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

VOLUME II

TEXT

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Thesis submitted for the Degree of
Doctor of Philosophy
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MARCH 1975

PART IV THE EFFECT OF DIFFERENT HEATING PERIODS BELOW DECOMPOSITION TEMPERATURE ON THE OPTICAL PROPERTIES OF VITRINITE

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A. General Introduction

The influence of the length of time during which heating is maintained at a constant temperature is here referred to as 'holding time'. In this Chapter, the effect of holding time on the optical properties of vitrinites (carbon = 77.0, 82.0, 85.4, 87.9 and 90.0% daf and 94.2 dmmf) will be considered and compared with the natural maturation of coal. The levels of temperature used in previous investigations, which considered the effect of holding time, were usually higher than the temperature levels influencing coals during coalification in the crust, i.e. temperatures were higher than 200°C which, according to Cook *et al.* (1972), is the maximum level of temperature for the production of anthracite during regional coalification. However, the length of holding time used in previous investigations was considerably shorter than the periods employed in the present project. In most geological processes, coal is heated for periods of time which are outside of the lifespan of man. Such considerable lengths of time, even with very low temperatures, may contribute effectively to the improvement and development of coal structure. It should be clear that the influence of holding time is only noticeable when other factors such as temperature are involved. When coal is carbonised in the laboratory, the period of the experiments is normally limited to short periods, so by increasing the temperature, a similar level of 'carbonisation' to the natural maturation of coal may be obtained, although the products may not be precisely the same.

One of the temperature levels used in the present project (350°C) is just below the temperature of 'active decomposition' of coal (Berkowitz 1967), which starts at about 400°C and the other (150°C) is closer to normal coalification temperatures suggested for bituminous coal (about 80° to 140°C - Teichmüller and Teichmüller 1967) and anthracite formation (approximately 200°C - Cook *et al.* 1972).

B. Previous related studies

1. Introduction

The influence of holding time on the natural coalification process and on the laboratory carbonisation of coal has been studied by Dulhunty (1954); van Krevelen *et al.* (195^{6}); M.Teichmüller and R.Teichmüller (1967, 1968). Dulhunty (1954) considered the effect of time on the metamorphism of the coal and concluded that time alone does not play an important role, but in combination with other factors (such as temperature and pressure) its role is vital. M.Teichmüller and R. Teichmüller (1967) support Dulhunty's opinion, giving an example of a certain Russian coal of Lower Carboniferous age in the Moscow Basin, which, at the present time, is still a hard brown coal, because this area was never exposed to the minimum temperature necessary for the formation of bituminous coal. In contrast, however, some of the German coals of Lower Carboniferous were in later Mesozoic and Cenozoic times buried at depths of 2000 to 4000 metres for a period of about

100 million years. These coals were converted to low-volatile bituminous coals (V.M. = 10 to 20%).

