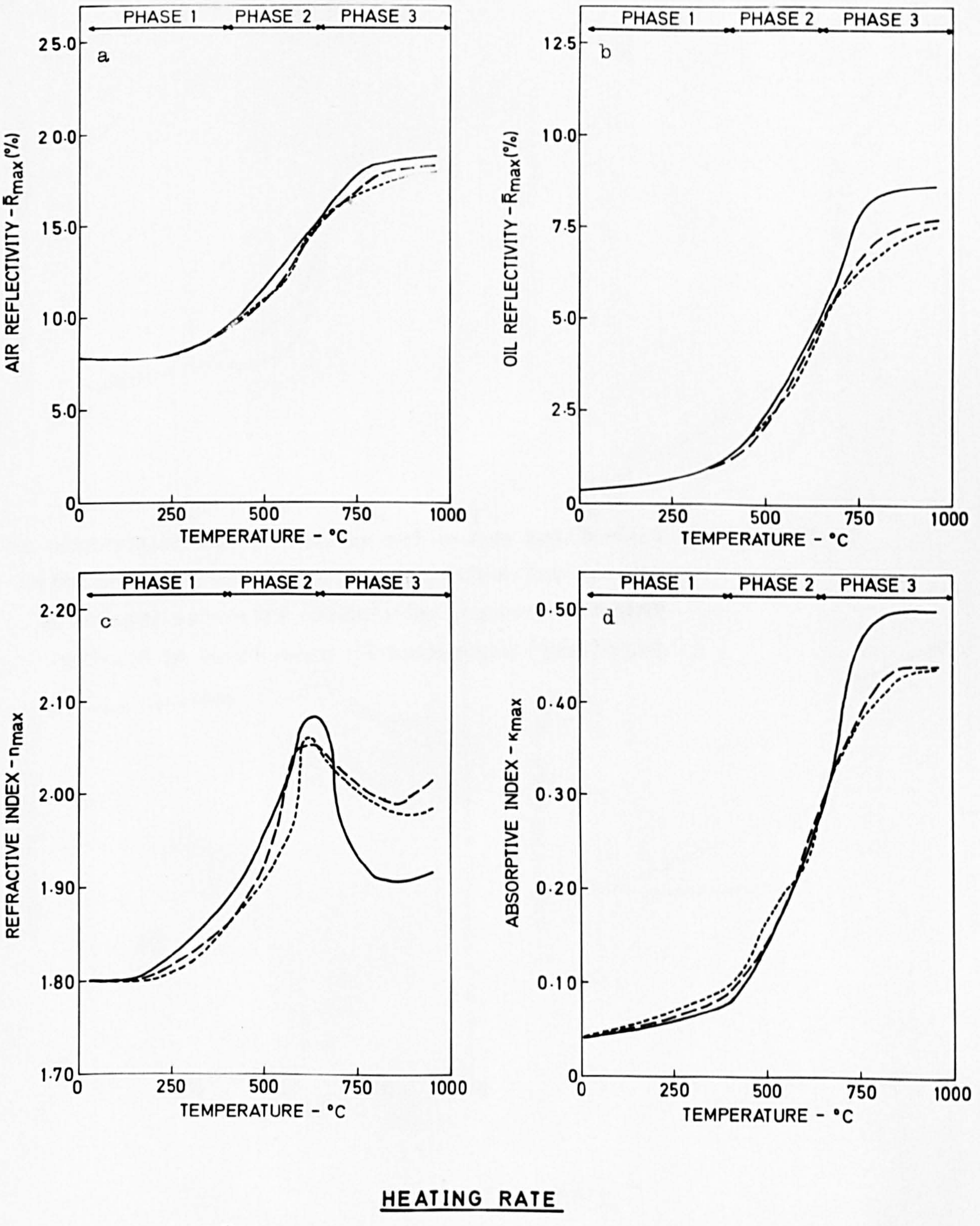

PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$(%)
25.0
20.0
15.0
10.0
5.0
0
TEMPERATURE - °C
0
250
500
750
1000
b
OIL REFLECTIVITY - $\bar{R}_{max}$(%)
12.5
10.0
7.5
5.0
2.5
0
c
REFRACTIVE INDEX - n_{max}
2.20
2.10
2.00
1.90
1.80
1.70
d
ABSORPTIVE INDEX - κ_{max}
0.50
0.40
0.30
0.20
0.10
0
HEATING RATE
60°C/min
10°C/min
1°C/min

Fig 47 Generalised curves for variation with temperature of air and oil reflectivity, refractive and absorptive index of low-rank anthracitic vitrinite (carbon = 93.5% dmmf) carbonised at three rates of heating.

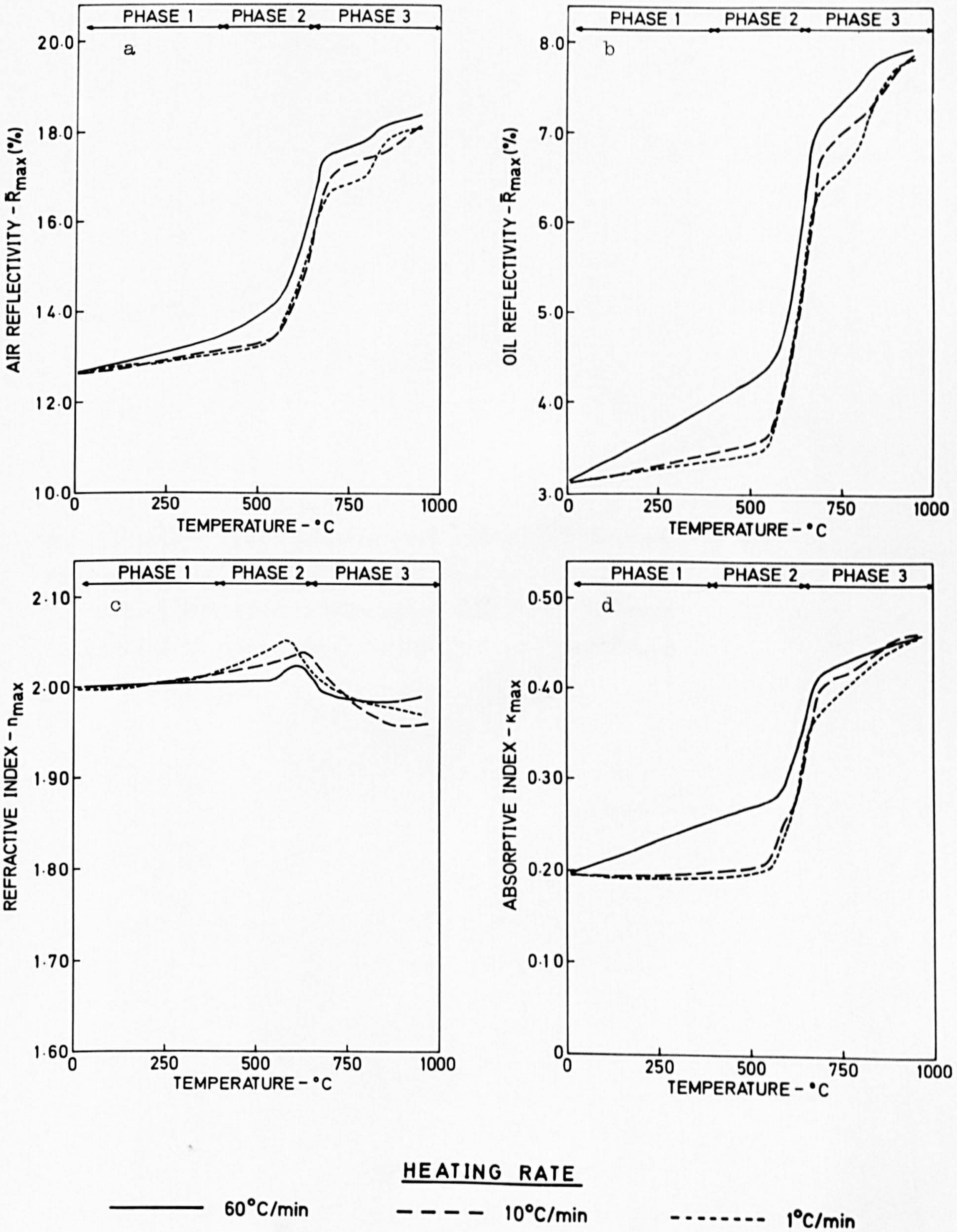

a
PHASE 1
PHASE 2
PHASE 3
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
20.0
18.0
16.0
14.0
12.0
10.0
0
250
500
750
1000
TEMPERATURE - °C
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
8.0
7.0
6.0
5.0
4.0
3.0
c
REFRACTIVE INDEX - n_{max}
2.10
2.00
1.90
1.80
1.70
1.60
d
ABSORPTIVE INDEX - κ_{max}
0.50
0.40
0.30
0.20
0.10
0
HEATING RATE
60°C/min
10°C/min
1°C/min

Fig 48 Generalised curves for variation with temperature of air and oil reflectivity, refractive and absorptive index of high-rank anthracitic vitrinite (carbon = 94.2% dmmf) carbonised at three rates of heating.

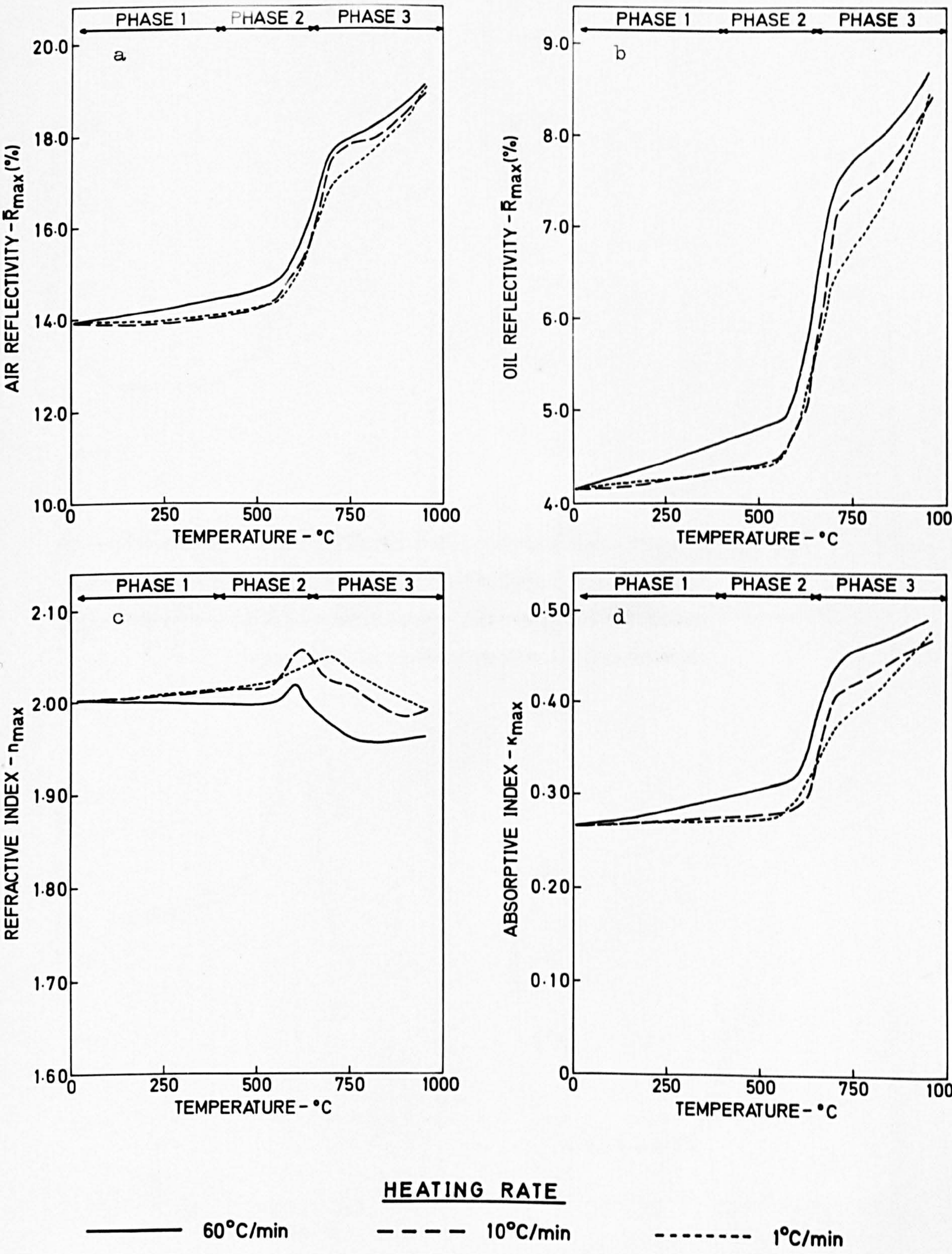

PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
20.0
18.0
16.0
14.0
12.0
10.0
0
250
500
750
1000
TEMPERATURE - °C
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
9.0
8.0
7.0
6.0
5.0
4.0
c
REFRACTIVE INDEX - n_{max}
2.10
2.00
1.90
1.80
1.70
1.60
d
ABSORPTIVE INDEX - κ_{max}
0.50
0.40
0.30
0.20
0.10
0
HEATING RATE
60°C/min
10°C/min
1°C/min

Fig 49 Generalised curves for variation with temperature of air and oil reflectivity, refractive and absorptive index of caking coal vitrinite (carbon = 85.4% daf), carbonised at three rates of heating.

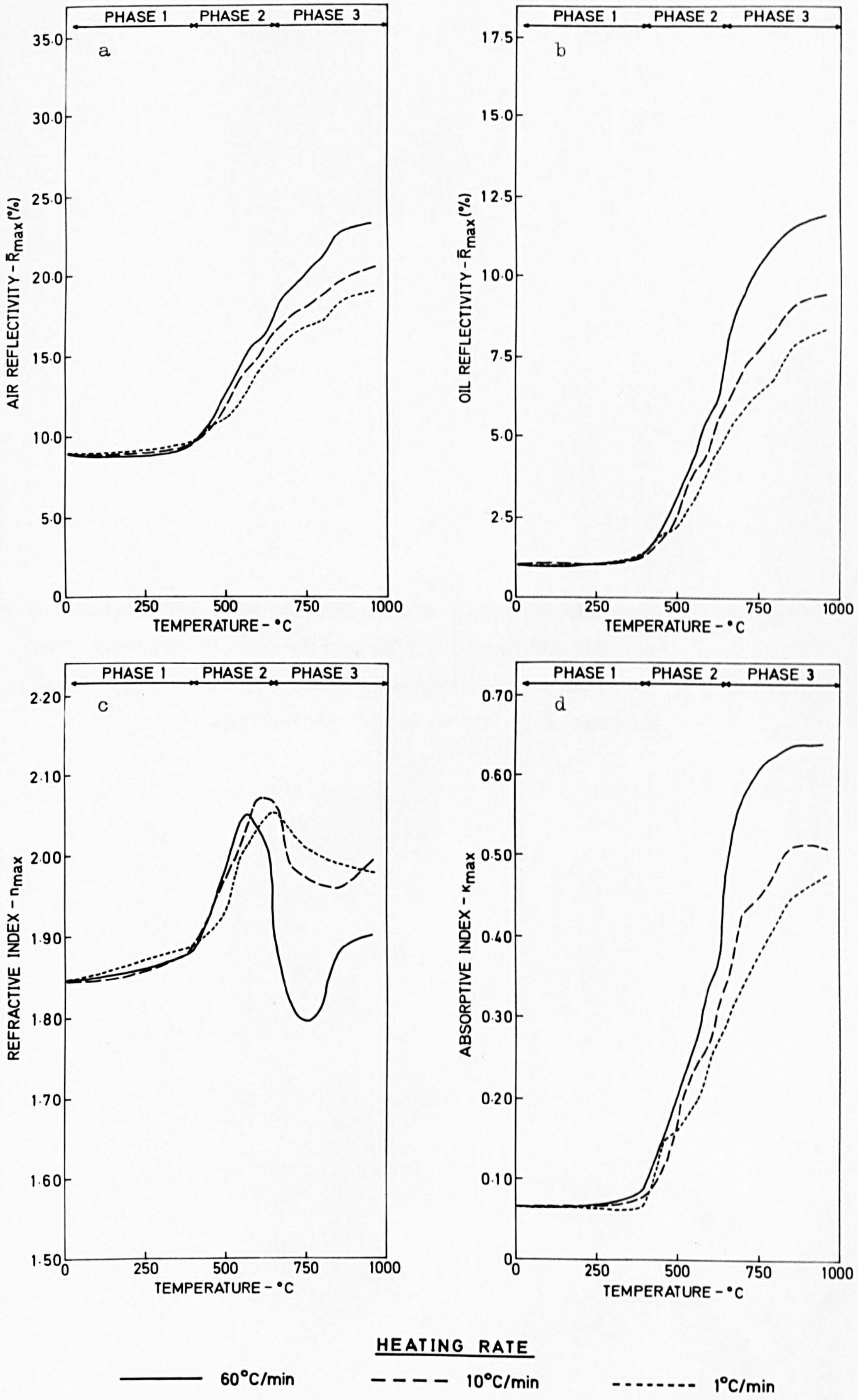

PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
0
250
500
750
1000
TEMPERATURE - °C
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17.5
15.0
12.5
10.0
7.5
5.0
2.5
c
REFRACTIVE INDEX - n_{max}
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
d
ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
HEATING RATE
60°C/min
10°C/min
1°C/min

Fig 50 Generalised curves for variation with temperature of air and oil reflectivity, refractive and absorptive index of low-rank coking coal vitrinite (carbon = 87.9% daf), carbonised at three rates of heating.