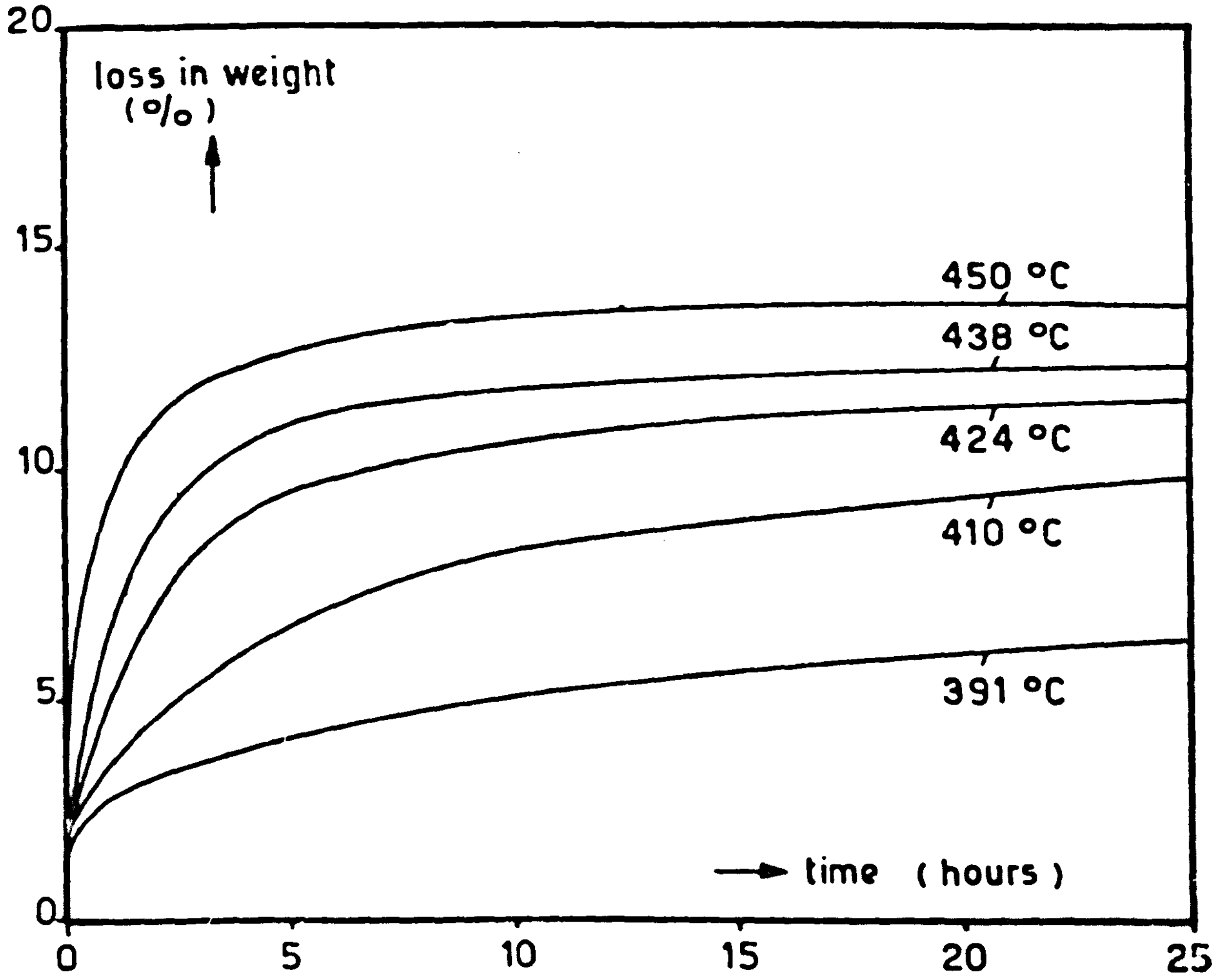
M. Teichmüller and R. Teichmüller (1968) have also considered in detail the effect of time on the coalification process and concluded that if the temperature is high enough, then the length of time to which coal is subjected to increased temperature will have an influence and the rank of coal will be higher the longer the temperature acts. For example, a particular Carboniferous coal in the Ruhr, subsided gradually to a depth of 5100 metres; the temperature at the present day is almost 147°C at that depth. Coaly inclusions of Upper Miocene age (16 ± 3 million years) on the Gulf Coast of Louisiana at a depth of 5440 metres have been heated to approximately 141°C. The German coal has been heated for about 270 million years at almost the same temperature as the American Miocene coal and has reached the level of low-volatile coking coal (V.M. = 16%), whereas the American coal has only reached the stage of high-volatile bituminous coal with 37% V.M. The only parameter which varied in this case was the time of heating which was much longer for the German coal, assuming of course a constant crustal temperature over the period.

Van Krevelen _et al._ (1956) also recognises the influence of holding time on the rate of decomposition of bituminous coals carbonised at different temperatures. On heating at a constant temperature, the rate of decomposition passes through a maximum which is dependent on the temperature. The rate of devolatilisation, after reaching its peak, shows a regular decrease with increasing length of time. A medium-volatile (23.3%) bituminous coal did not reach the peak of decomposition on heating to 391°C, even after 25 hours, whereas at 450°C it reached its maximum after about a 5 hour 'soak period'. (Fig 70).

These studies show that coal heated to a particular temperature, after attaining maximum decomposition at a particular temperature level, develops a certain level of molecular structure; further lengthening of the time will tend to improve the molecular structure to an even more advanced molecular structure until the equilibrium is reached.

2. Morphology

The morphology of the carbonised residues of carbonaceous materials such as coking coal and coal-tar pitch etc. prepared at low temperatures is again dependent upon the length of holding time. The appearance and growth of the spherical mesophase at low temperatures is also a function of holding time, as is the development of different types of mosaic structures in coke. Taylor (1961) anticipates the possibility of the formation of large spherical bodies in thermally metamorphosed vitrinites with prolonged heating at low temperatures. Honda *et al.* (1970); Whittaker and Grindstaff (1972) and Sanada *et al.* (1973) show that the appearance, growth and nucleation of spherical mesophase in



20
15
10
5
0
loss in weight (%)
450 °C
438 °C
424 °C
410 °C
391 °C
time (hours)
0
5
10
15
20
25

carbonaceous materials, such as coal-tar pitch, is dependent upon the length of time and takes place progressively; the isotropic liquid phase finally disappears completely with a sufficiently long holding time.

Sugimura et al. (1969) and Sanada et al. (1973) show that the amount of the anisotropic fraction of coking coal (carbon = 89.8% daf) carbonised at 400°C increases with length of time up to 4 hours and that the percentage of the anisotropic texture varies with the time (Fig 71). Considering the above investigation, it is possible to anticipate the formation of mosaic structures at temperatures lower than that required to produce the plastic stage, e.g. around 400°C during carbonisation under atmospheric pressure.

3. Optical Properties - Reflectivity

The reflectivity of vitrinites carbonised for different lengths of time have been measured by Mackowsky (1961); Ghosh (1968) and de Vries et al. (1968). Most of these studies have been carried out on vitrinites carbonised above the decomposition point.

Mackowsky (1961) observed an increase in reflectivity at a temperature of 350°C when coal (V.M. = approximately 35 - 40%) was heated for a period of 24 to 48 hours, but no increase in reflectivity was observed at temperatures below 380°C if there was no 'soak period'.

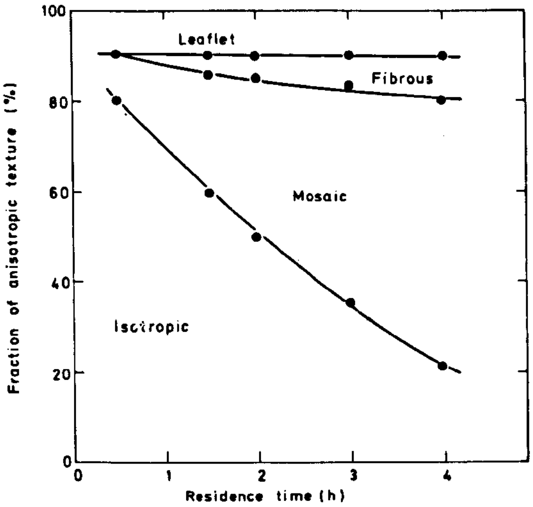


Fig 71 Variation with residence time of various anisotropic textures for high rank coking coal vitrinite (carbon = 89.8% daf) (after Sanada <u>et al.</u> 1973).

Ghosh (1968) studied the influence of 'soak periods' ('residence times') of up to five hours on the reflectivities of three different ranks of coal (carbon = 76.2, 83.5 and 91.1% daf) carbonised at temperatures of 500°, 700° and 1000°C. The reflectivity of these coals increased with residence time up to a maximum, after which it maintained the same level with further increase of time. The rate of the initial increase of the reflectivity to its maximum value depended on many factors, including the carbonisation temperature, the original rank of the coals and the rate of heating (Fig 72). The initial increase of reflectivity was sharper the higher was the temperature of the carbonisation. The differences between rates of heating became less evident with increase of residence time. Ghosh did not study these effects on a true coking coal (carbon = 88% daf).

De Vries *et al.* (1968) also studied the reflectivity of a range of vitrinites of different rank (from 78.8 up to 92.4% daf) carbonised at 450°, 520° and 600°C for periods up to 72 hours. The effect of residence time is more pronounced in the coking range (carbon = 88.6, 89.6 and 89.7% daf). The reflectivities of coking coal vitrinites at all three levels of carbonisation temperature maintain their increase and even after 72 hours holding time the reflectivity rise still does not seem to have ended (Fig 73). The phenomenom is at its maximum at 89.6% carbon. The reflectivity of the lowest-rank coal (carbon = 78.8% daf), when carbonised at 450°C, increases with time up to 24 hours and