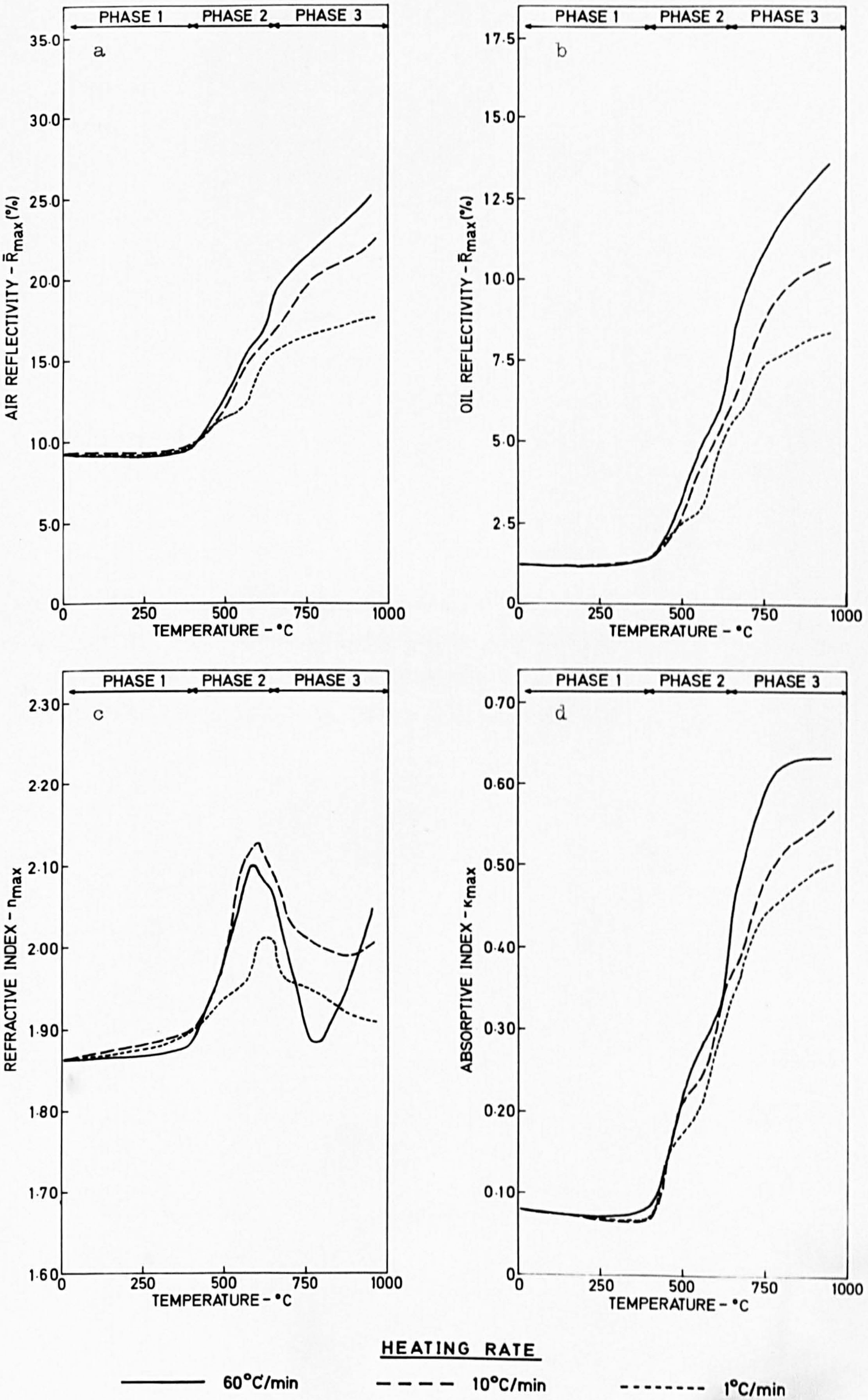
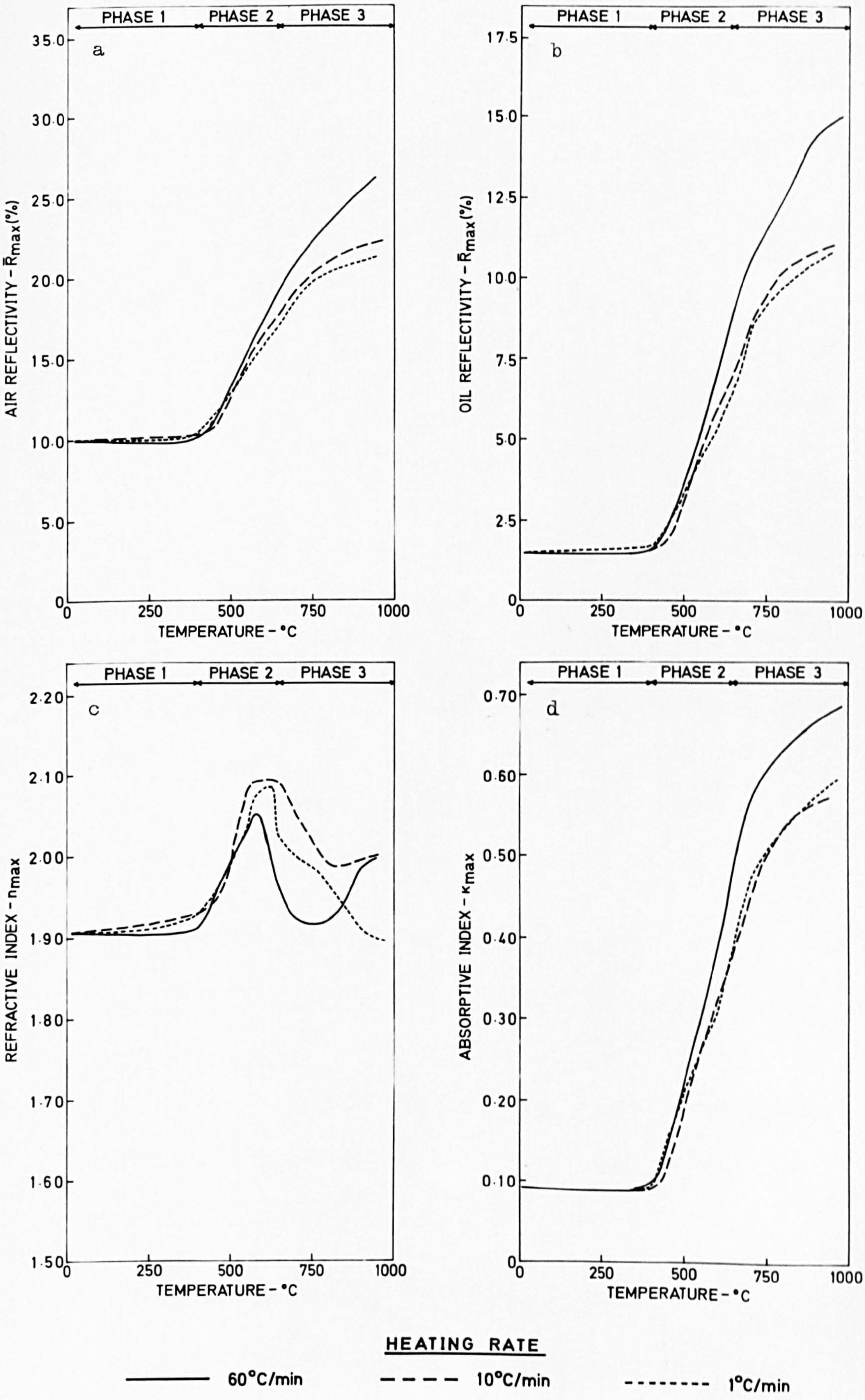

PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
0
250
500
750
1000
TEMPERATURE - °C
PHASE 1
PHASE 2
PHASE 3
b
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0
0
250
500
750
1000
TEMPERATURE - °C
PHASE 1
PHASE 2
PHASE 3
c
REFRACTIVE INDEX - n_{max}
2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
0
250
500
750
1000
TEMPERATURE - °C
PHASE 1
PHASE 2
PHASE 3
d
ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
60°C/min
10°C/min
1°C/min

Fig 51 Generalised curves for variation with temperature of air and oil reflectivity, refractive and absorptive index of high-rank coking coal vitrinite (carbon = 90.0% daf), carbonised at three rates of heating.


PHASE 1
PHASE 2
PHASE 3
a
AIR REFLECTIVITY - $\bar{R}_{max}$(%)
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0
TEMPERATURE - °C
0
250
500
750
1000
b
OIL REFLECTIVITY - $\bar{R}_{max}$(%)
17.5
15.0
12.5
10.0
7.5
5.0
2.5
c
REFRACTIVE INDEX - n_{max}
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
d
ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
HEATING RATE
60°C/min
10°C/min
1°C/min

curves of the carbonised residues of each rank level in this group appear only after carbonisation to about 500°C, when the reflectivity curves become separated, with the curves for 60°C the highest with the 1°C curve at the base, the curves for 10°C/min maintaining an intermediate position. The reflectivity curves for the three heating rates maintain their distinct trends with progressive increase of temperature up to 950°C. The reflectivity curves of the high-rank, coking coal vitrinite at 10°C and 1°C/min follow one another more closely with rise of carbonisation temperature, but still the reflectivity curve for 10°C/min maintains a higher level than that at 1°C/min. The above trends show that in the softening group, the reflectivity at any one temperature is the higher, the faster is the rate of heating. The separation between the curves is much more distinct than in the non-softening group.

(iii) Bireflectance in oil (a and b Figs 52 to 57)

Bireflectance-temperature curves of non-softening vitrinites are plotted on a larger scale than those of the softening vitrinites, again to bring out the differences between the bireflectance-temperature curves at the different rates of heating, which are small for the non-softening group.

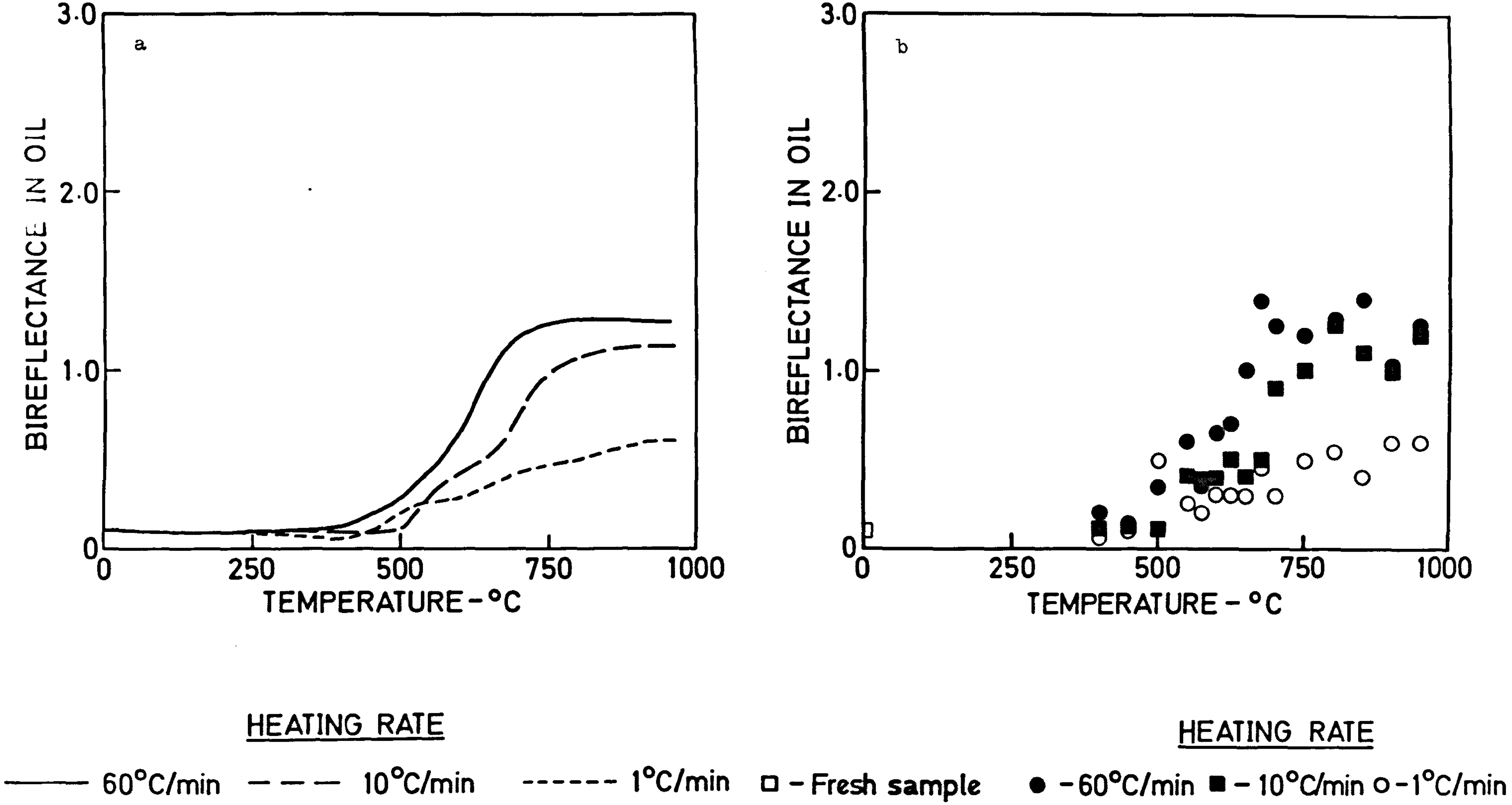
(a) Non-softening Group (a and b Figs 52 to 54)

Low-rank bituminous vitrinite (Figs 52a and b)

There is little change in the bireflectance-temperature

Fig 52 Variation with temperature of oil bireflectance of carbonised low-rank bituminous vitrinite (carbon = 80.0% daf)

(a) generalised curve
(b) experimental data


a
BIREFLECTANCE IN OIL
3.0
2.0
1.0
0
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
60°C/min
10°C/min
1°C/min
b
BIREFLECTANCE IN OIL
3.0
2.0
1.0
0
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

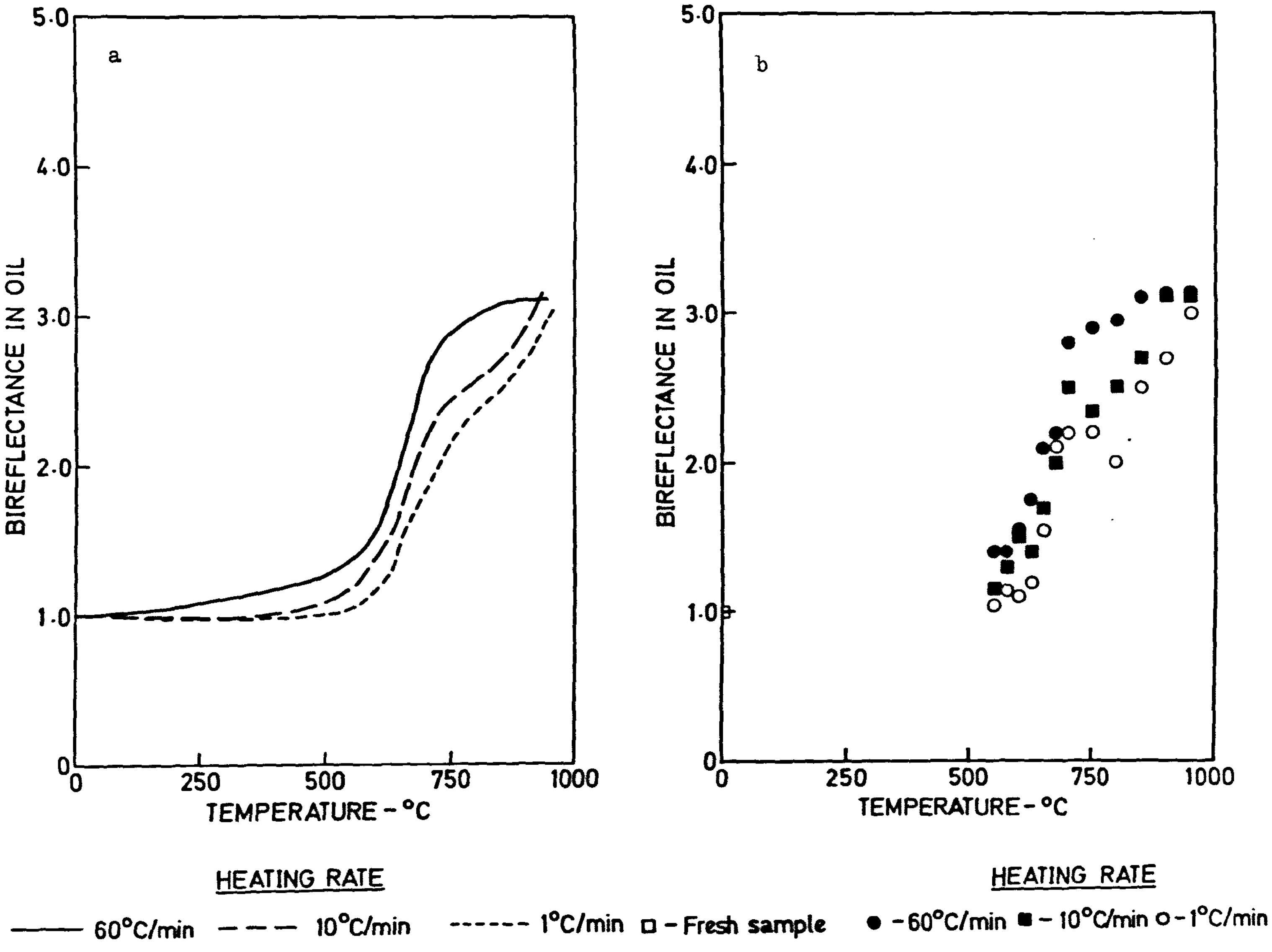
curves at the three rates of heating up to 450°C. At 500°C bireflectance starts to increase and this increase is more pronounced at 60°C/min than at either 10°C or 1°C/min. The bireflectance curve at 60°C/min after rising continuously to 700°C then maintains the same level or decreases slightly, but at 10°C/min, it is only after rising to 850°C that a constant level is maintained to 950°C. The bireflectance at 1°C/min increases slowly with increase of temperature up to 950°C. The bireflectance curves maintain a sequential pattern after about 600°C with the curves of 60°C/min above and 1°C/min at the base, with the 10°C/min curve maintaining an intermediate position.

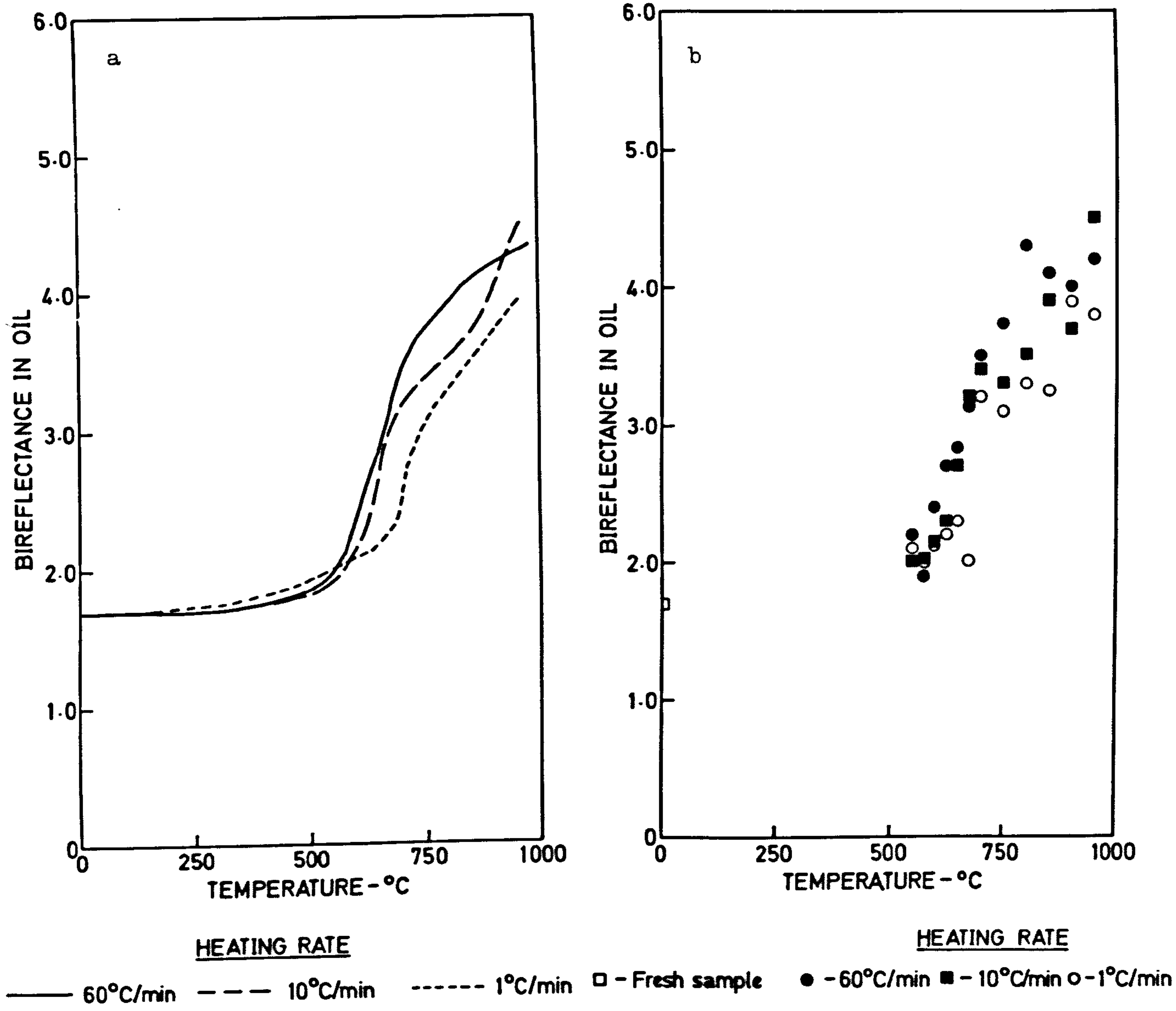
2. Anthracitic vitrinite (a and b Figs 53 and 54)

The bireflectance curves of the two anthracitic vitrinites at all three rates of heating show similar and sequential trends, with the curves for 60°C/min on top and the 1°C/min curves at the base. The curves show three stages. There is little change in bireflectance up to about 600°C for the high-rank anthracite and up to approximately 550°C for the lower-rank anthracite. Then the bireflectance increases rapidly up to about 700°C. After this point the bireflectance increases at a much reduced rate between 700°C and 950°C.

(b) Softening Group (a and b Figs 55 to 57)

The curves of bireflectance at the three rates of heating in general increase with rise of temperature after 450°C and they


a
b
BIREFLECTANCE IN OIL
TEMPERATURE - °C
0
1.0
2.0
3.0
4.0
5.0
0
250
500
750
1000
HEATING RATE
—— 60°C/min
– – – 10°C/min
------ 1°C/min
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min


a
6.0
5.0
4.0
3.0
2.0
1.0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
60°C/min
10°C/min
1°C/min
b
6.0
5.0
4.0
3.0
2.0
1.0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

follow different upward paths again with the curves for 60°C/min above and the 1°C/min at the base. Several of the curves show minima between approximately 400° to 450°C.

1. Caking coal vitrinite (Figs 55a and b)

The bireflectance curves at 1°C and 10°C/min, after an initial slight decrease, increase with rise of temperature. At 1°C/min the bireflectance curve shows little change up to 750°C, the larger increase of bireflectance lying between 750° and 950°C. The bireflectance curve for 10°C/min increases very sharply to about 750°C and then maintains a roughly constant level up to 950°C. The bireflectance curve at 60°C/min increases continuously with temperature. This increase is slow up to 450°C, but is followed by a very sharp increase up to 750°C, then the bireflectance curve rises more slowly up to 950°C.