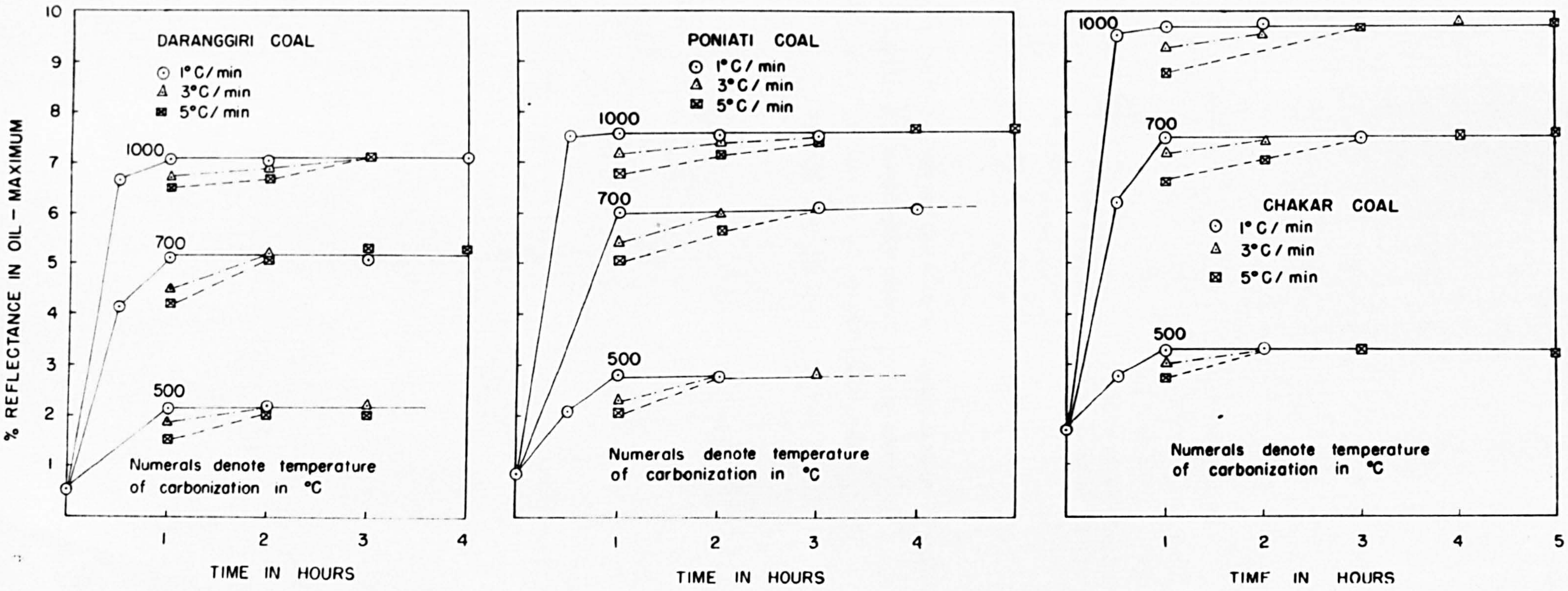
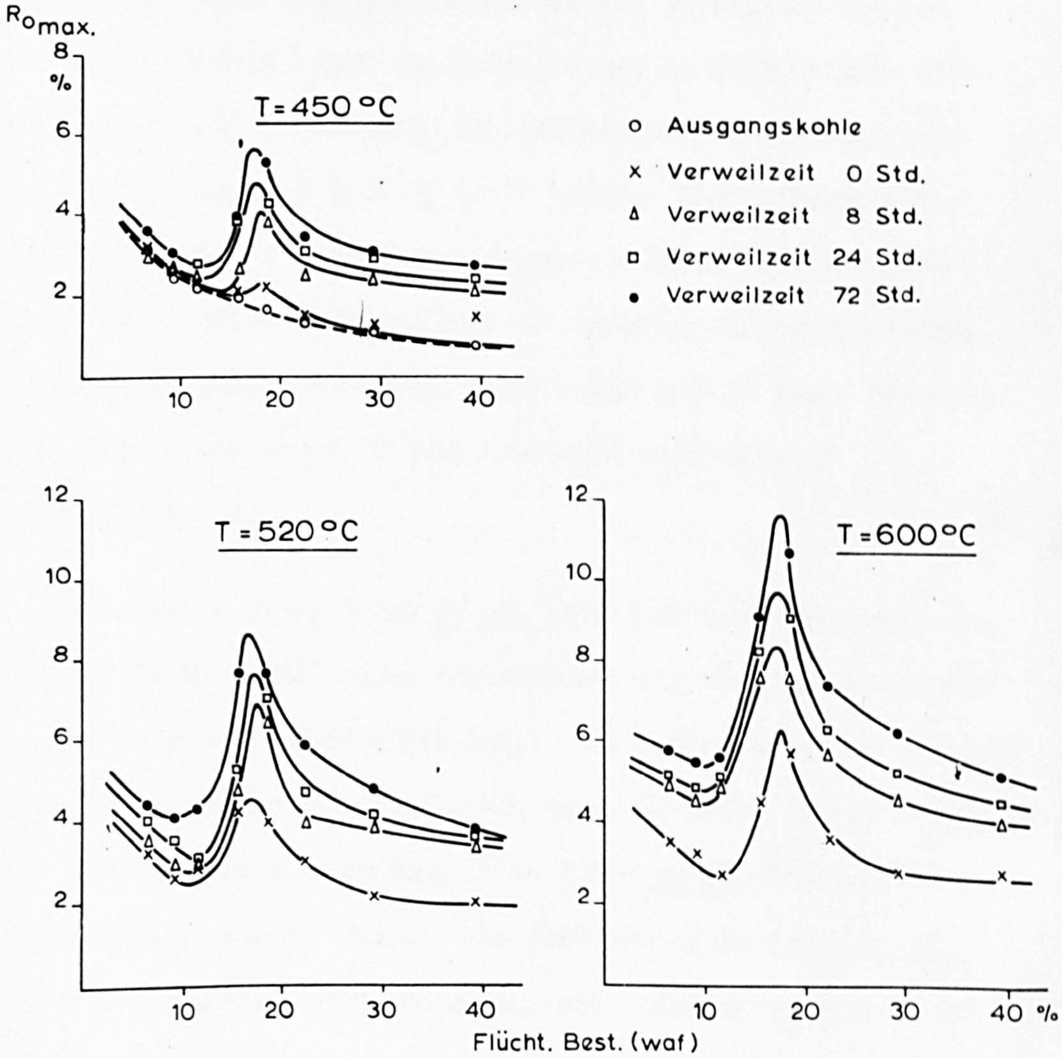

% REFLECTANCE IN OIL - MAXIMUM
1
2
3
4
5
6
7
8
9
10
DARANGGIRI COAL
⊙ 1°C/min
△ 3°C/min
⊠ 5°C/min
1000
700
500
Numerals denote temperature of carbonization in °C
1
2
3
4
TIME IN HOURS
PONIATI COAL
⊙ 1°C/min
△ 3°C/min
⊠ 5°C/min
1000
700
500
Numerals denote temperature of carbonization in °C
1
2
3
4
TIME IN HOURS
CHAKAR COAL
⊙ 1°C/min
△ 3°C/min
⊠ 5°C/min
1000
700
500
Numerals denote temperature of carbonization in °C
1
2
3
4
5
TIME IN HOURS

Fig 73 Variation of oil reflectivity with volatile matter content of fresh vitrinites carbonised at 450°, 500°, and 600°C for 0, 8, 24 and 72 hours 'soak periods'. (after de Vries *et al.* 1968).


$R_{o\,max.}$
8
%
6
4
2
T = 450 °C
○ Ausgangskohle
× Verweilzeit 0 Std.
△ Verweilzeit 8 Std.
□ Verweilzeit 24 Std.
● Verweilzeit 72 Std.
10
20
30
40
12
10
8
6
4
2
T = 520 °C
10
20
30
40
12
10
8
6
4
2
T = 600 °C
10
20
30
40 %
Flücht. Best. (waf)

then only increases slightly thereafter, up to 72 hours; at 600°C the reflectivity increases continuously up to 72 hours. (Fig 74). As might be expected anthracitic vitrinites (carbon = 91.3 and 92.4% dmmf) show the least change in reflectivity with time after an initial increase, the reflectivity increasing only slightly with length of time up to 72 hours. The reflectivity-holding time curve of caking coal (carbon = 87.5% daf) exhibits behaviour intermediate between that of low-rank and coking coals. Reflectivity differences between zero 'soak' and 72 hours 'soaking time' for different ranks of coal increases with rise of temperature (Fig 74).

The results of de Vries *et al.* (1968) do not agree with the findings of Ghosh (1968) even for reflectivity changes in similar ranks of vitrinite (carbon = 91% daf). According to Ghosh vitrinite of this rank maintains the same level of reflectivity after a holding time of 3 hours, while according to de Vries *et al.* (the reflectivity increases with length of time. The findings of de Vries *et al.* show that the increase of reflectivity with time is more pronounced the higher is the temperature of carbonisation, whereas the results of Ghosh suggest only an initial sharp increase of reflectivity and maintenance of the maximum level of reflectivity after a short period of time (between 2 and 3 hours).