2. Low-rank coking coal vitrinite (Figs 56a and b)

All three bireflectance curves,, after showing a minimum at 400°C, increase to 500°C, after which the curves branch out and follow three distinct paths. The bireflectance curves at 10°C and 60°C/min exhibit similar trends, increasing very sharply up to 950°C. At 1°C/min the bireflectance plots are more scattered but the bireflectance maintains the same general level up to 750°C, but increases rapidly to 700°C and less quickly to 950°C.

3. High-rank coking coal vitrinite (Figs 57a and b)

The bireflectance curves for the three different rates of

Fig 55 Variation with temperature of oil bireflectance of carbonised caking coal vitrinite (carbon = 85.4% daf)

(a) generalised curve
(b) experimental data

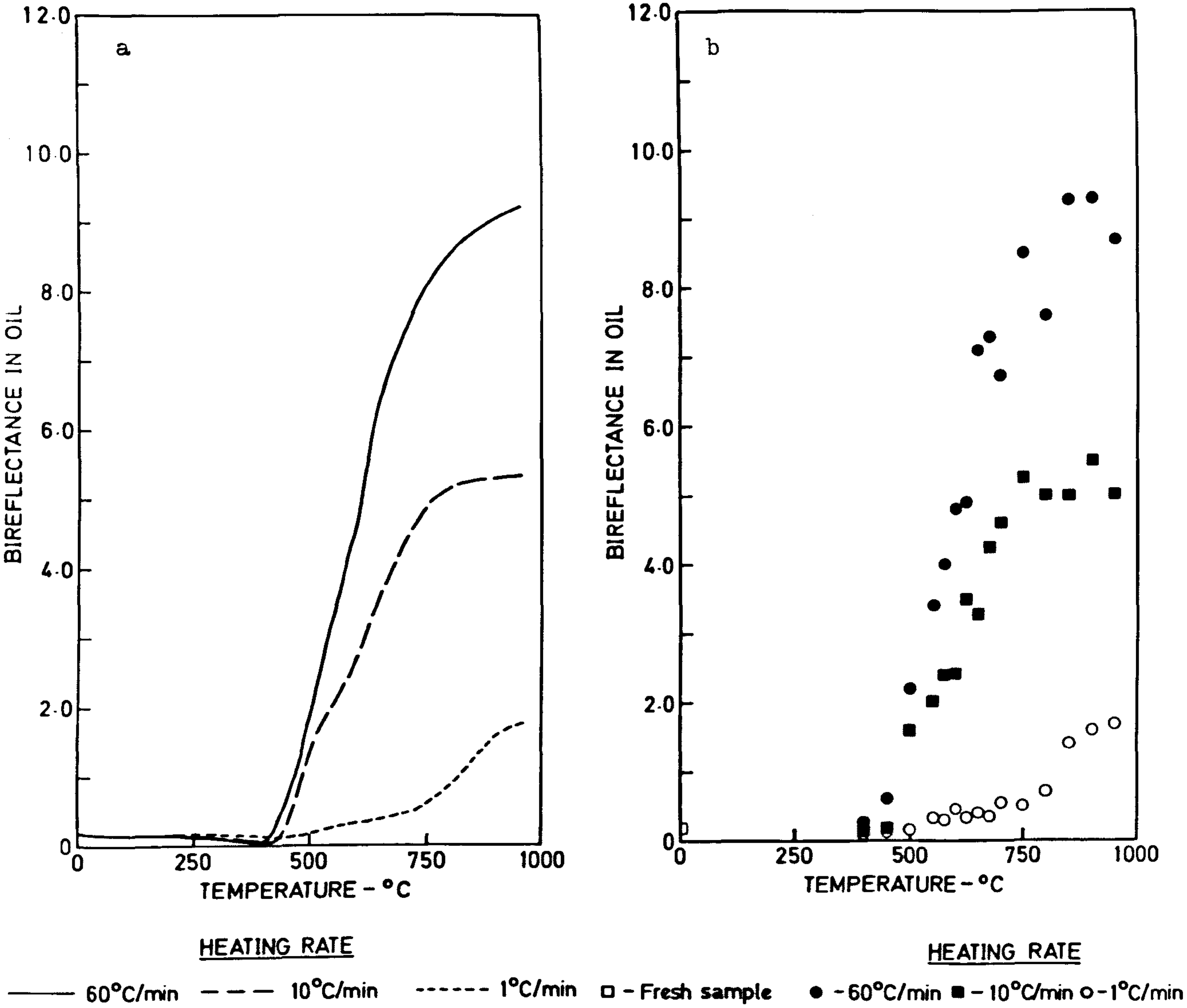

a
b
BIREFLECTANCE IN OIL
0
2.0
4.0
6.0
8.0
10.0
12.0
0
250
500
750
1000
TEMPERATURE – °C
HEATING RATE
60°C/min
10°C/min
1°C/min
□ – Fresh sample
● – 60°C/min
■ – 10°C/min
○ – 1°C/min

Fig 56 Variation with temperature of oil bireflectance of carbonised low-rank coking coal vitrinite (carbon = 87.9% daf)

(a) generalised curve
(b) experimental data

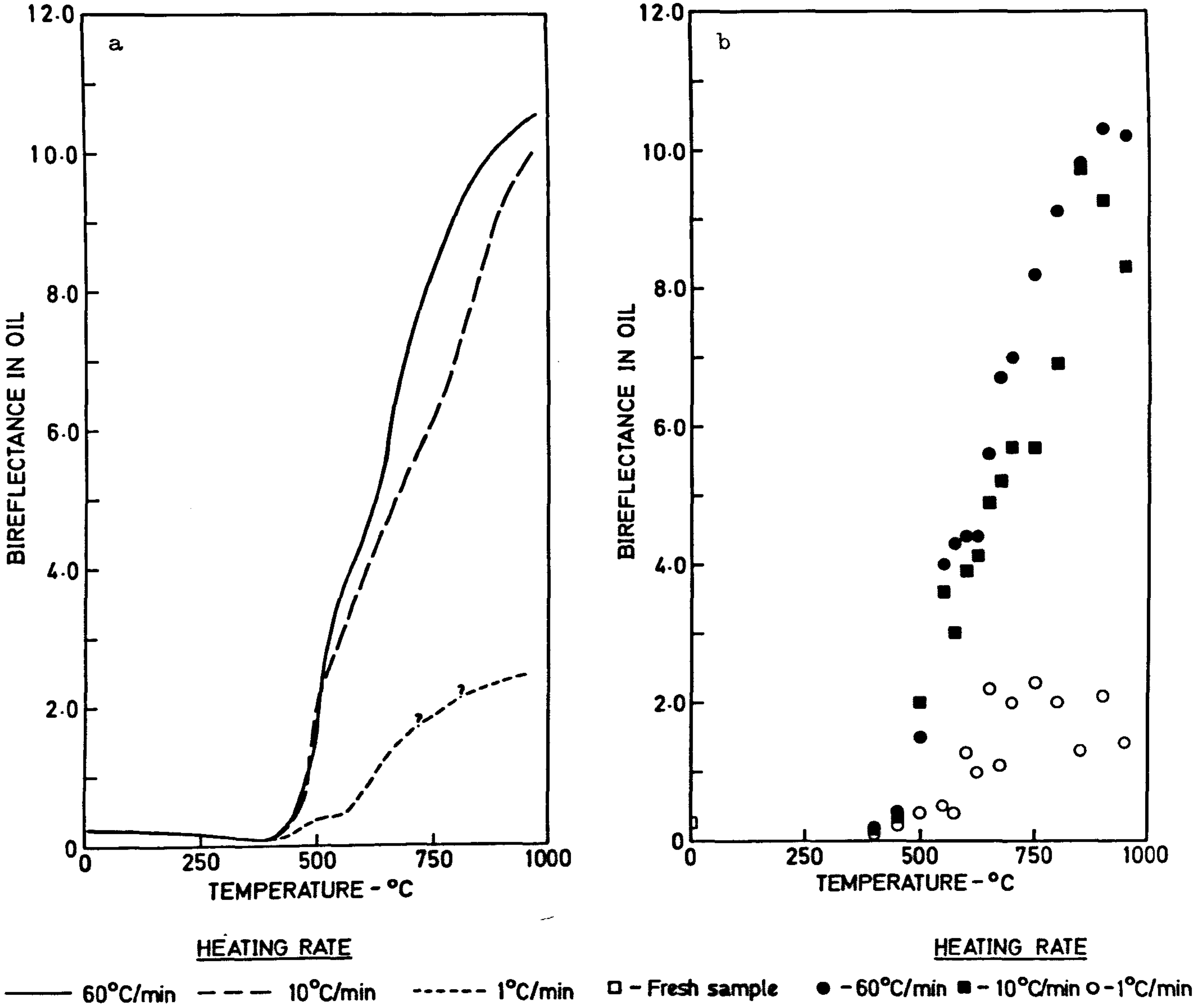
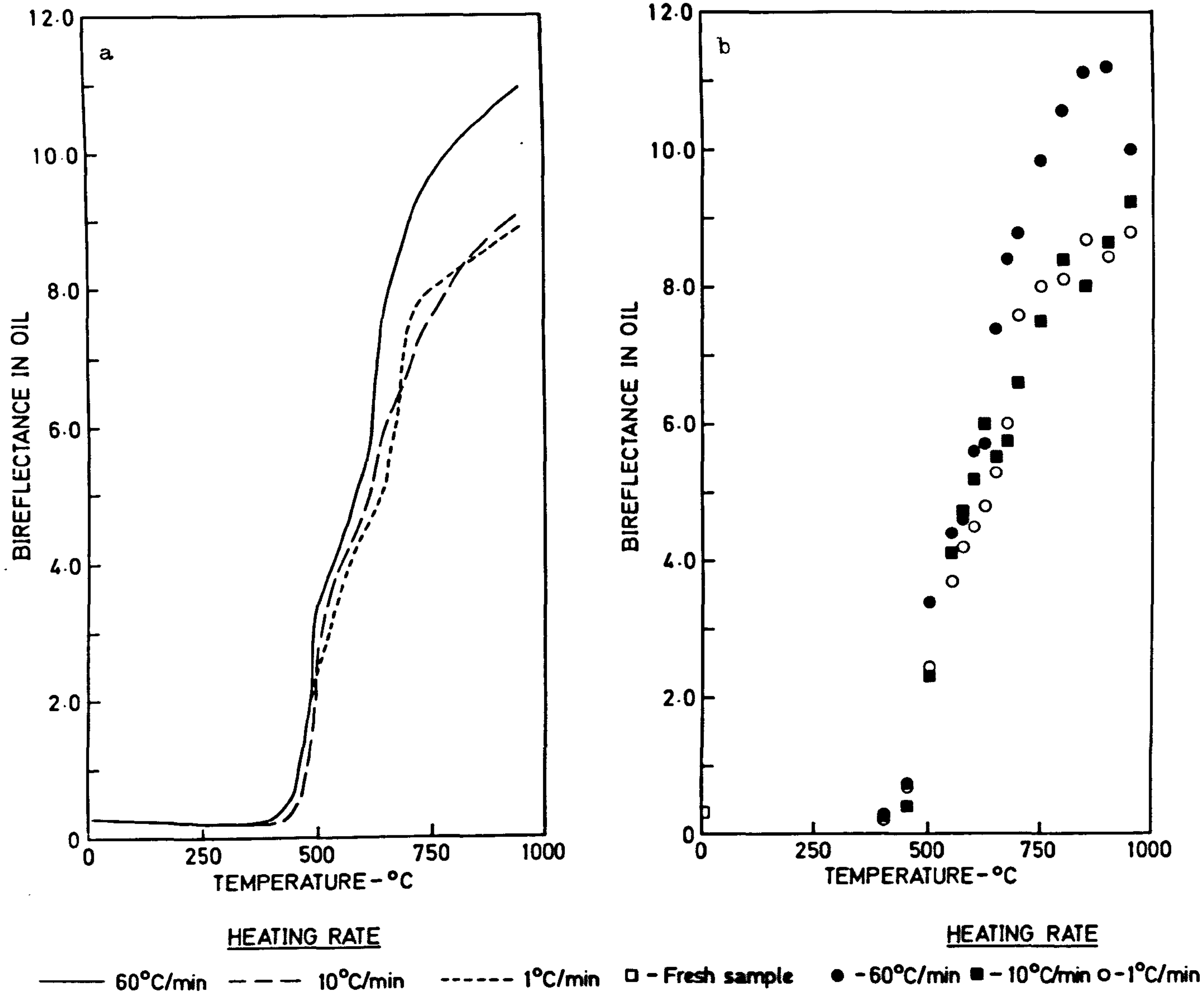

12.0
10.0
8.0
6.0
4.0
2.0
0
BIREFLECTANCE IN OIL
a
0
250
500
750
1000
TEMPERATURE - °C
?
?
HEATING RATE
60°C/min
10°C/min
1°C/min
12.0
10.0
8.0
6.0
4.0
2.0
0
BIREFLECTANCE IN OIL
b
0
250
500
750
1000
TEMPERATURE - °C
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

Fig 57 Variation with temperature of oil bireflectance of carbonised high-rank coking coal vitrinite (carbon = 90.0% daf)

(a) generalised curve
(b) experimental data


a
b
BIREFLECTANCE IN OIL
TEMPERATURE - °C
0
2·0
4·0
6·0
8·0
10·0
12·0
0
250
500
750
1000
HEATING RATE
60°C/min
10°C/min
1°C/min
HEATING RATE
□ - Fresh sample
● - 60°C/min
■ - 10°C/min
○ - 1°C/min

heating increase with rise of temperature and follow similar trends up to 625°C, but the bireflectance for 60°C/min maintains a slightly higher level, increasing sharply to 850°C and then more slowly up to 950°C. The bireflectance curves at 1°C and 10°C/min maintain similar trends up to approximately 700°C after which bireflectance rises at a reduced rate to 950°C. The three curves show a similar pattern; a slight increase to 450°C is followed by a sharp rise to 850°C at 60°C/min, 750°C at 10°C/min and 700°C at 1°C/min.

(iv) Refractive Index (cFigs 40 to 51)

The refractive index-temperature curves of the six vitrinites are all plotted on the same scale, because it is possible to illustrate the changes which occur during the carbonisation process at different heating rates for each vitrinite without scale adjustment. The form of the refractive index-temperature curves of the carbonised residues of the six vitrinites are later compared with the refractive-index curves of vitrinites examined previously by Goodarzi and Murchison (1973) (Fig 13).

(a) Non-softening group (cFigs 40 to 42 and 46 to 48)

1. Low-rank bituminous vitrinites (cFigs 40 and 46)

The refractive indices at the three rates of heating exhibit a maximum at about 625°C, but this peak is very sharp at 60°C/min, broader and lower for 10°C and 1°C/min. The refractive index curve at the fastest rate of heating passes through a minimum at about 800°C, which is much lower than for the 10°C/min and the 1°C/min curves. The refractive index curves for 10°C and 1°C/min, after 625°C, decrease more slowly and are close together, with the curve for 10°C/min above the 1°C/min curve up to 850°C. Then the refractive-index curve for 10°C/min starts to rise, whereas the curve for 1°C/min maintains the same level or only increases very slightly.

2. Low-rank anthracite(cFigs 41 and 47)

The refractive index curve at 60°C/min shows a small but sharp peak at 600°C, followed by a broad minimum over a range of 200°C between 700°C and 900°C. At 10°C/min, the refractive index again exhibits a broad peak with its maximum at 625°C, but lies higher than the 60°C/min curve. However, this peak is followed by a continuous decrease to a minimum at about 900°C. The refractive index curve at 1°C/min shows a sharp maximum which is higher than peak for either the 60°C or 10°C/min curves and lies at a lower temperature; then the refractive index decreases continuously with temperature without showing signs of arrest, even at 950°C.

3. High-rank anthracitic vitrinite(cFigs 42 and 48)

The refractive index curve at 60°C/min exhibits a sharp but very low peak, with a maximum at 600°C, which is followed by a decrease that produces a very broad minimum over the range from 650° to 900°C. At 10°C/min a less sharp peak but one with a higher maximum than for 60°C/min is produced, again followed by a decrease virtually to 950°C; there appears to be a slight rise at this temperature. The refractive index curve at 1°C/min shows a broad maximum peak and then a continuous decrease to higher temperatures.

(b) Softening group (cFigs 43 to 45 and 49 to 51)

The behaviour of the refractive index curves for each vitrinite of the softening group is described separately because of the greater complexity in the curves.

1. Caking coal vitrinite (cFigs 43 and 49)

60°C/min: the refractive index curve increases very sharply to a maximum at 575°C, then decreases rapidly to a pronounced minimum at 750°C, after which the refractive index increases with temperature to 950°C

10°C/min: the curve increases sharply to a maximum at about 25°C, nearly maintains its level for the next 25°C, then decreases rapidly to 700°C before falling at a slower rate to a minimum at approximately 850°C. The refractive index starts to rise once more after 850°C.

1°C/min: the curve increases sharply to a maximum at about 650°C, after which it decreases continuously to 950°C, producing only a broad maximum peak.

The maximum level of refractive index for a heating rate of 10°C/min is higher than for either the 60°C or 1°C/min curves, the peak values for the latter being similar. The minimum refractive index developed is the lower, the faster is the rate of heating.

2. Low-rank coking coal vitrinite (cFigs 44 and 50)

60°C/min: the refractive index curve increases sharply to a maximum at about 575°C and then decreases quickly to a minimum at approximately 750°C to give a broadly symmetrical trough. The index again rises sharply to 950°C.

10°C/min: the refractive index curve increases sharply to 600°C, then decreases very rapidly to 700°C and less rapidly to a minimum value at about 850°C, followed by a further slight rise up to 950°C.

1°C/min: the refractive index curve increases slowly to 575°C and then more sharply to 600°C, maintains its level for the next 50°C, then decreases sharply to 675°C and more slowly thereafter to 950°C resulting in a broad peak with a sharp subsidiary peak to give the maximum value.

3. High-rank coking coal vitrinite. (cFigs 45,51)

60°C/min: the refractive index curve increases sharply to a maximum at about 575°C, when it decreases very rapidly to a minimum at about 750°C, before increasing once more up to 950°C. There is a sharp maximum peak and a broad minimum.

10°C/min: the refractive index increases sharply to a maximum at 575°C, maintains the same level for the next 75°C to give a broad maximum, then decreases with rise of temperature to a minimum at about 800°C; once more the refractive index curve increases slightly with rise of carbonisation temperature to 950°C, producing a very shallow trough.

1°C/min: the refractive index increases sharply to 575°C and then more slowly to 625°C, after which it decreases sharply to 650°C, then more slowly to 950°C, resulting in a sharp peak above a broad maximum.

(v) Absorptive index (dFigs 40 to 51)

The absorptive index curves of the non-softening and softening groups follow similar and parallel trends to the reflectivity curves at the same rates of heating. Although the absorptive index is a less precisely determined parameter than the reflectivity, it still shows good agreement with the changes produced by the different rates of heating.

4. DISCUSSION

A. Morphology

(i) Development of mosaic structures in the carbonised vitrinites at different heating rates

The above observations clearly show the influence of heating rate on the morphology of the carbonised residues of vitrinites. It will be remembered that the six vitrinites of different rank in the present studies fall into two arbitrary groups on the basis of their plastic properties: non-softening and softening.

(a) Non-softening vitrinites

These vitrinites consist of low-rank bituminous and anthracitic vitrinites. They do not soften but produce slightly swelling, non-coherent and vesicular residues. The extent and size of the vesicles and eventually the plastic deformation, is the greater the lower is the rank (see for example Davis 1965 and Marshall and Murchison 1971). The low-rank vitrinitic particles become rounded and lose their original angular shape, whereas anthracitic vitrinite particles maintain their angular shape and/or become subangular with rise of temperature. Mosaic structures are not developed in the anthracitic group of vitrinites.

Low-rank bituminous vitrinite (Plates 3a, 5a, 6, 7 and 8)

The progressive increase of temperature and heating rate enhances the swelling and increases any limited plasticity of this vitrinite. The plasticity is apparent by the deformation and loss of the original angular shape of the particles and the size and extent of the vesicles, which increase with rise of heating rate. The plasticity of this vitrinite is limited, but its limited plasticity is enhanced by increasing the heating rate. The higher level of bireflectance in the carbonised residues at the fast heating rate is not surprising, because the rapid swelling and expansion of particles due to rapid degasification results in the development of a level of internal pressure at periphery of the particles and it is known that pressure increases the ordering of the molecular structure and hence raises the bireflectance (see for example Hryckowian et al. 1963; Huck and Patteiskey 1964; Chandra 1965 and Melvin 1974).