4. Optical Properties and Molecular Structure

De Vries *et al.* (1968) state that the continuous increase of reflectivity with time of heating in vitrinites of coking rank

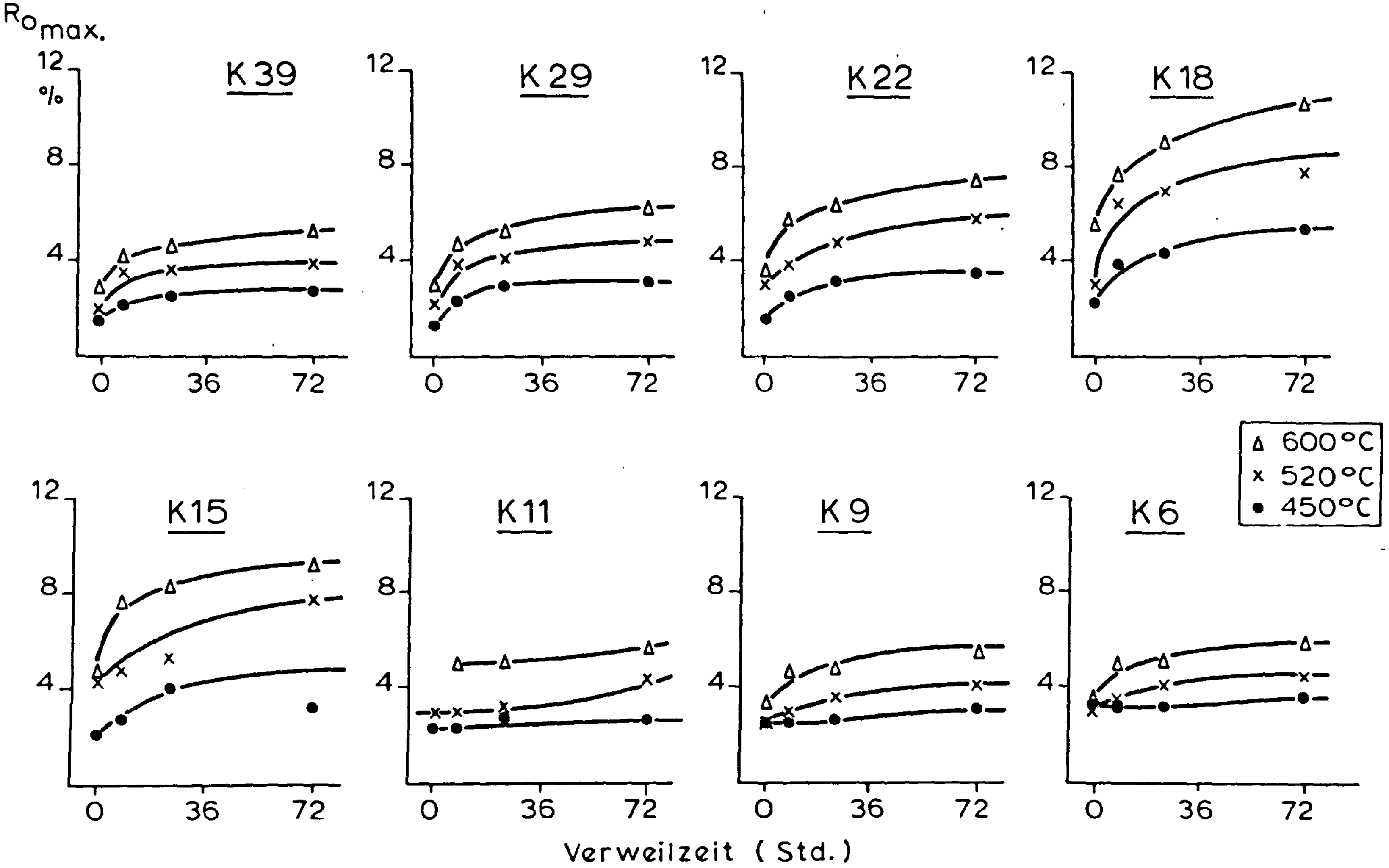
Fig 74 Variation of oil reflectivity curves with holding time for a range of vitrinite carbonised at 450°, 520° and 600°C (after de Vries *et al.* 1968)

Carbon
% daf.

K39 = 78.8
K29 = 87.5
K22 = 88.6
K18 = 89.6
K15 = 89.7
K9 = 91.3
K6 = 92.4

V.M.%
daf

K11 = 11.6



Romax.
%
K 39
K 29
K 22
K 18
K 15
K 11
K 9
K 6
12
8
4
0
36
72
Δ 600°C
× 520°C
● 450°C
Verweilzeit (Std.)

is maintained because of gradual condensation of aromatic material. The condensation of aromatic material in anthracites is very slight, even at 600°C after 72 hours, and results in only a slight rise of reflectivity. The above results suggest that on heating, lengthening the time modifies the molecular structure of vitrinite by distillation and condensation reaction. These molecular changes are also obviously influenced by the initial structure of the vitrinite, e.g. vitrinite of low-rank is more sensitive to time of heating than is anthracite, because low-rank vitrinite has a relatively less ordered structure than does anthracitic vitrinite and so is more liable to the influence of time of heating.

5. X-Ray Diffraction

Honda *et al.* (1970) and Sanada *et al.* (1973), using X-ray diffraction, studied the molecular changes brought about by different residence times on coal-tar pitch, but unfortunately there is no evidence from X-ray diffraction studies of molecular changes in carbonised vitrinites in relation to length of time.

Honda *et al.* (1970) examined the changes in the stack heights of the lamellae (L_c) for different residence times and constant temperatures of 390°, 400° and 410°C for coal-tar pitch. The (L_c) increases with the length of residence time, with the increase rapid up to about 8 hours, after which it rises at a reduced rate up to 20 hours. Support for Honda was given by the results of Sanada *et al.* (1973). The crystallite height (L_c)

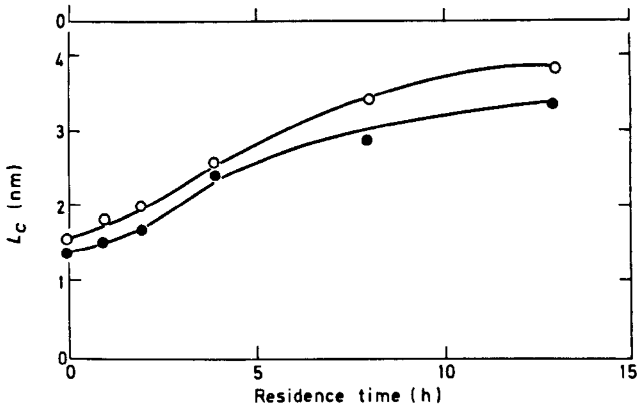


Fig 75 Variation of crystallite height (L_c) with holding time for coal tar pitch carbonised at 420°C (after Sanada et al 1973).

- ● original
- o extract

of coal-tar pitch carbonised at 420°C over a period of up to 13 hours, increased progressively with the length of time (Fig 75).

The behaviour of a carbonaceous material, such as coking-rank vitrinite and coal-tar pitch is rather similar. Thus, if the molecular structure of coal-tar pitch is modified as described above by the time of heating, then the molecular structure of vitrinite, in particular vitrinite of coking rank, might be assumed to change in a similar manner by heating at constant temperatures for prolonged periods.

6. Summary

The above studies indicate that time of heating can have a considerable influence on the properties of vitrinites. It is possible to produce a more ordered molecular structure, which is reflected in the optical properties and in the morphological structure of the carbonised residues at relatively low temperatures if the length of heating is sufficient. Even mosaic structures, which commonly appear at about 425° to 450°C, can apparently form at lower temperatures and the optical properties, e.g. reflectivity reach higher levels which, with continuously rising temperature, would not normally be reached until temperatures 100° to 150°C higher with 'zero soak periods'. What is, however, missing from these earlier studies is a detailed examination of the effect of time and temperatures on the optical properties of vitrinites heated well below their decomposition points, although a slight indication of what may happen is given by the early brief work of Mackowsky.

C. Results. Description

1. Introduction

The morphological changes and optical properties of heat-treated vitrinites (carbon = 77.0, 82.3, 85.4, 87.9, 90% daf and 94.2 dmmf) are discussed and compared with one another.as follows:-

(a) variation at 150°C and

(b) variation at 350°C.

2. Morphology

(a) 150°C (Plates 61, 63, 65, 67, 69 and 71)

The residues of sub-bituminous (carbon = 77.0% daf) and low-rank bituminous vitrinite (carbon = 82.3% daf) show the greatest morphological changes with rise of holding time, i.e. the microspores disappear, vitrinite becomes brighter and slightly subangular and the mottled structure disappears. The residues of caking, low and high-rank coking vitrinites (carbon = 85.4, 87.9 and 90.0% daf) develop occasional small vacuoles at the maximum length of holding time (32 weeks). Anthracitic vitrinite (carbon = 94.2% dmmf) remains unchanged.

(b) 350°C (Plates 62, 64, 66, 68, 70 and 72)

The sub-bituminous vitrinite up to strongly caking coal vitrinite (carbon = 77.0, 82.3 and 85.4% daf) becomes subangular and develop devolatilisation vacuoles of up to 25um diameter with increase of holding time. Particles of the two coking vitrinites (carbon = 87.9 and 90.0% daf) develop vacuoles of up to 50 um diameter, become rounded (Plate 68c) and develop granular mosaic structure (Plates 68c and 70c); anthracitic vitrinite (carbon = 94.2% dmmf) again remains unchanged.