Anthracitic vitrinites (Plates 4, 36 to 46)

The increase in size and number of vesicles in these vitrinites with increasing heating rate indicates a rise in plasticity; indeed the results of Mackowsky and Wolff (1966) indicate that the number of vesicles in anthracitic vitrinites increases greatly with faster heating rates. A system of cracks and fracturing also develops as the heating rate rises, which is the greater the lower is the rank of anthracitic vitrinite. This is probably due to limited swelling and expansion of these vitrinites, which increases the faster is the heating rate. One interesting feature of the anthracitic vitrinites carbonised at about 900° - 950°C is the reduction in the number of small vesicles, which was reported previously by Goodarzi (1971) for anthracitic vitrinite (carbon = 93.1% daf) when carbonised at relatively slow heating rates (2.45°C/min). This is due to further expansion of the carbonised residues within the temperature range 900°-950°C which results in the destruction of vesicles and the development of extensive fracturing and the fissuring of the residues (see Plates 39, 40 and 46). It is also interesting to observe the different macerals, e.g. megaspores and microspores (Plates 42b, 45c and 46c), cutinite (Plates 41b and c and 44b), resinoid bodies (Plate 43a) and inertinite macerals, particularly at the highest rate of heating (Plates 36b, 41c and 44c). Increase in carbonisation temperature apparently enhances the morphologies of these macerals and produces a higher level of anisotropy at the peripheries of inertinite macerals, perhaps due to localised pressure caused by the presence of inert material and the better ordering of molecular structure in this area. It is accepted that anthracitic vitrinites do not in general develop mosaic textures (see for example Davis 1965; Marshall and Murchison 1971; Goodarzi 1971), but the anthracitic vitrinites carbonised to 900°C at 10°C/min in the present study exhibit a granular type structure (see Plates 41a and 45d).

(b) Softening vitrinites

This group includes the bituminous-coal vitrinites which soften on heating and produce vesicular, melted, coherent and swollen residues at normal heating rates, e.g. 3°-5°C/min. The most striking feature of these vitrinites is the development of an intermediate plastic stage during the early stages of carbonisation. During this intermediate stage, an isotropic 'pitch' is formed which is subsequently transformed into a spherical 'mesophase'. Eventually the mesophase coalesces to form various types of 'mosaic' textures. The type of mosaic texture is dependent upon the rank of the starting material and the granular mosaic is the coarser the higher is the starting rank (see for example Taylor 1961; Brook and Taylor 1965; Goodarzi 1971; Goldrings 1973; Patrick et al. 1973 and Marsh et al. 1973).

In general, the faster is the heating rate, the coarser is the granular mosaic texture formed because of the greater plasticity produced with rise in heating rate (see Brown 1956 and van Krevelen et al. 1956). This faster heating rate results initially in the development of a larger mesophase, because of the prolonging of plasticity and the prevention of maximum viscosity to a higher temperature. (see for example Taylor 1961; Brooks and Taylor 1965). One interesting feature of the highest heating rate is the development of a flow-type texture and large anisotropic domains due to coalescence of the mosaic units (see Plates 50 to 54). The carbonised residues of this group develop larger vacuoles and a system of cracks and fracturing at the fastest heating rate, which further indicates increase in plasticity.

Comparing the development of mosaic textures with heating rate within and between the rank levels, an estimation of the degree of plasticity and the ordering of the molecular structure can be achieved. Caking coal vitrinite, which only develops a partial fine-grained mosaic at 1°C/min, due to its low plasticity (see Brown 1956; van Krevelen et al. 1956), develops various types and sizes of completely granular mosaic textures at 10°C/min. At 60°C/min it not only develops the flow-type mosaic texture,, but also it develops large anisotropic domains which are a typical feature of high-temperature residues of prime coking coal vitrinite (see Marsh 1973). The low-rank coking coal vitrinite develops only a granular mosaic structure at 1°C/min, but due to the original high level of plasticity of this vitrinite, which is greatly reduced at 1°C/min, a number of mosaic units are still able to align themselves and develop a common orientation (Plates 21 and 24). The high-rank coking coal vitrinite also develops fine to medium-grain granular textures but remains non-coherent, non-vesiculated at 1°C/min (Plates 27, 30 and 33), because of the reduced plasticity at this slow heating rate. Increase of heating rate to 10°C/min results in a rise of plasticity and an increase in size and amount of vesicles with development of cracks in the carbonised residues. The cracking and fracturing is abundant the higher is the rank of the coking vitrinite (Plates 22, 25, 31 and 34), indicating the greater degree of expansion and contraction with increased plasticity. The high-rank coking vitrinite develops large anisotropic domains (Plates 52 to 54) and the mosaic texture mainly consists of medium-grained, flow-type textures. The development of large mosaic units is again due to increased plasticity in this vitrinite. At 60°C/min carbonised residues of all softening vitrinites are coherent, cracked and vesiculated, but the size of the vesicles is also larger, which indicates the increased plasticity.

The morphological features of the caking and the two coking coal vitrinites become increasingly similar at the fastest heating rate. The caking coal vitrinite, which only partially develops a fine-grained mosaic texture at 10°C/min, develops a flow-type mosaic texture at 60°C/min (Plate (Plates 11, 14 and 17) and the mosaic units show similar optical extinctions, which suggests development of a better-ordered structure due to the increase in plasticity. Plate 50 demonstrates the higher fluidity of this vitrinite at the fast heating rate, resulting in large flow-type anisotropic domains.

The coking coal vitrinites develop mainly medium-grained, flow-type mosaic textures and coarse-grained to flow-type in the high-rank coking vitrinite. The amount and size of large anisotropic domains are also greatly increased in the coking coal vitrinites (Plates 18 to 35). The increase in the size of the mosaic units indicates the rise in the plasticity in these two vitrinites at 60°C/min and is in agreement with statements by Goldring (1973), who anticipated a drastic change in the scale of mosaic texture with rise of heating rate.

(ii) Summary and practical use of the morphological studies

Having dealt at some length with the morphological features of carbonised residues of vitrinites at different levels of heating rate, it may be possible to make an assessment of the original rank of carbonised vitrinite in mixtures of various ranks of coals by morphological studies of polished coke surfaces. It is evident from the foregoing studies that the softening vitrinites develop various mosaic textures and that the size of the mosaic units increases with increase of rank and heating rate; the non-softening vitrinites do not show these features, so the vitrinites can firstly be divided into these two groups. Then, knowing that in the non-softening group, low-rank vitrinites develop relatively larger vacuoles than anthracitic vitrinites, these two sub-groups can be quite easily established. However, if morphological study is accompanied by other optical studies (e.g. bireflectance measurements), then a more accurate method of original rank determination will be achieved (see later in this Chapter).

Moving now to the softening vitrinites which develop mosaic textures, it appears at first glimpse that an estimation of rank of these vitrinites will be difficult, but in fact, by measuring the size of the mosaic units and also the types of mosaic texture, a satisfactory parameter can be established. This method of original rank estimation has been considered previously (see Goldring 1973; Patrick *et al.* 1973), but it chiefly deals with the size of mosaic units and not with the mosaic textures. It is known that the size of mosaic units increases with rank and is related to increase in plasticity and decrease in oxygen content (see for example Patrick et al. 1973; Goldring 1973). In the present study, at the rate of 1°C/min, the caking vitrinite develops partial fine-grained mosaic units, which show weak optical extinction (and a low level of bireflectance), whereas medium-rank, coking coal vitrinite, which also develops a fine-grained mosaic texture, but has a greater intensity of anisotropy than caking vitrinite, exhibits a more regular extinction pattern. Further, the residues of caking and medium-rank coking vitrinites develop a coherent residue. The high-rank, coking coal vitrinite, which develops a fine to coarse-grained mosaic texture (and a higher level of bireflectance), shows particles that are not fused to one another and does not develop vacuoles.

Thus, in a mixture of the above six vitrinites, the non-softening vitrinites should be easily recognised and indexed. The softening vitrinites can also be easily indexed according to their general morphology and the mosaic sizes and mosaic, e.g. the caking vitrinite by its partial fine-grained mosaic, but a low level of common orientation within the mosaic structure, the medium rank, coking coal by a completely converted, fine-grained mosaic texture and a high level of common orientation (high level of bireflectance), the high-rank coking coal by subangular but fine to coarse-grained mosaic texture, with no vesicles and highly orientated mosaic units (higher level of bireflectance). There is also interaction between the vitrinites of different rank levels in a mixture during carbonisation (see for example Alpern 1956), which results in a transition of mosaic size from one softening vitrinite to another, but still these transformations are gradual and it is possible to recognise different rank levels by the size of mosaic structure (this will be discussed later in detail).

By increasing the rate of heating to 10°C/min, the softening vitrinites become increasingly similar, whereas the non-softening vitrinites greatly differ, but once again using the mosaic size type and texture and the level of common orientation of the mosaic units, differentiation within the softening group is possible. However, with further increase of the heating rate to 60°C/min, the differentiation of softening vitrinites becomes difficult, because of similarities in morphology, e.g. size and type of mosaic, common orientation, etc.

(iii) Development of Mesophase (Plates 47 to 49)

One of the interesting morphological features of the coking coal vitrinites is the formation of a spherical mesophase (see for example Taylor 1961; Brooks and Taylor 1965). Plate 47a shows the formation of a few isotropic spherical bodies at about 450°C at a rate of 10°C in low-rank coking coal. It was impossible to show the anisotropic spherical mesophase in the present studies, because the growth and conversion of mesophase to a mosaic structure probably takes place between approximately 450° and 460°C. In the present work an interval of 50°C was used over the temperature range between 400° and 500°C and further investigation, using a very much smaller temperature interval would be required to demonstrate the development of a mesophase in British coals. However, at about 500°C, the spherical bodies are still present (Plates 47b, 48 and 49), and show many features of a coalesced mesophase, such as poles and attachment of smaller spherical bodies to the larger bodies (Plate 46). However, individual spheres develop a fine-grained mosaic texture (Plates 45–47). Plate 47 shows spherical bodies displaying pleochroism extinction. It is rather interesting that only at a rate of 10°C/min do the spherical bodies appear. Probably the rate of 1°C/min is too slow and plasticity too much reduced, while the rate of 60°C/min would be too fast and/or the mesophase starts to develop at a higher temperature than 450°C (465° or 475°C perhaps), due to enhanced plasticity.

(iv) Types of nuclei in nucleated domains (Plates 50 to 54)

Nucleated domains (see Hartshorne and Stuart 1970) are present at the relatively fast heating rates (10°C and 60°C/min). They are present in residues of caking coal vitrinite carbonised at the fastest rate of heating (Plate 50) and low-rank coking coal vitrinite develops various types of 'nucleated domains'. The 'node-type' extinction (Plate 51a) surrounded by strong anisotropy indicates a high degree of structural reordering in this area, and is caused by deformation of the mesophase due to the degasification and the formation of gas bubbles (see White et al. 1967). A helical arrangement of coalesced mesophase is also evident in Plate 51c in the residue from low-rank coking coal carbonised at 60°C/min. While nucleated domains are present in the residues of high-rank coking coal carbonised at 10°C/min, it is the residues from carbonisations at 60°C/min which exhibit various types of nuclei in nucleated domains (Plates 52 to 54), probably because of the greater fluidity enhanced by the fast rate of heating and also because of the relatively low oxygen content of this vitrinite (see for example Kipling _et al._ 1964; 1966; White _et al._ 1967; Sanada _et al_ 1973 and Patrick _et al._ 1973). Plate 53a shows the 'Y-type node' (delta shape) (White _et al._ 1967; Honda _et al._ 1971) or half-nucleus 'turning' type (Hartshorne and Stuart 1970) with a three-fold symmetry, where the layer planes are perpendicular to one another. An 'O-type' domain, showing a circular arrangement of lamellar planes is illustrated in Plate 53c (see Honda _et al._ 1971); note the development of large and long fibrous textures (see White _et al._ 1967). Plate 54a shows the 'U-type' node (see Honda _et al_ 1971) Plates 53b and 54b show the development of large anisotropic domains, which are reported by Marsh (1973) for high-temperature coke (about 1800°C) from a coking coal. It is interesting to observe that such structures develop at low temperatures in semi-cokes at the fast rate of heating, again probably because of the high level of plasticity.(see Brown 1956; van Krevelen _et al._ 1956). It is also interesting that the nucleated domains are only present at 10°C/min and 60°C/min, because it appears that increase in plasticity and the length of time which the residues remain in the plastic state result in the formation of a large anisotropic mesophase at the expense of the isotropic medium, whereas at 1°C/min, because of the lower plasticity and the shorter length of time when the vitrinite remains plastic, little or no nucleation takes place.

In summary it appears that increase in plasticity due to rise of heating rate facilitates the development of a larger mesophase and results in the formation of 'nucleated domains' which are more evident the higher is the original level of plasticity of the vitrinite and the increased plasticity brought about by fast heating. Only the high-rank, coking coal vitrinite at the fast rate of heating frequently exhibits areas of 'nucleated domains'; these are not so common in the residues of caking coal vitrinite at the same heating rates.

(v) Cell Structure (Plates 55 to 58)

The only vitrinite of the six which exhibits botanical-cell structure on carbonisation is that from the high-rank coking coal (Plates 55 to 58). The cell structure remains practically unchanged, but the vitrinite is converted to a fine to medium-grained mosaic texture, which indicates that the particles become plastic, because vitrinite only develops a mosaic texture when it softens (see for example Sanada *et al.* 1973 and Patrick *et al.* 1973). The fresh vitrinite did not exhibit such distinct cellular structure, but on carbonisation, perhaps due to depolymerisation and because of differences in the structure and composition of the cell walls and the material forming the modified cell contents, the cell walls react differently to the contents. The cell contents behave as a softening carbon or vice versa. Then, the shape of the cell structure remains intact, but a granular mosaic structure develops within the cell. Increase of heating rate results in deformation and loss of the original cell structure, particularly at temperatures above the resolidification point (Plates 56d, 57b and d, 58b), indicating that the particles showing cell structure are not inert or semi-inert. However, it appears that there are variations within these particles and where one particle shows cellular structure and softens, another (Plates 58a and b) will keep its original cellular shape and does not alter.

According to Benedict et al. (1968), coking coal vitrinite showing remains of cellular structure behaves as semi-inert material on carbonisation, i.e. it does not develop a mosaic texture and the particles keep their original angular shape. The retention of cellular structure indicates resistance of these materials to homogenisation due to alteration at an early stage in their history and the original cell structure resists reaction on carbonisation. The present work indicates that cellular structures in coking coal vitrinite are not necessarily semi-inert, because they may develop mosaic structure. Goodarzi (1971) also demonstrated that coking coal vitrinite displaying such structure when fresh, could lose this structure on carbonisation.

B. VARIATION OF OPTICAL PROPERTIES OF SINGLE VITRINITES IN RELATION TO THREE RATES OF HEATING.

A number of points emerge from the results obtained by the carbonisation of the six vitrinites at the three different heating rates. As stated earlier, the vitrinites of different rank levels in the present studies can be divided into two groups, a softening and a non-softening group. The discussion will follow this grouping.

(i) Reflectivity (a and b Figs 40 to 51)

(a) General

The reflectivity of all six vitrinites carbonised at the different rates of heating increases with the carbonisation temperature, which agrees with the results of Mackowsky (1961); Davis (1965); Ghosh (1968); de Vries *et al.* (1968); Marshall and Murchison (1971) and Goodarzi and Murchison (1972). However, the reflectivity curves of all six vitrinites of different rank exhibit patterns which show that the faster is the rate of heating, the higher is the reflectivity at any particular temperature. This observation is contrary to the results of Ghosh (1968) (Fig37)., who shows that the reflectivity is higher, the lower is the rate of heating. There are differences between the experimental conditions of the two studies, although in both investigations, the relation between the reflectivity of different ranks of vitrinite and rates of heating were studied. The range of heating rate employed by Ghosh (1968) was very restricted (1°C, 3°C and 5°C/min), whereas in the present work the range of heating rates is much wider

(1°C, 10°C and 60°C/min). It would, therefore, be reasonable to assume that any molecular changes that occur on carbonisation will be better illustrated by the present study. What is also surprising is that the reflectivity differences observed by Ghosh are much greater at temperatures around 500°C than noted in the present work with a wider range of heating rates and less at higher temperatures.

Although no other systematic study of the variation of optical properties of vitrinites with heating rate has been attempted, support for the present findings is also given by Brown and Taylor (1961). They suggested the possibility of a fast rate of heating to explain the development of an unusually high reflectivity in a naturally metamorphosed Antarctic coal. Also, the results of Cook <u>et al.</u> (1972) quoting a vitrinite (carbon = 93.8% daf) which exhibits a reflectivity level that would be associated with much higher carbon content (about 96.5% daf) are explained by a fast rate of heating.

Why should reflectivity be the higher the faster is the rate of heating? It is accepted that the reflectivity of carbonised vitrinites is a function of the concentration of aromatic structures (Davis 1965; de Vries <u>et al.</u> 1968 and Goodarzi and Murchison 1972). De Vries <u>et al.</u> (1968) states that the gradual increase of reflectivity of vitrinite during carbonisation is due to gradual degasification of volatile groupings in the vitrinite and the results of van Krevelen <u>et al.</u> (1956) and Brown (1956) show that the rate of degasification is higher the faster is the rate of heating. It can then be assumed that at a fast rate of heating, due to rapid degasification, a higher concentration of aromatic carbon will result and so the reflectivity should be higher. The findings of Dulhunty and Harrison (1953); van Krevelen et.al. (1956) and Brown (1956) indicate that plasticity rises as the rate of heating increases. Taylor (1961) observed, although only qualitatively, that the reflectivity of plastic vitrinite increases steadily throughout the plastic stage and Goodarzi and Murchison (1972) demonstrated that reflectivity increases sharply during primary carbonisation. Since plasticity increases with rate of heating, then because of enhanced plasticity, the reflectivity at fast rates of heating should be higher than at slow rates of heating, when the plasticity is greatly reduced.

Because of the similarity between the reflectivity curves and absorptive index curves of the carbonised residues of vitrinite and since the absorptive index is believed to be related to the number of mobile electrons, which increases with the size and degree of condensation of the aromatic molecules in vitrinite (McCartney and Teichmüller 1972), then the reflectivity curves of the carbonised vitrinites can also be assumed in large part to be an indication of crystallite diameter (L_a). Thus, the increase of reflectivity with carbonisation temperature is probably also a function of increase in the size of aromatic layers.

With increase of the heating rate and the consequent extension of plasticity, the mobility of the aromatic lamellae is also enhanced. Rapid degasification probably leaves the aromatic layers free to coalesce and to produce larger aromatic structures; at slow rates of heating, due to suppression of the plastic stage, the aromatic lamellae are not able to coalesce to produce such large aromatic layers.

Finally, the reflectivity curves for medium and high-rank vitrinites at the different rates of heating are more distinctive and well separated than those for either anthracitic or low-rank bituminous vitrinites. This is probably due to the rate of degasification and the condensation of aromatic structures, which are higher in medium and high-rank bituminous vitrinites than in low-rank bituminous or anthracitic vitrinites.

(b) Non-softening (Figs a and b 40, 46)

1. Low-rank bituminous vitrinites

The behaviour of the reflectivity-temperature curves indicates that the influence of rate of heating on the molecular structure of the carbonised residues is very small up to the third stage of the carbonisation process (Berkowitz 1967). After 700°C, however, the reflectivity-temperature curves follow different paths with the reflectivity curve for the fastest rate of heating being highest and the curve for the slowest rate of heating being at the base. The difference increases with rising temperature and is probably due to the higher level of aromaticity and the development of larger aromatic layers as the heating rate increases.

2. Anthracitic vitrinites (Figs a and b 41,42,47,48)

The behaviour of the reflectivity curves of the anthracitic vitrinites is similar to that for the low-rank vitrinite (Fig 46). However, in Figs 47 and 48 the scale has had to be enlarged to show the small differences that exist between the reflectivity curves at different heating rates; these curves would otherwise be very close, but the difference between them becomes evident at about the temperature when molecular rearrangement in the solid state (approximately 650°C) occurs. The small differences between the curves indicate the rate of degasification is very low at this rank level (van Krevelen et al. 1956 and Brown 1956), but still it appears that thermal treatment at a fast rate of heating is sufficient to promote a higher degree of condensation of aromatic structures than slower rates of heating in anthracites.

(b) Softening Vitrinites (Figs a and b 43 to 45, 49 to 51)

The differences between the reflectivity curves at different rates of heating of the softening vitrinites becomes distinct by about 500°C, which is the onset of resolidification (Goodarzi and Murchison 1972) and is considerably lower than the temperature of differentiation of the non-softening vitrinites (about 700°C) which occurs in the temperature range where molecular rearrangements in the solid occur (Goodarzi and Murchison 1972). According to Brown (1956) the maximum degasification temperature in coking coal is at about 500°C, so it appears that the differentiation of the reflectivity curves in softening vitrinites begins before the time of maximum decomposition. The higher level of reflectivity with rising heating rate is again probably due to the greater rate of degasification of amorphous material and/or concentration of the aromatic structures, as well as to the coalescence into larger aromatic layers (Diamond 1960). The reflectivity-temperature curves of the high-rank coking vitrinite at the slower rates of heating (10°C and 1°C/min) are not as well differentiated as in the caking and low-rank coking coal vitrinites (Figs b49 to 51), but still, it is evident that the aromaticity at any temperature is lower (apparent from the reflectivity curves), the slower is the rate of heating (Fig 51).

(ii) Bireflectance

(a) General

Bireflectance for all six vitrinites at the different rates of heating increases with rising carbonisation temperature. This general observation is also supported by several investigations viz., Davis (1965); Ghosh (1968); de Vries *et al.* (1968); Marshall and Murchison (1971) and Goodarzi and Murchison (1972). In contrast, however, to the results of the present study, Ghosh states that bireflectance decreases as the rate of heating rises. The present work shows the bireflectance curves for the different ranks of carbonised vitrinite increasing with temperature and showing this increase to be the sharper the faster is the rate of heating. Brown and Taylor (1961) recognise that the bireflectance of a metamorphosed coal is an expression of its degree of graphitisation and also Marshall and Murchison (1971) and Goodarzi and Murchison (1972) relate the increase in the level of bireflectance with increasing temperature of carbonisation to improvement in the degree of ordering of the structural units. Support for an increase of bireflectance with rise of heating rate comes from Taylor (1957) and other studies. Abramski and Mackowsky (1951) and Taylor (1961) state that the faster is the rate of heating, the better will be the ordering of the molecular structure. Thus the bireflectance will rise in these circumstances with increase in the rate of heating. Brown and Taylor (1961) also relate the unusually strong bireflectance of a metamorphosed anthracitic coal to the possibility of a fast rate of heating in the crust, due to intrusions. Further, Cook et al. (1972) recognise a high level of bireflectance of a vitrinite with a carbon content of approximately that of anthracitic vitrinite, but a bireflectance of a much higher level. This strong anisotropy was attributed to rapid heating.

(b) Non-softening vitrinites (Figs 52 to 54)

The behaviour of the bireflectance curves suggests that relatively little change in molecular ordering of these vitrinites takes place with rise of temperature when compared with the changes in softening vitrinites. However, the changes in ordering of the structure is still substantial. The bireflectance curves of this group of vitrinites do not show the reduction in their initial level of bireflectance in the plastic stage (between 400° and 500°C) because they are non-softening.

1. Low-rank bituminous vitrinite (Fig. 52)

The bireflectance curves of this vitrinite at different rates of heating indicate only relatively slight but distinct improvement in the ordering of the aromatic units takes place, probably because of the original randomly orientated and strongly cross-linked aromatic lamellae. But the increase of molecular ordering is still higher the faster is the rate of heating (Figs 52a and b). The rise of bireflectance begins at about 500°C, which is in agreement with the findings of Goodarzi and Murchison (1972) for low-rank bituminous vitrinite. However, Goodarzi and Murchison (1972) demonstrated a rapid increase of bireflectance for a low-rank bituminous vitrinite (carbon = 82.5% daf) after carbonisation beyond about 800°C; in the present study this rapid increase in the bireflectance of a low-rank bituminous vitrinite was not observed, but this vitrinite is, however, substantially lower in rank (carbon = 80.0% daf) and would not soften to the same extent.

2. Anthracitic vitrinites (Figs 53, 54)

The behaviour of the bireflectance curves of the anthracitic vitrinites show that these vitrinites have an initial strongly preferred orientation. Relatively little improvement in the ordering of the molecular structure takes place up to 600°C at the different rates of heating (see Goodarzi and Murchison 1972). The sequential trends of the curves with the curve of the fast rate of heating above and the curve for the slow rate of heating at the base probably indicates that further ordering of the aromatic structure is in general more rapid the faster is the rate of heating. The form of all the curves is similar to that shown by Goodarzi and Murchison (1972) for variation of bireflectance with temperature of anthracite (2.45°C/min).

(c) Softening Vitrinites (Figs 55 to 57)

This group of vitrinites shows a much greater degree of sensitivity in the behaviour of their bireflectances with the different rates of heating. The bireflectance curves of this group show a decrease in bireflectance between 400° and 500°C (plastic stage), as was demonstrated by the results of Goodarzi and Murchison (1972) for bituminous-rank vitrinites, but since the temperature interval in the present study is not as small as in the earlier investigation, it is not surprising that the bireflectance curves of a softening vitrinite at a particular level of heating rate does not exhibit the reduction in level of bireflectance curves.

1. Caking and low-rank coking vitrinites (Figs 55,56)

The trends of bireflectance of these vitrinites indicate that the reordering of the molecular structure is very rapid at the fastest rate of heating, almost certainly because of the increase of plasticity caused by the rapid heating (Brown 1956; van Krevelen et al. 1956), which results in better ordering of molecular structure (Abramski and Mackowsky 1951). The much lower rate of rise of the bireflectance curve for 10°C/min is due to the lower rate of reordering of the molecular units, because the plasticity of the vitrinite is decreased. At the slowest rate of heating, the bireflectance curves indicate relatively a much lower rate of ordering. The behaviour of the bireflectance curves of the caking coal vitrinite shows that it is possible to promote the coking ability of caking coal to the level of coking coal at lower heating rates. This conclusion is in accordance with the statement by Mackowsky and Wolfe (1966), who maintain that non-coking or weakly caking vitrinite can produce coke if a fast rate of heating is employed.

2. High-rank coking coal vitrinite (Fig 57).

The behaviour of the bireflectance curves for this vitrinite is not the same as for the other vitrinite in the softening group, because, even at 1°C/min the bireflectance curve maintains a high rate of rise and is due to this vitrinite being highly plastic. It seems that taking the results of the present study into account along with the earlier work of Goodarzi and Murchison (1972), the general increase in the rate of rise of bireflectance is directly related to how severe is the breakdown in the initial molecular ordering. The more plastic a vitrinite becomes, the more severe is the breakdown, but the high degree of ordering ensues, even at a slow rate of heating. The behaviour of the bireflectance again illustrates the basic structural difference between the two groups of vitrinites.

(iii) Refractive Index (cFigs 40 to 51)

(a) General

Goodarzi and Murchison (1972, 1973) have described the refractive index curves of carbonised vitrinites of different rank and have shown that no matter what is the original rank of vitrinite, the general form of the curves is the same, but that the curves vary in detail for graphitising and non-graphitising vitrinites. In general the variation in the refractive index-temperature curve can be attributed to the following molecular structural changes:-

<u>initial rise:</u> due to increase of the crystallite height (L_c), and improvement in the ordering and packing of the aromatic lamellae within the crystallites,

<u>subsequent fall:</u> due to deterioration in the packing and to buckling of the aromatic lamellae as the layer diameter (L_a) increases, which results in reduction of the crystallite height (L_c), and

<u>secondary rise:</u> due to further improvement of packing of aromatic lamellae within the crystallites and an increase in the crystallite height (L_c).

The refractive index-temperature curves of all the carbonised vitrinites in the present study, irrespective of the starting rank of the vitrinite and the heating rate, show the above general form, but the rate of increase in the refractive index, the particular temperature at which the maximum level of refractive index is achieved and the precise shape of refractive index-temperature curves, depends on the rate of heating and the rank of starting vitrinites.

The results of Franklin (1951) show that vitrinites which soften at low temperature provide graphitising carbons at high temperature, whereas non-softening vitrinites do not. The crystallite height is higher in graphitising vitrinites than non-graphitising vitrinite for a particular layer diameter (Fig 22 to 24).

Over the temperature range employed, the secondary increase of refractive index can only be observed if the heating rate is relatively fast. Marsh (1971), using a heating rate of about 5°C/min, showed a secondary increase of crystallite height (see also Diamond 1960), whereas at lower heating rates (about 0.5 - 2°C/min), this secondary increase of crystallite height was not observed. The earlier results of Goodarzi and Murchison (1972) do not show such an increase of refractive index, due again to the slow heating rate (about 2.4°C/min).

(b) Non-softening Vitrinites (cFigs 40 to 42; 46 to 48)

1. Low-rank Bituminous Vitrinites (cFigs 40; 46)

The refractive index curves at 1°C and 10°C/min behave as those for a non-graphitising vitrinite. The findings of Goodarzi and Murchison (1972) indicate that the refractive-index curves of non-graphitising vitrinites follow similar trends after achieving their maximum refractive-index level. The increase of heating rate to 60°C/min results in sharper peak for the refractive index curve, which is probably due to rapid devolatilisation of amorphous material and a rapid improvement in crystallite height. The sharp decrease of the refractive index between temperatures of 625°C to 800° or 850°C indicates a rapid deterioration of the packing of the aromatic layers and a decrease in the crystallite height. The form of the refractive index curve at 60°C/min is very similar to the curve for graphitising vitrinite reported by Goodarzi and Murchison (1972). It seems that the high heating rate indicates structural changes similar to those taking place in the carbonised graphitising vitrinite. All the refractive index curves after a decrease to 850°C begin to rise with further increase of temperature, due to improvement in the packing of the aromatic lamellae and increase of the crystallite height.

2. Anthracitic vitrinites (c Figs 41,42,47,48)

The patterns of the refractive index-temperature curves of anthracitic vitrinites are similar to the form of the refractive index curve for anthracitic vitrinite reported by Goodarzi and Murchison (1972). The present results show that in general the differences between the refractive index curves at various levels of heating rate are quite small, presumably because of the few changes of molecular structure caused by the heating. There is some lack of consistency in the pattern of the refractive index curves for the higher-rank anthracitic vitrinite (Fig 48c) compared with the lower-rank anthracitic vitrinite (Fig 47c). The reason for the anomalous results is not clear. However, the structural changes brought about by the fast rate of heating, although taking place more rapidly, are probably less than for slower heating rates.

(c) Softening vitrinites (c Figs 43 to 45, 49 to 51)

The shape of refractive index-temperature curves of the coking coal vitrinites at 1°C/min are similar to the form of the refractive index curves of the graphitising (coking coal) vitrinite (carbon = 88.0% daf) examined by Goodarzi and Murchison (1972), while the form of refractive index of the caking coal vitrinite at the slow rates of heating is also similar to the carbonised lower-rank vitrinite (carbon = 82.5% daf) examined by the same authors. Here, in this 'intermediate' carbon (85.4%daf) (Franklin 1951), the slow rate of heating causes a degree of modification of the molecular structure similar to that for non-graphitising vitrinite, which consists of aromatic lamellae strongly cross-linked to each other, whereas in coking coal vitrinite, the pattern of the refractive index indicates that also the general level of ordering within the aromatic structure is high, but that the cross-linking between the aromatic lamellae is also weak. This results in a rapid development and breakdown.

The form of the peaks and the temperature at which maximum occurs are most useful. The shape of the refractive index curves of softening vitrinites becomes increasingly similar with increase of heating rate of 10°C/min, although the pattern of the curves change. The more rapid increase of the temperature clearly results in a rapid devolatilisation of the vitrinite and a much sharper peak in the refractive index curves, due to a more rapid increase of crystallite height (L_c) and better packing of aromatic lamellae within the crystallites. This is followed by a more rapid breakdown of ordering within the molecular structure which is reflected by a sharp decrease in the level of the refractive index that is more pronounced in coking coal vitrinite than in the coking coal vitrinite. The refractive index curve only begins to rise again at about 850°C. The results of Diamond and Hirsch (1958) and Diamond (1960) indicates that the number of aromatic lamellae per crystallite increases after carbonisation to about 700°C due to improvement of packing of the aromatic lamellae and alignment of the aromatic lamellae parallel to one another (Fig 20). The secondary rise of the refractive index-temperature curves is satisfactorily in agreement with the above structural improvement.

Further increase in heating rate to 60°C/min produces the sharpest peak, which has its highest level at the lowest temperature, probably indicating even more rapid evaporation of amorphous material that forms the cross-links between the aromatic structures. The drastic fall of refractive index may be due to buckling of aromatic structures, as well as to deterioration in the packing of aromatic lamellae which is arrested at about 750°-800°C. The further marked rise of the refractive index curves with further increase of temperature is, again, probably due to improvement in the molecular structure. It is interesting that the breakdown of the molecular structure and its rebuilding is most pronounced for the fast heating rate. The similarity between the refractive index-temperature curve for caking coal vitrinite and those of coking coal vitrinites at the heating rates of 10° and 60°C/min suggests that the changes of molecular structure occurring during carbonisation for this vitrinite are similar to those in true softening vitrinites at high heating rates.

(iv) Absorptive Index (d Figs 40 to 51)

The behaviour of the absorptive index-temperature curves of the softening and non-softening vitrinites carbonised at different rates of heating can be attributed to the same causes suggested for the behaviour of the reflectivity-temperature curves, namely, an increase in aromatic layer diameter (L_a) with carbonisation temperature. The present results show that the aromatic layer diameter increases as the rate of heating rises. Not only is the phenomenon more pronounced for softening vitrinites than non-softening vitrinites, but in the softening vitrinites the increase in aromatic layer diameter is much more rapid as the rate of heating rises.

C. VARIATION OF THE OPTICAL PROPERTIES OF VITRINITES OF DIFFERENT RANK IN RELATION TO PARTICULAR RATES OF HEATING

(i) Introduction

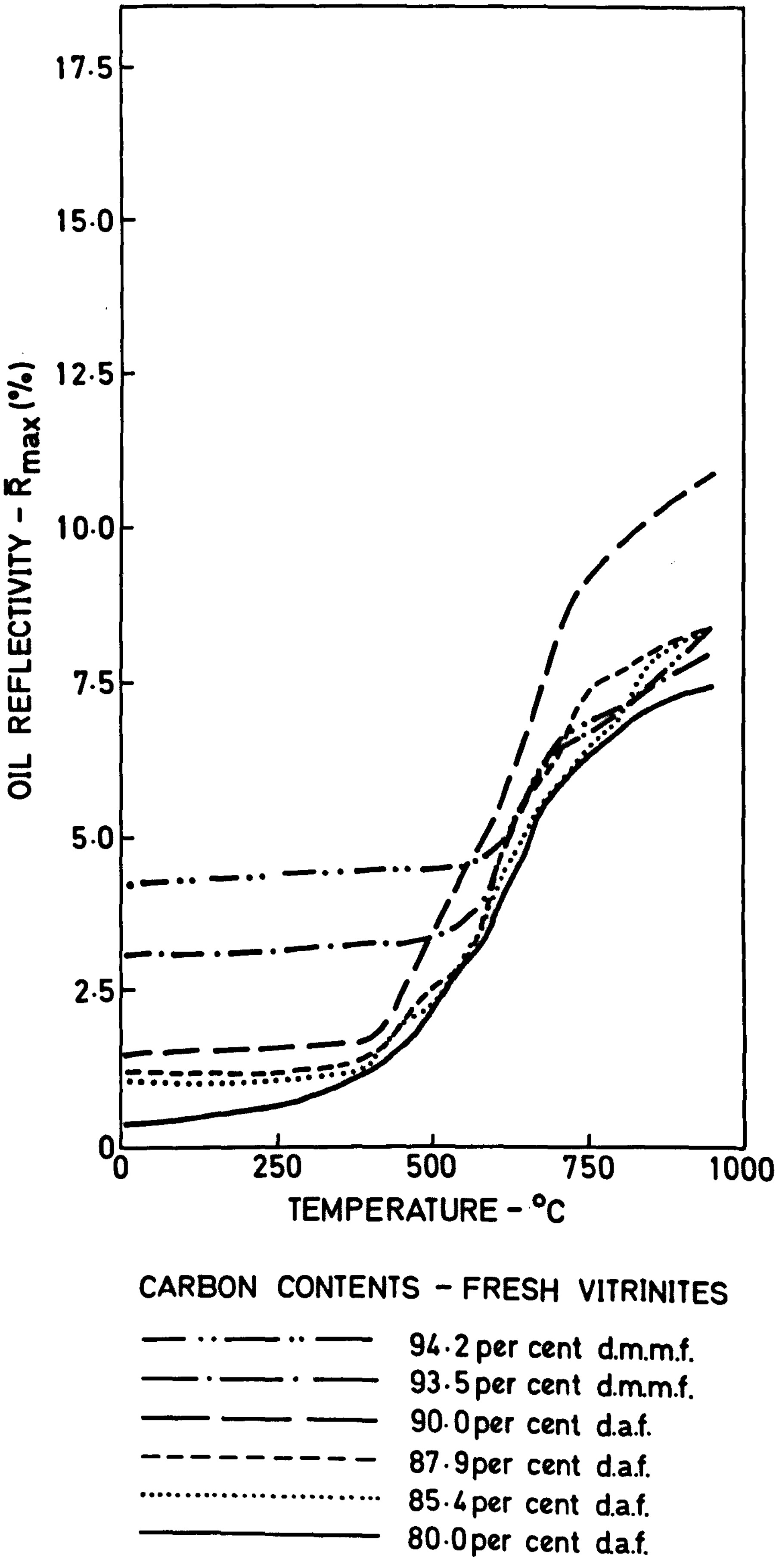
Having now compared the behaviour of the optical properties of individual vitrinites carbonised at three different heating rates, it is now useful to group the six curves for specific optical properties at each heating rate, to compare these. The grouped curves will be found in Figs 58 - 69.

(ii) Reflectivity (Figs 58 - 60)

(a) Rate of 1°C/min (Fig 58)

All vitrinites apart from the high-rank coking coal vitrinite eventually follow approximately similar and coincident paths at this rate of heating, suggesting that, due to slow degasification, similar levels of condensation of the aromatic structures at different levels occur. However, the curve for high-rank, coking coal vitrinite, crosscuts and reaches (after 700°C) a higher level of reflectivity than the remainder of the vitrinites of this group, probably due to development of larger aromatic layer structures. The behaviour of the reflectivity of the other five vitrinites is similar to that described by Goodarzi and Murchison (1972) for vitrinite of similar rank (Fig 13) during carbonisation up to about 950°C at a heating rate of about 2.5°C/min and includes low and high-rank bituminous vitrinites. The higher level of the reflectivity

Fig 58 Generalised curves for the variation with temperature of oil reflectivity of six vitrinites carbonised at a heating rate of 1°C/min.

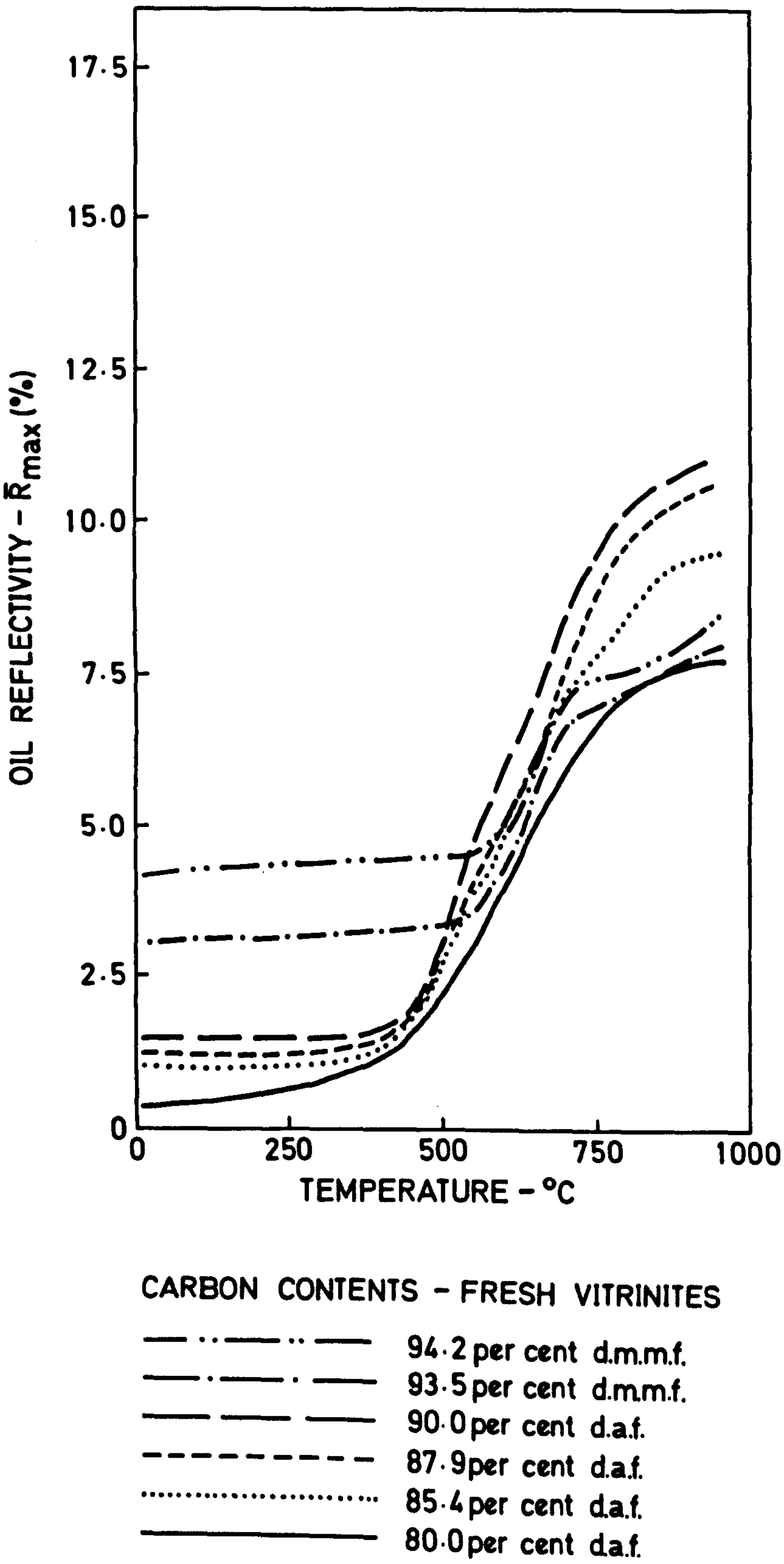

OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17·5
15·0
12·5
10·0
7·5
5·0
2·5
0
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

curves for the high-rank coking coal vitrinite at this rate of heating is in accord with the results of de Vries *et al.* (1968) (Fig 10) who indicate that the residues of carbonised high-rank, coking vitrinite exhibit higher reflectivity values than either carbonised low-rank or anthracitic vitrinites, and even most coking coal vitrinites.

(b) Rate of 10°C/min (Fig 59)

At this heating rate, the different vitrinite groups can begin to be distinguished in terms of their softening characteristics and by the behaviour of their reflectivity curves. The vitrinites can be divided into three groups (Fig 59), the first consisting of the two coking coal vitrinites, which eventually show the highest reflectivity values of their carbonised products, indicating a higher degree of aromaticity and aromatic layers of larger diameter. The second group includes only the caking coal vitrinite. The behaviour of the caking-coal vitrinite is interesting, because at this heating rate it maintains an intermediate trend between the truly softening and non-softening vitrinites (Fig 59), indicating the development of an intermediate moleculare structure in the carbonised products for this vitrinite. Franklin (1951), examining a caking coal vitrinite at graphitising temperatures, states that the vitrinite possesses molecular structure intermediate between graphitising and non-graphitising vitrinite. The present results tend to support the above findings for

Fig 59 Generalised curves for the variation with temperature of oil reflectivity of six vitrinites carbonised at a heating rate of 10°C/min.



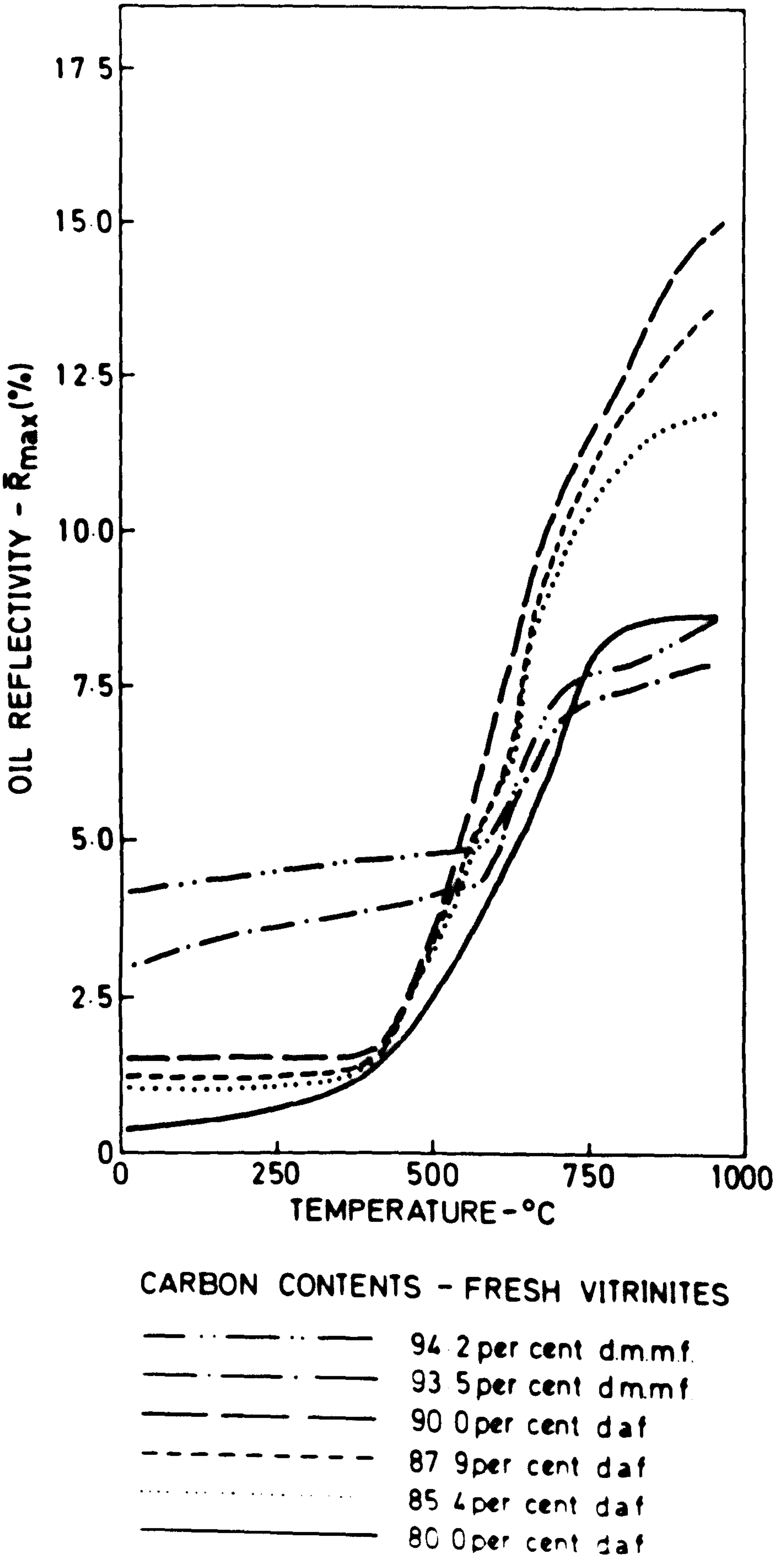
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
17·5
15·0
12·5
10·0
7·5
5·0
2·5
0
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

caking vitrinite when carbonised to much lower temperatures and also indicates the importance of rate of heating on the optical properties of vitrinites. The third group consists of the two anthracitic and the low-rank vitrinite, whose carbonised residues still follow a lower reflectivity path than either the coking or caking coal vitrinites. The rank sequence however is maintained in this group during carbonisation, which agrees with the results of de Vries et al. (1968), although only one rate of heating was used in these experiments.

(c) Rate of 60°C/min (Fig 60)

The vitrinites now fall into two groups on the basis of the behaviour of their reflectivity curves, the residues of the caking coal, medium-rank and high-rank coking vitrinites in one group following much higher trends, and the low-rank and two anthracitic vitrinites reaching lower levels. The caking coal vitrinite residues still yield substantially lower reflectivity level than do those from the coking coal vitrinites even at 950°C, but the vitrinite now truly softens on carbonisation and is able to develop aromatic lamellae of larger diameter and more condensed aromatic structures due to the rapid degasification. The higher level of the reflectivity curves of the softening vitrinites indicates the basic molecular-structural differences between this group and non-softening vitrinites. What is also interesting is the behaviour of the reflectivity curve for the residues from low-rank vitrinite, which now show a

Fig 60 Generalised curves for the variation with temperature of oil reflectivity of six vitrinites carbonised at a heating rate of 60°C/min.


17.5
15.0
12.5
10.0
7.5
5.0
2.5
0
OIL REFLECTIVITY - R̄max (%)
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94.2 per cent d.m.m.f.
93.5 per cent d.m.m.f.
90.0 per cent d.a.f.
87.9 per cent d.a.f.
85.4 per cent d.a.f.
80.0 per cent d.a.f.

reflectivity at leasts as high as that of anthracitic vitrinite at 950°C, which suggests that the condensation of aromatic material for this vitrinite is greater than for anthracitic vitrinite: de Vries (1968) also states that during carbonisation the rate of condensation of low-rank vitrinite is higher than for anthracitic vitrinite. Also the behaviour of the caking coal vitrinite in the first group needs some attention, since carbonisation at this rate of heating apparently promotes the molecular structure of caking coal vitrinite towards the general level of that of coking-rank vitrinite (apparent from the reflectivity curve). The influence of the original rank of the vitrinites in each group is still evident from the behaviour of their reflectivity curves, which follow an upward sequential trend with reflectivity of the highest-rank vitrinite on top and the lowest rank vitrinite at the base. In the second group there is a rank sequence between the anthracitic vitrinites, but the curve for the low-rank vitrinitic residues eventually lies above the anthracitic vitrinites.

In summary it is now possible to draw a relationship between the reflectivity curves of carbonised vitrinites and the rate of heating. At the slowest heating rate it is possible only to distinguish the true softening vitrinite. The differences between the reflectivities of carbonised vitrinites become more evident with increasing of heating rate. Groups of carbonised vitrinites can be distinguished by the level of their reflectivities which are related to their softening characters after carbonisation to about 650°C at 10°C/min heating rate; at a heating rate of 60°C/min the vitrinite groups can be recognised after the resolidification temperature (about 550°C).

(iii) Bireflectance (Figs 61 to 63)

To some extent the behaviour of the bireflectance curves at the different rates of heating parallel to those for reflectivity, but the curves for bireflectance are perhaps surprisingly more sensitive than the reflectivity curves.

(a) Rate of heating 1°C/min (Fig 61)

The bireflectance-temperature curves of five of the vitrinites show an upward sequential trend that is related to their initial ranks and to carbonisation temperature, but the curve for the carbonised high-rank coking vitrinite increases very sharply after the softening temperature (450°C) to reach a much higher level than the curves for the other carbonised residues. This behaviour indicates that highly fluid vitrinites display high bireflectance and thus show greater ordering of their molecular structures. The plasticity of the other vitrinites is much reduced due to the slow heating rate (Brown 1956, van Krevelen et al. 1956) but the rate is still sufficient to mobilise and reorder the molecular structure to some degree.

(b) Rate of heating 10°C/min (Fig 62)

The bireflectance curves of the residues of the two coking vitrinites at this rate of heating follow a rising and steeper trend than either the caking and/or non-softening group. The bireflectance curves for the carbonised non-softening vitrinites

Fig 61 Generalised curves for the variation with temperature of oil bireflectance of six vitrinites carbonised at a heating rate of 1°C/min.

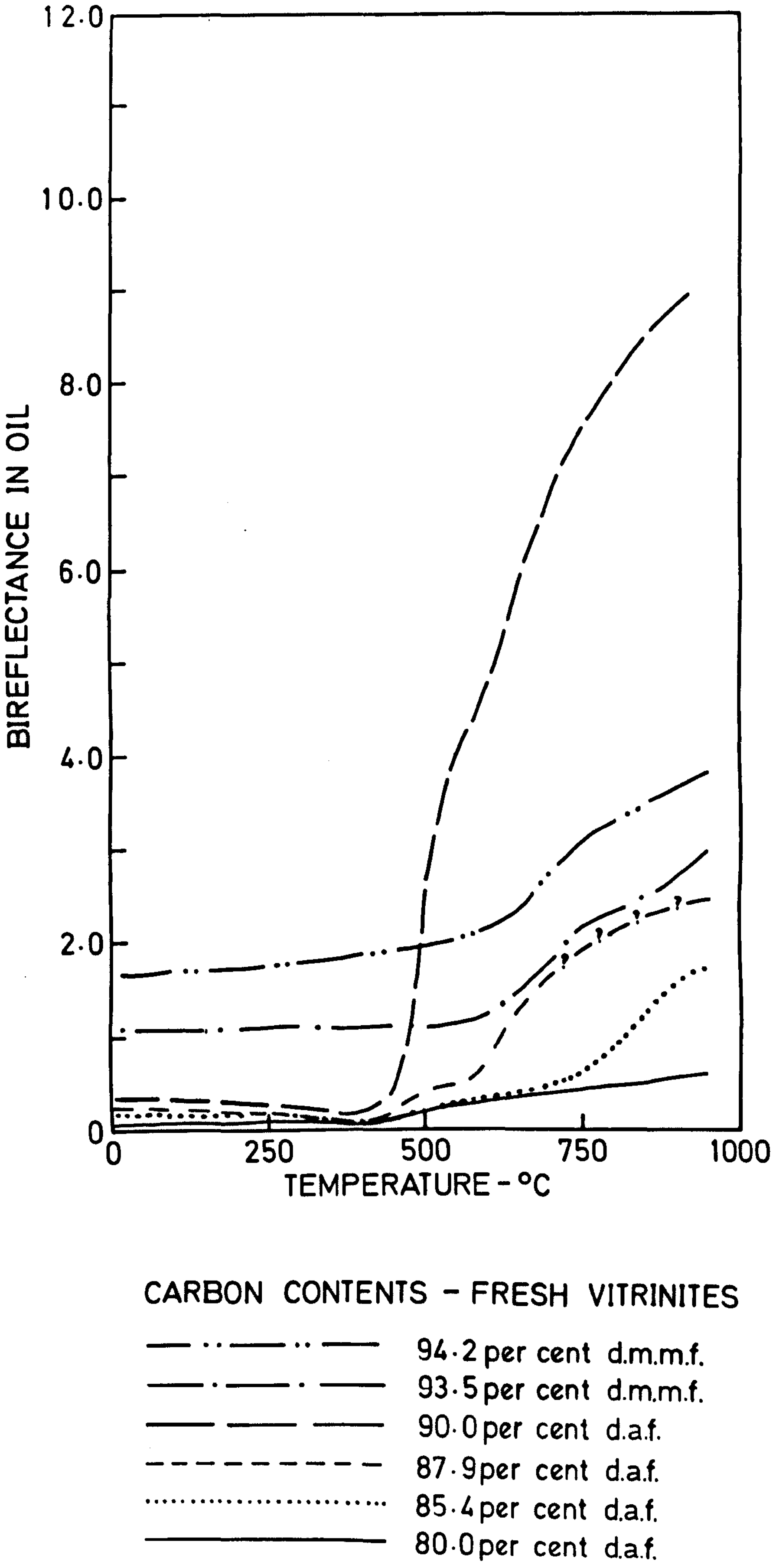
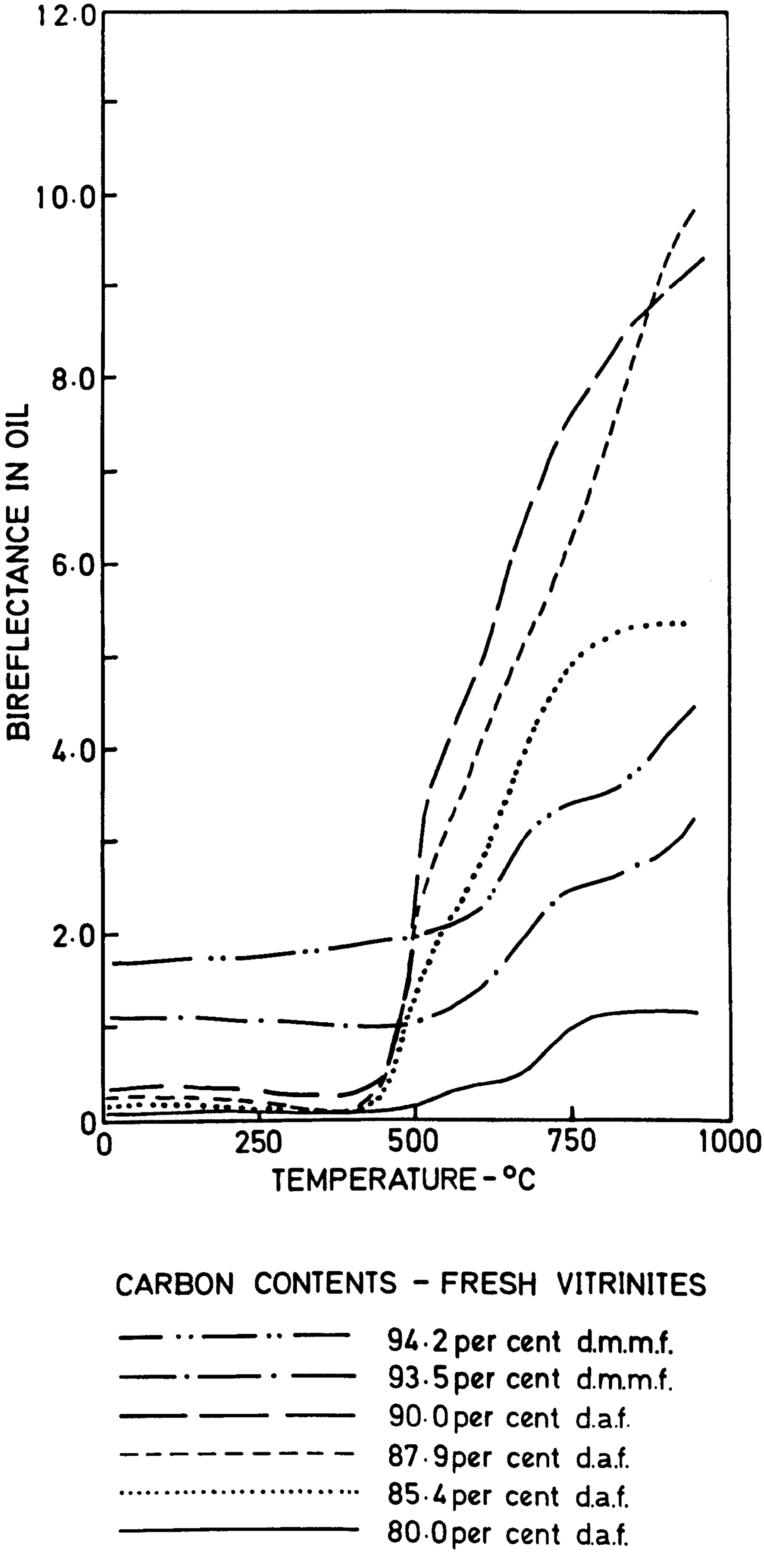

12.0
10.0
8.0
6.0
4.0
2.0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

Fig 62 Generalised curves for the variation with temperature of oil bireflectance of six vitrinites carbonised at a heating rate of 10°C/min.

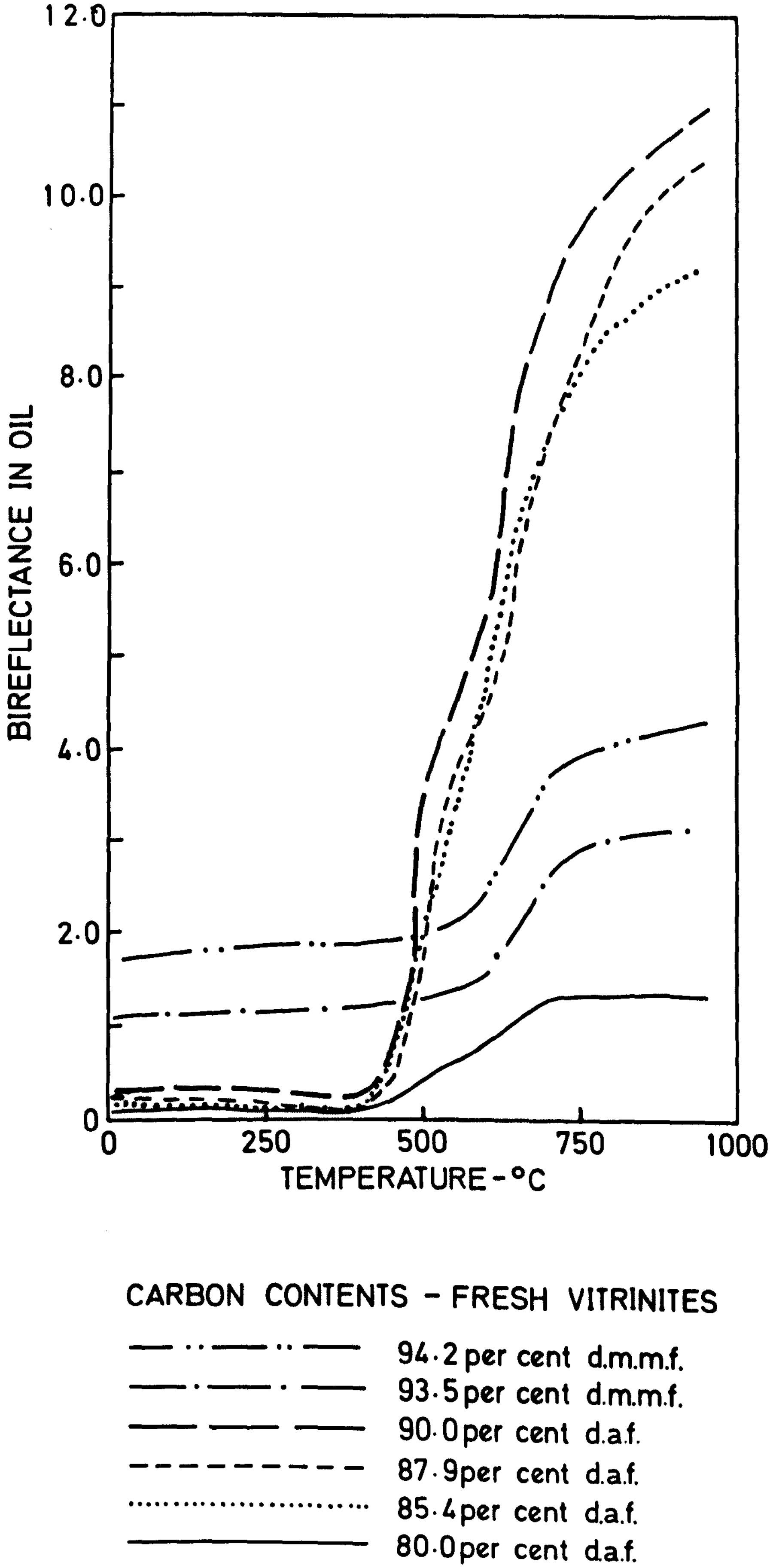

12.0
10.0
8.0
6.0
4.0
2.0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

show relatively little change to those produced at a heating rate of 1°C/min. The bireflectance curve for the caking coal vitrinite now shows an intermediate behaviour, maintaining a trend between the residues of the softening and non-softening vitrinites. This intermediate behaviour of the bireflectance curve of the caking coal vitrinite is again due to the 'intermediate'molecular structure of this vitrinite (Franklin 1951). The gradual separation or expansion of the bireflectance curves is a reflection of the greater degree of reordering possible because of the higher fluidities produced at higher heating rates (see for example van Krevelen _et al._ 1956 and Brown 1956).

(c) _Rate of heating 60°C/min (Fig 63)_

The bireflectance curves for the carbonised residues of the coking and caking vitrinites group together and follow a rising, very sharp and much higher trend than that for the non-softening vitrinites, the contrast now being the stronger because of the high fluidities induced in any vitrinites which softens at this high heating rate and so a high degree of ordering of the molecular structure in those vitrinites is now possible. It is clear from Fig 63 that even the plasticity of the caking coal vitrinite is greatly enhanced and a structural ordering similar to that of the coking coal vitrinite is achieved. But still the original structural differences within this group are maintained in relation to the rank sequence, where the bireflectance

Fig 63 Generalised curves for the variation with temperature of oil bireflectance of six vitrinites carbonised at a heating rate of 60°C/min.


12.0
10.0
8.0
6.0
4.0
2.0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94.2 per cent d.m.m.f.
93.5 per cent d.m.m.f.
90.0 per cent d.a.f.
87.9 per cent d.a.f.
85.4 per cent d.a.f.
80.0 per cent d.a.f.

curve of the carbonised high-rank coking vitrinite is above and the curve for the caking coal vitrinite is at the base. This sequence shows the relative degree of ordering of the aromatic structures of the vitrinites in this group. The bireflectance curves for the carbonised anthracitic and low-rank vitrinites again show relatively small changes, probably because any increase in the ordering of their molecular structures is relatively small due to immobility of the aromatic lamellae during the early stages of carbonisation (Franklin 1951). The influence of the rank of the original vitrinite is also again evident in the behaviour of the bireflectance curves of the non-softening group.

It is quite clear from a comparison of Figs 61 and 63 that the influence of heating rate on the trends of bireflectance of non-softening vitrinites is relatively small, the group not showing any great variation with heating rate, while the softening vitrinites display great changes in bireflectance with heating rate. It appears that there is a strong relationship between the degree of plasticity and bireflectance. While the plasticity of the six vitrinites was not determined directly, it is known that plasticity rises with increasing heating rate (Brown 1956 and van Krevelen _et al._ 1956), and the present results show that the level of the bireflectance curves of softening vitrinites rises with rate of heating. That the bireflectance should increase with increasing plasticity is not unreasonable, because the greater the plasticity the better can be the reordering of the original molecular structure and consequently the higher will be the bireflectance. High-rank coking vitrinite, due to its greater degree of plasticity at all times than that of other vitrinites examined in this study, exhibits higher bireflectance even at a low rate of heating. Modification to the rate of bireflectance with increasing heating rate through the softening bituminous-rank vitrinites is the greater the lower is the rank, e.g. the caking coal vitrinite has its bireflectance curve most modified by changing the heating rate.

The above results suggest that it might be possible to use bireflectance as a means of distinguishing between the different carbonised residues of vitrinites in a mixture. Commonly rates of 1° to $5^{\circ}C$ are used in commercial coke ovens and comparing Fig 61 and Fig 62, it is possible to see contrasts, broadly speaking, between true softening, intermediate and non-softening vitrinites. It may even be possible to subdivide each of the above groups according to the rank of the starting materials, because apparently at $1^{\circ}C$/min, only truly softening vitrinites can be distinguished, whereas at $10^{\circ}C$/min, softening, intermediate and non-softening groups are present. Thus if bireflectance is used in combination with the morphology of the carbonised residues, a better estimation of the rank of the original carbonised residues may be achieved.

(iv) Refractive Index (Figs 64 - 66)

(a) Introduction

The refractive index curves for the six vitrinites carbonised at each of three heating rates are shown in Figs 64 - 66. Because of the confusion of the curves around their maxima, interpretation may apparently be rather difficult, but in fact resolution is quite possible, and reasonable interpretations can be put forward for the patterns.

In the earlier work published by Goodarzi and Murchison (1972), in discussion of changes in refractive index in relation to carbonisation temperature and molecular structure, emphasis was laid on the relative heights of the peaks in the refractive index curves for graphitising and non-graphitising vitrinites (see previous work, P. 50). The more detailed results produced in the present project suggest that this earlier interpretation is probably too simple a view and that it is also important to consider not only the relative heights of the peaks, but also the shape of the curves as well. A further factor, in the graphitising vitrinites particularly, is the original rank levels (which of course governs the initial ordering of molecular structure) of the vitrinites. And so, it seems that the refractive index curve of a graphitising vitrinite (Fig 13), after an initial sharp rise to a maximum, falls at a much faster rate than does a curve for a non-graphitising vitrinite, which, after an initial increase that is the sharper the lower is the rank of the vitrinite, decreases at a slower rate, producing a much broader peak.

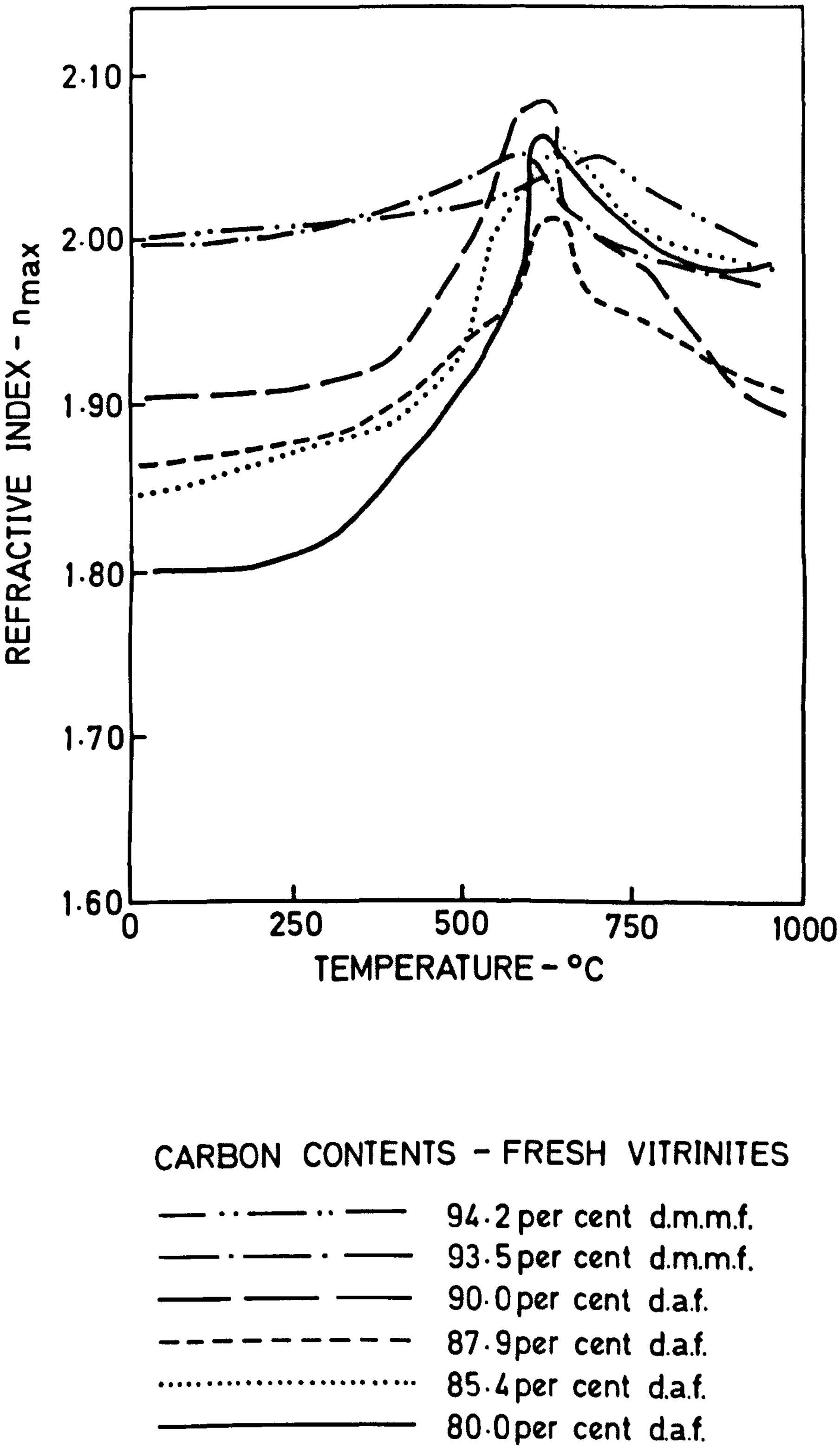
The sharp maximum of the refractive index-temperature curve of a graphitising vitrinite is probably due to the more rapid development and subsequent breakdown of the molecular structure of this form of vitrinite. The mobility of weakly cross-linked aromatic lamellae within the crystallites allow them to align and enlarge themselves parallel to one another in a vertical or a lateral sense more easily. The broad maximum peak of the refractive index-temperature curve of non-graphitising vitrinites suggest that the development of the molecular structure and the subsequent breakdown is relatively slow due to the strongly cross-linked aromatic lamellae within the crystallites. Because of this rigid cross-linking, the aromatic lamellae are relatively less mobile than in graphitising vitrinites, so the vertical or lateral development of crystallites here is slower and requires a higher level of thermal energy to destroy the cross-linking (see for example Franklin 1951). Rather similar curve forms can be seen in the variation of crystallite height (L_c) with temperature (Diamond 1960) (Fig 20).

The point about the curves, namely the variation with rank within the graphitising vitrinites, can be seen easily in the description below on vitrinites heated at 1°C/min.

(b) Rate of heating 1°C/min (Fig 64)

The form of the refractive index-temperature curves for

Fig 64 Generalised curves for the variation with temperature of refractive index of six vitrinites carbonised at a heating rate of 1°C/min.

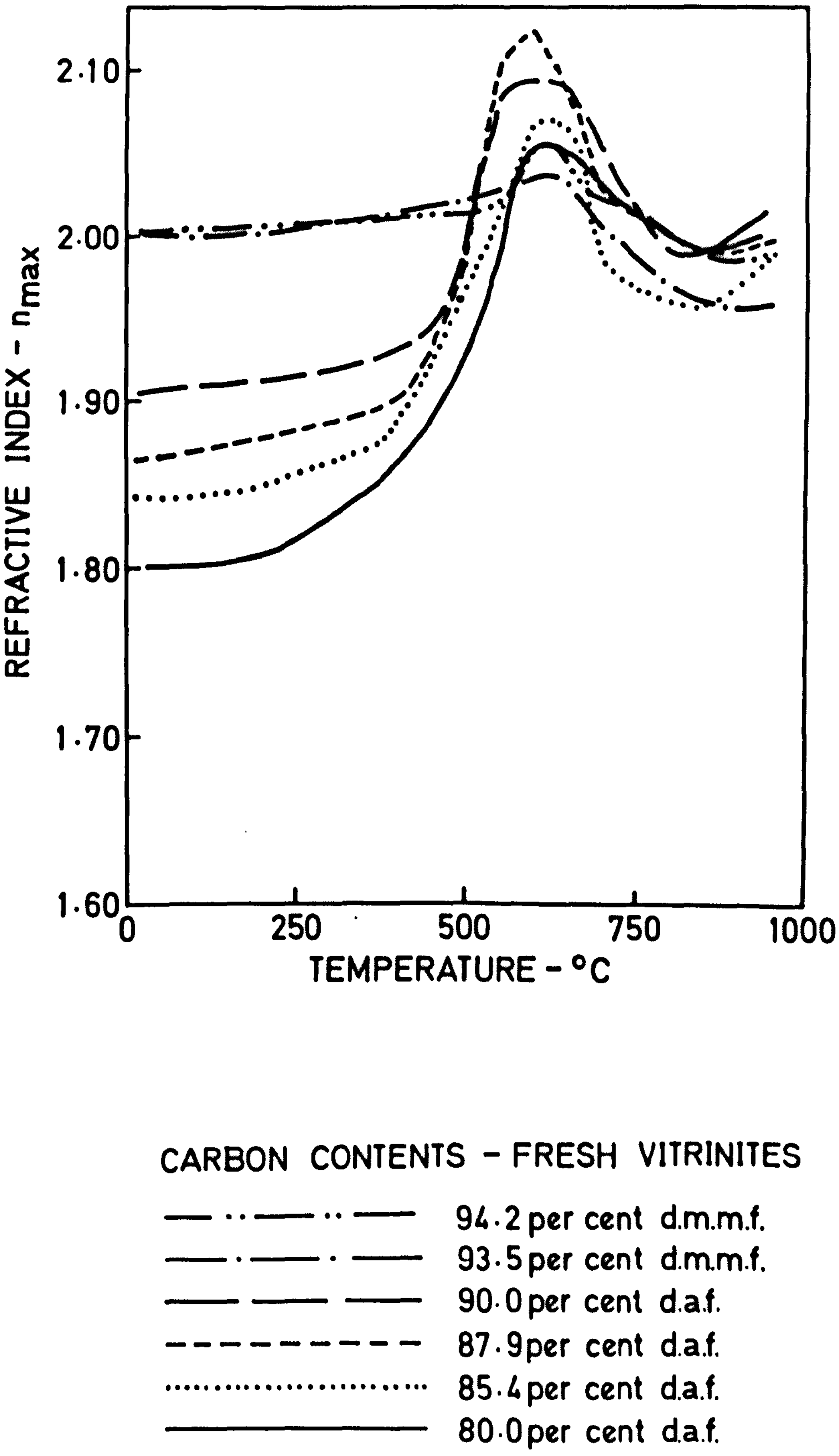

REFRACTIVE INDEX - n_{max}
2·10
2·00
1·90
1·80
1·70
1·60
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

the residues of the two coking coal vitrinites is similar, being sharp and showing much less broad peaks than the curves for the low-rank, caking and the two anthracitic vitrinites; the curves for the non-softening vitrinites are similar to those for non-graphitising vitrinites (see Goodarzi and Murchison 1972). It should be noted at this point that in the earlier work by Goodarzi and Murchison a heating rate of 2.45°C/min was employed, whereas the rate here is lower, so that an immediate direct comparison is not possible. Despite the fact that plasticity must be much reduced at 1°C/min, the contrast between the refractive index curves for non-softening and softening vitrinites is still quite visible. What is also apparent from the data here, is that the level of the refractive index peak for graphitising carbonised vitrinites is not always lower than that for non-graphitising as suggested by Goodarzi and Murchison (1972). The level of the refractive index peak is apparently also dependant on the original ordering of the molecular structure of the graphitising vitrinite which improves with increasing rank.(see for example Hirsch 1954, McCartney and Teichmüller 1972). It can then be expected that, during carbonisation, the initial development and subsequent breakdown of molecular structure be greater for high-rank coking (softening) than for low-rank coking vitrinite. The higher level of the refractive index maximum for residues of high-rank coking coal vitrinite than for any of the non-graphitising vitrinites may also be due to the development of a greater crystallite height (L_c). The mobility of the aromatic layers combined with better original ordering of the aromatic lamellae within the crystallites and the lower level of amorphous material could result in the development of a greater level of crystallite height (L_c). Franklin (1951) shows that graphitising carbons develop a greater level of (L_c) than do non-graphitising carbons.

(c) Rate of heating 10°C/min (Fig 65)

The form of the refractive index-temperature curves of the softening vitrinites are now more similar to one another, but they still differ from the curves of non-softening vitrinites. It must, of course, be noted that with the increase of the heating rate to 10°C/min, instead of 1°C/min, that the plasticity of all the vitrinites, and particularly the caking coal vitrinite, will be considerably enhanced. The bituminous-rank vitrinites (caking and coking vitrinites), which soften on heating, produce an initially higher refractive index maximum than the non-softening (non-graphitising) vitrinites and they also begin to exhibit a secondary increase in their refractive index curves at approximately 800° to 850°C. This secondary increase will be due to a further improvement of the packing of the aromatic lamellae and development of crystallite height after the earlier breakdown (Diamond 1960). The caking coal vitrinite, which behaved as a non-softening vitrinite at 1°C/min, now exhibits a similar refractive index behaviour to the true coking vitrinites at this rate of heating, and the maximum crystallite height developed (apparent from the refractive index curve) has an intermediate level between that for the softening and non-softening vitrinites.

Fig 65 Generalised curves for the variation with temperature of refractive index of six vitrinites carbonised at a heating rate of 10°C/min.



REFRACTIVE INDEX - n_{max}
2·10
2·00
1·90
1·80
1·70
1·60
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

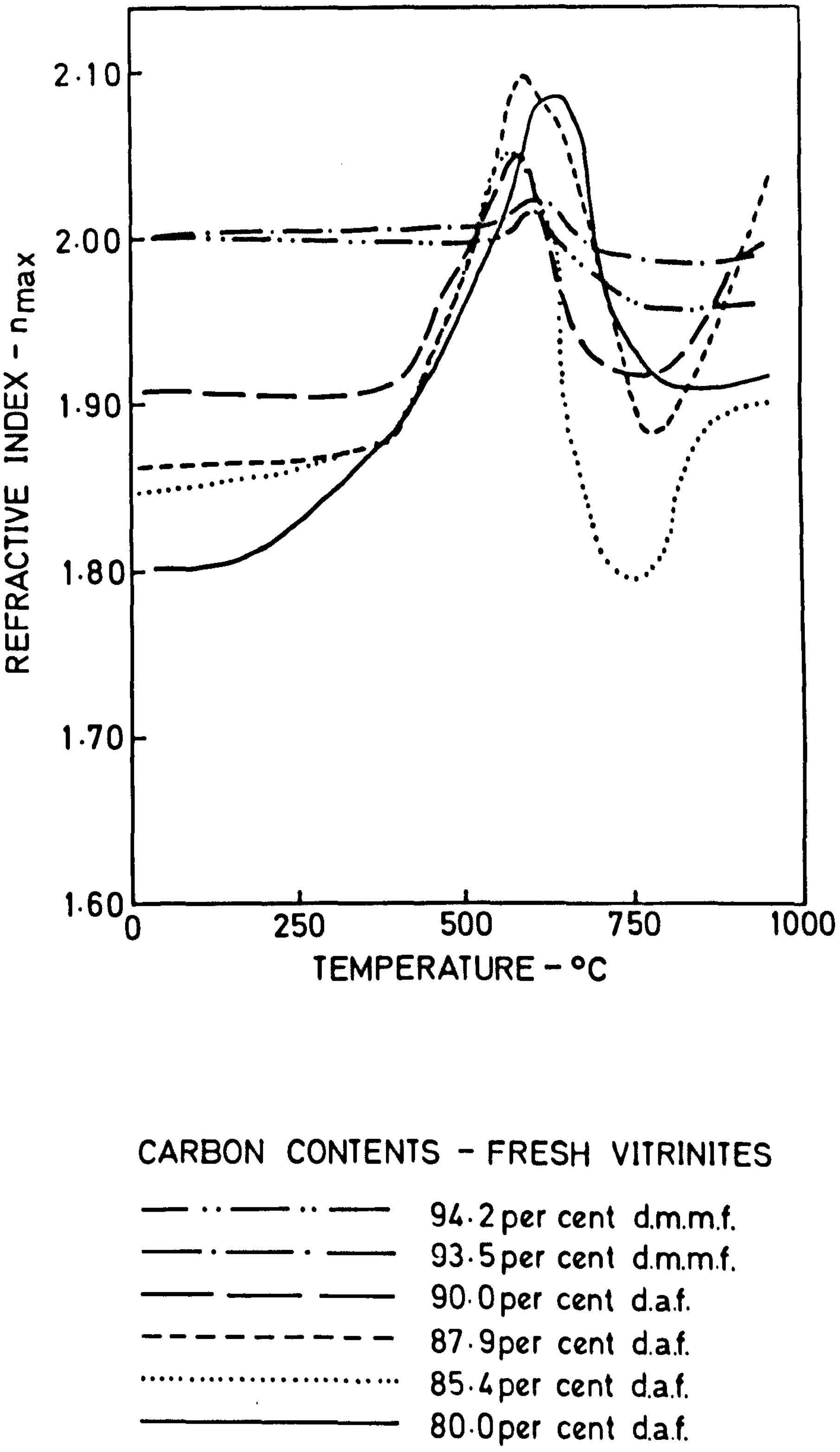
The results of Marsh (1971) show the crystallite height of a carbonised caking coal at slow rates of heating (5°C/min), after an initial increase, decreasing with further rise of temperature. The decrease of crystallite height is, however, arrested at about 700°C, at the fastest heating rate (5°C/min) employed and once more the crystallite height begins again to rise. The refractive indices of the low-rank vitrinite and two anthracitic vitrinites still behave as non-graphitising vitrinites (see Goodarzi and Murchison 1972).

(d) Rate of heating 60°C/min (Fig 66)

The softening vitrinites now display markedly contrasting curves to the non-softening group, showing sharp maxima and also pronounced minima. Even the low-rank vitrinite is affected at this high heating rate and it actually now displays a high level of refractive index with a much sharper peak. All these softening vitrinites exhibit high levels of refractive index, indicating that these vitrinites undergo greater modification within their molecular structures over this temperature range than do the anthracitic vitrinites. The greater input of thermal energy, combined with typical bituminous molecular structure (Hirsch 1954 and Cartz and Hirsch 1960) enables these vitrinites temporarily to achieve greater crystallite heights than the non-softening vitrinites.

The secondary increase of refractive index beyond

Fig 66 Generalised curves for the variation with temperature of refractive index of six vitrinites carbonised at a heating rate of 60°C/min.


REFRACTIVE INDEX - n_{max}
2·10
2·00
1·90
1·80
1·70
1·60
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94·2 per cent d.m.m.f.
93·5 per cent d.m.m.f.
90·0 per cent d.a.f.
87·9 per cent d.a.f.
85·4 per cent d.a.f.
80·0 per cent d.a.f.

approximately 800°C can only be observed in the truly softening vitrinites, not in the low-rank vitrinites.

The increase again indicates that the packing of the aromatic lamellae is improving and that the crystallite height has begun to increase once more. The non-graphitising vitrinites do not show this secondary increase in crystallite height, at least up to 1000°C.

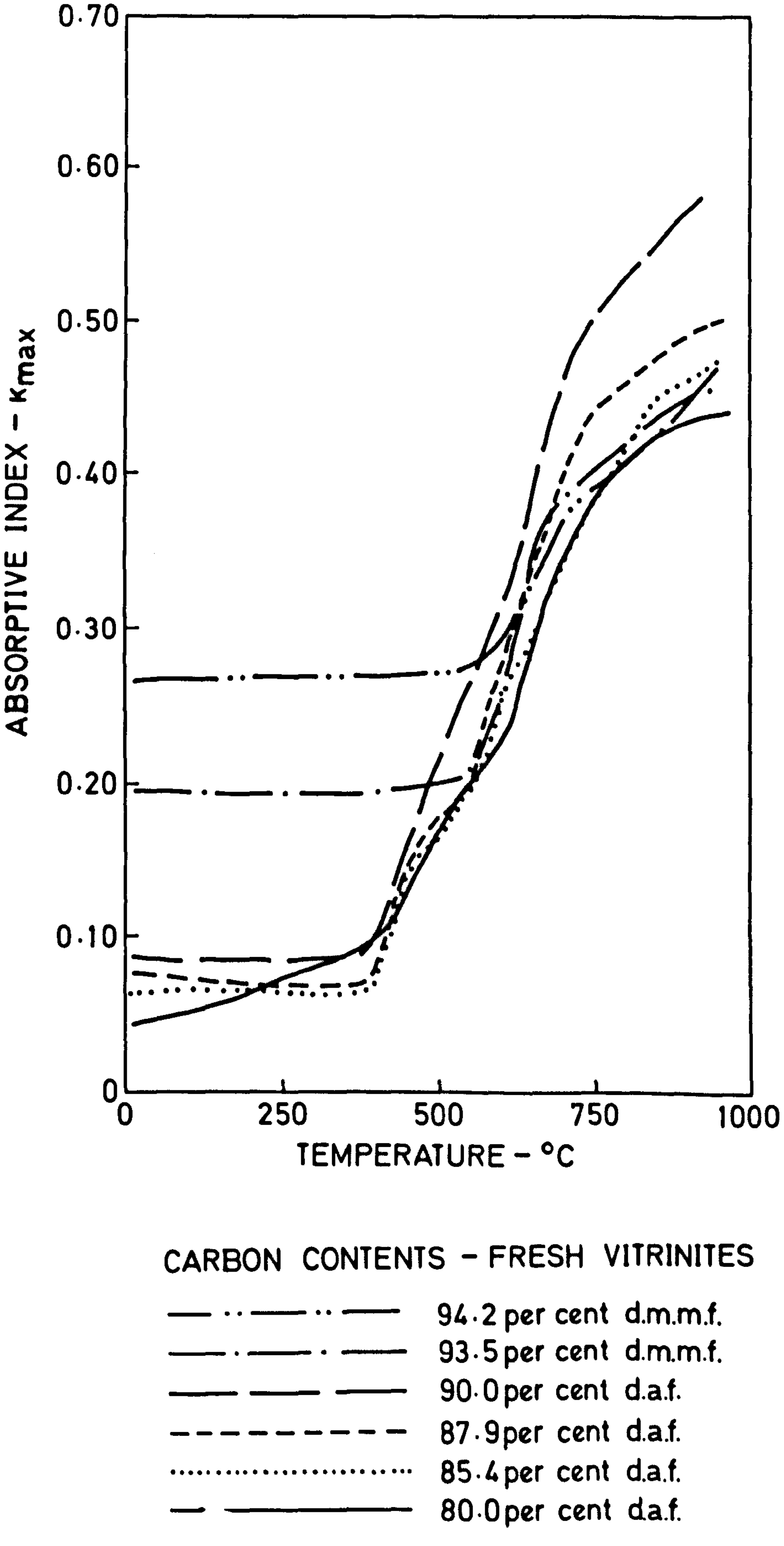
(v) Absorptive Index (Figs 67 - 69)

The curves for each heating rate show parallel changes to those of the reflectivity-temperature curves, but the differences between the graphitising and non-graphitising vitrinites are perhaps surprisingly in general better defined than in the reflectivity-temperature curves for each heating rate. All the variations with heating rate are discussed without any subdivision.

It appears that the softening vitrinites develop larger aromatic-layer diameters (apparent by the high level of the absorptive index curve) at any temperature than do the non-softening vitrinites. The differences between the molecular structures of the two groups become more evident with increase in the heating rate.

Moving from the lowest to the highest rate of heating the behaviour of the coking coal and low-rank bituminous vitrinites is most interesting. The residues of the caking coal vitrinite show the greatest level of shift of the absorptive index curve from the non-graphitising to the graphitising group and seemingly the rapid rise in thermal energy provided by the increased heating rate facilitates lateral growth of the crystallites. Lateral growth of the crystallite layers in non-softening vitrinites is limited at low heating rates due to the strong cross-linking between the aromatic layers, whereas in the softening vitrinites the cross-linking is not sufficiently strong and so the increased

Fig 67 Generalised curves for the variation with temperature of absorptive index of six vitrinites carbonised at a heating rate of 1°C/min.


ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94.2 per cent d.m.m.f.
93.5 per cent d.m.m.f.
90.0 per cent d.a.f.
87.9 per cent d.a.f.
85.4 per cent d.a.f.
80.0 per cent d.a.f.

thermal energy combined with rapid evaporation of cross-linked material leaves the aromatic lamellae free to coalesce and to develop an 'intermediate' molecular structure. The present results show that, at the fastest rate of heating, the 'intermediate' molecular structure of caking coal is shifted so that a molecular structure similar to that of a graphitising carbon is formed.

The other large although gradual shift in the absorptive index curve is shown by the carbonised low-rank vitrinite in the non-softening group, which, at high temperature, shows a gradual shift from the lowest value in the group at the slowest rate of heating to the highest level in the group at the fastest rate of heating. This behaviour probably indicates that this vitrinite of the non-graphitising group is partially able to overcome the restricting factors, such as strong cross-linking and also the disordered aromatic layers, to develop larger aromatic lamellae at fast rates of heating.

Fig 68 Generalised curves for the variation with temperature of absorptive index of six vitrinites carbonised at a heating rate of 10°C/min.

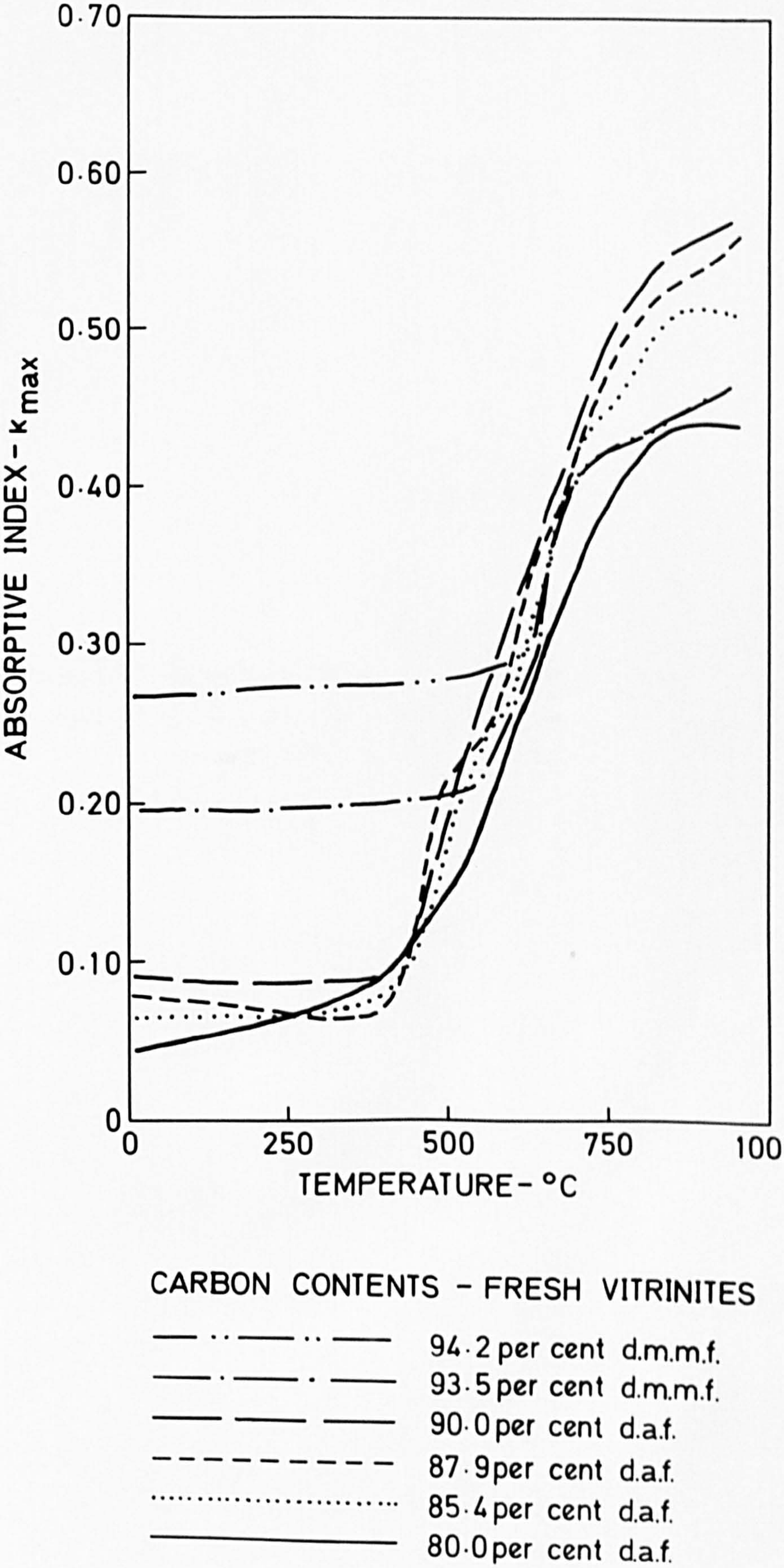
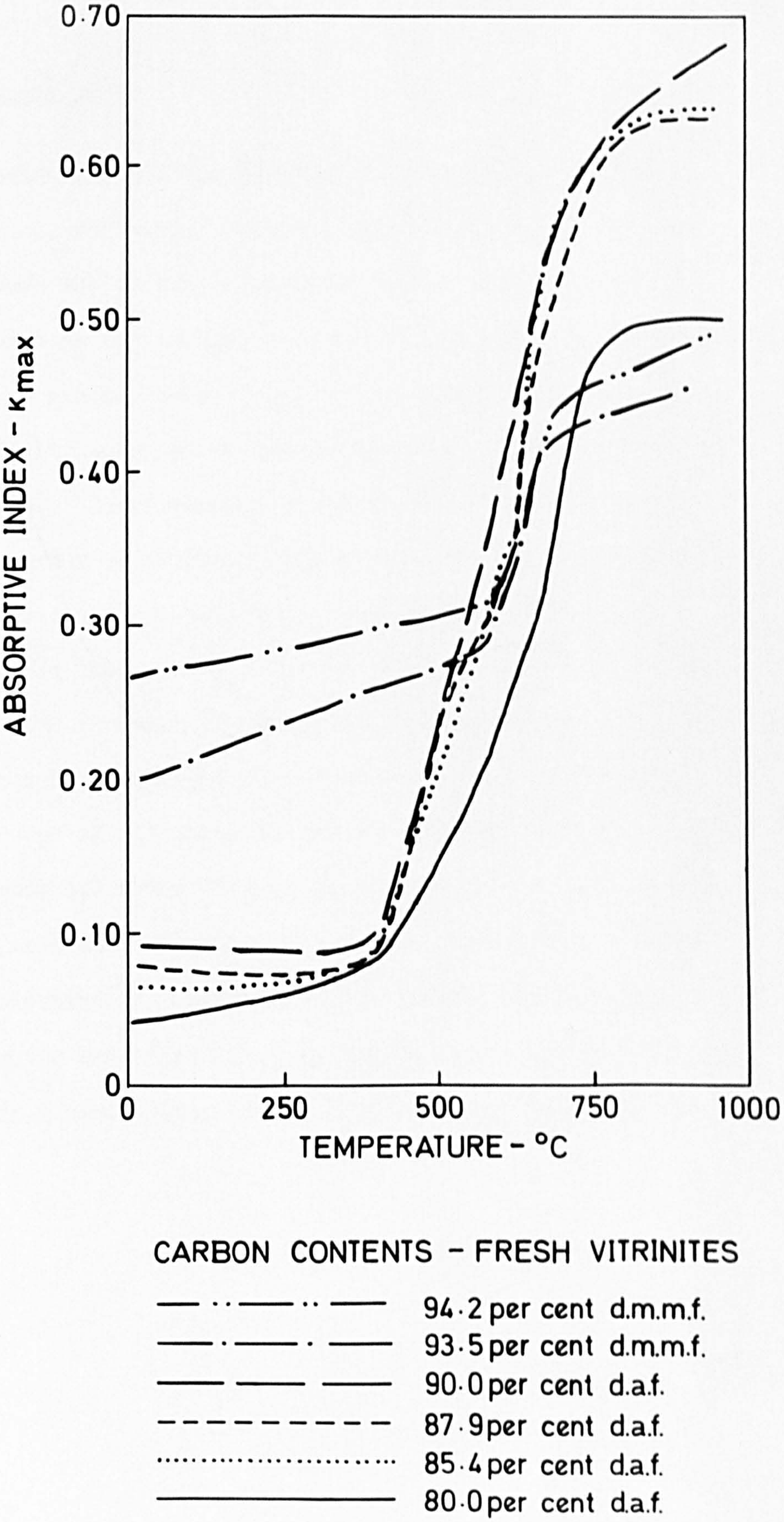

ABSORPTIVE INDEX - κ_{max}
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94.2 per cent d.m.m.f.
93.5 per cent d.m.m.f.
90.0 per cent d.a.f.
87.9 per cent d.a.f.
85.4 per cent d.a.f.
80.0 per cent d.a.f.

Fig 69 Generalised curves for the variation with temperature of absorptive index of six vitrinites carbonised at a heating rate of 60°C/min.


0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
ABSORPTIVE INDEX - κ_{max}
0
250
500
750
1000
TEMPERATURE - °C
CARBON CONTENTS - FRESH VITRINITES
94.2 per cent d.m.m.f.
93.5 per cent d.m.m.f.
90.0 per cent d.a.f.
87.9 per cent d.a.f.
85.4 per cent d.a.f.
80.0 per cent d.a.f.

(vi) Summary

Considering all the above parameters, reflectivity, bireflectance, refractive and absorptive indices, it appears that although the precision and accuracy of determination of bireflectance is not as high as that of reflectivity, bireflectance shows a greater sensitivity to the original rank of the carbonised vitrinite and to the heating rate than does the reflectivity. Bireflectance particularly appears to be a better indicator of original rank at slow heating rates, where reflectivity is not so sensitive (compare Figs 58 and 61). The refractive index curve also indicates changes in molecular structure with increase in carbonisation temperature. First, it distinguishes the basic molecular structural differences between groups of vitrinite and second, the differences between the softening and non-softening vitrinites can be seen in the trends of refractive index curves for the carbonised products. The determination of a refractive index curve is, however, rather time-consuming and tiresome work, whereas the bireflectance can be determined more easily at any rank level in less time.

5. Conclusion

The following conclusions can be drawn from the foregoing studies:-

A. Morphological

(i) Softening vitrinites are the only vitrinites which develop different types of mosaic texture during carbonisation. The faster is the rate of heating, the larger are the granular mosaic units developed.

(ii) Low-rank vitrinites develop completely rounded cenospheres like semi-coke at fast rates of heating, whereas at slow rates of heating the vitrinite particles retain their original angular form.

(iii) Caking-coal vitrinite, which at a fast rate of heating develops mosaic structures with different textures, only develops a partial finely-grained mosaic at slow rates of heating.

(iv) Anthracitic vitrinites show the least morphological changes with heating rate.

(v) It is possible to identify carbonised residues of various rank level for specific heating rates by morphological studies; the faster is the heating rate the easier is the differentiation between softening and non-softening vitrinites and within the non-softening group, but the more difficult it becomes within the softening group.

(vi) The extent of 'nucleated domains' depends on the level of plasticity and is the greater the higher is the rank of the softening vitrinite and the faster is the heating rate.

B. <u>Optical</u>

(i) Graphitising (softening) vitrinites are more sensitive to heating rate than are non-graphitising (non-softening) vitrinites.

(ii) The reflectivity, bireflectance and absorptive index curves of carbonised vitrinites are the higher the faster is the rate of heating.

(iii) Differences in reflectivity, bireflectance and absorptive index curves between and within softening vitrinites and non-softening vitrinites increase as the rate of heating rises.

(iv) The refractive index curves of softening vitrinites exhibit different trends to those of non-softening vitrinites, irrespective of the level of heating rates. The peak shape (for softening vitrinites) and the rank level (for all vitrinites) are important in distinguishing between vitrinites.

(v) The form of the refractive index curves of softening vitrinites at fast rates of heating is different to that at slow rates of heating; there is a secondary increase which is due to further increase of crystallite height.

(vi) The optical properties of carbonised caking-coal vitrinite indicate how important is the influence of the plasticity on the optical properties of this vitrinite. The faster is the rate of heating, the greater is the plasticity and thus the better is the ordering of the molecular structure and the more similar the molecular structure becomes to that of truly softening vitrinite.

(vii) High-rank, coking-coal vitrinite, even at low rates of heating, exhibits a higher level of reflectivity and bireflectance than do anthracitic vitrinites after carbonisation.

(viii) The lower is the rank in each group of vitrinites the greater are the overall optical changes.