Complete details of the morphological changes are given in Appendix II(Volume III).

3. Optical Properties

The similar optical data of the six vitrinites of different rank are grouped depending on the temperatures at which they were carbonised.

(a) Variation at 150°C

(i) Reflectivity (Figs 76 and 77)

The reflectivity in air and oil are described together because of the similarity between the curves for each vitrinite. The reflectivities of the sub-bituminous and of the lower-rank bituminous vitrinites increase continuously with the length of time, the increase being more evident in the sub-bituminous vitrinite. The caking and two coking vitrinites show a very slight but continuous increase of reflectivity with time and the same trend is possibly present in the anthracitic vitrinite.

Fig 76 Variation of reflectivity in air of different ranks of vitrinite heated for different periods of time at 150°C.

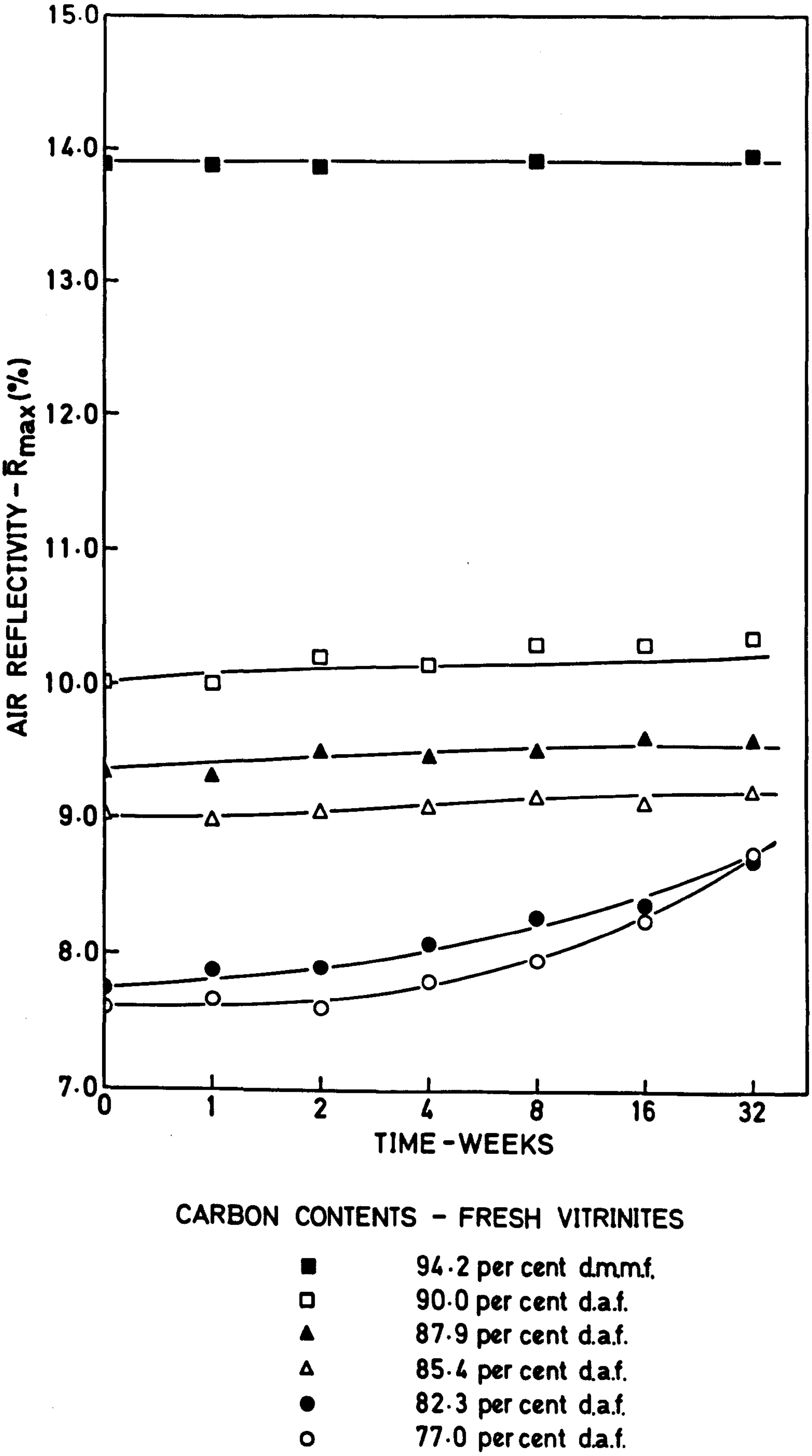
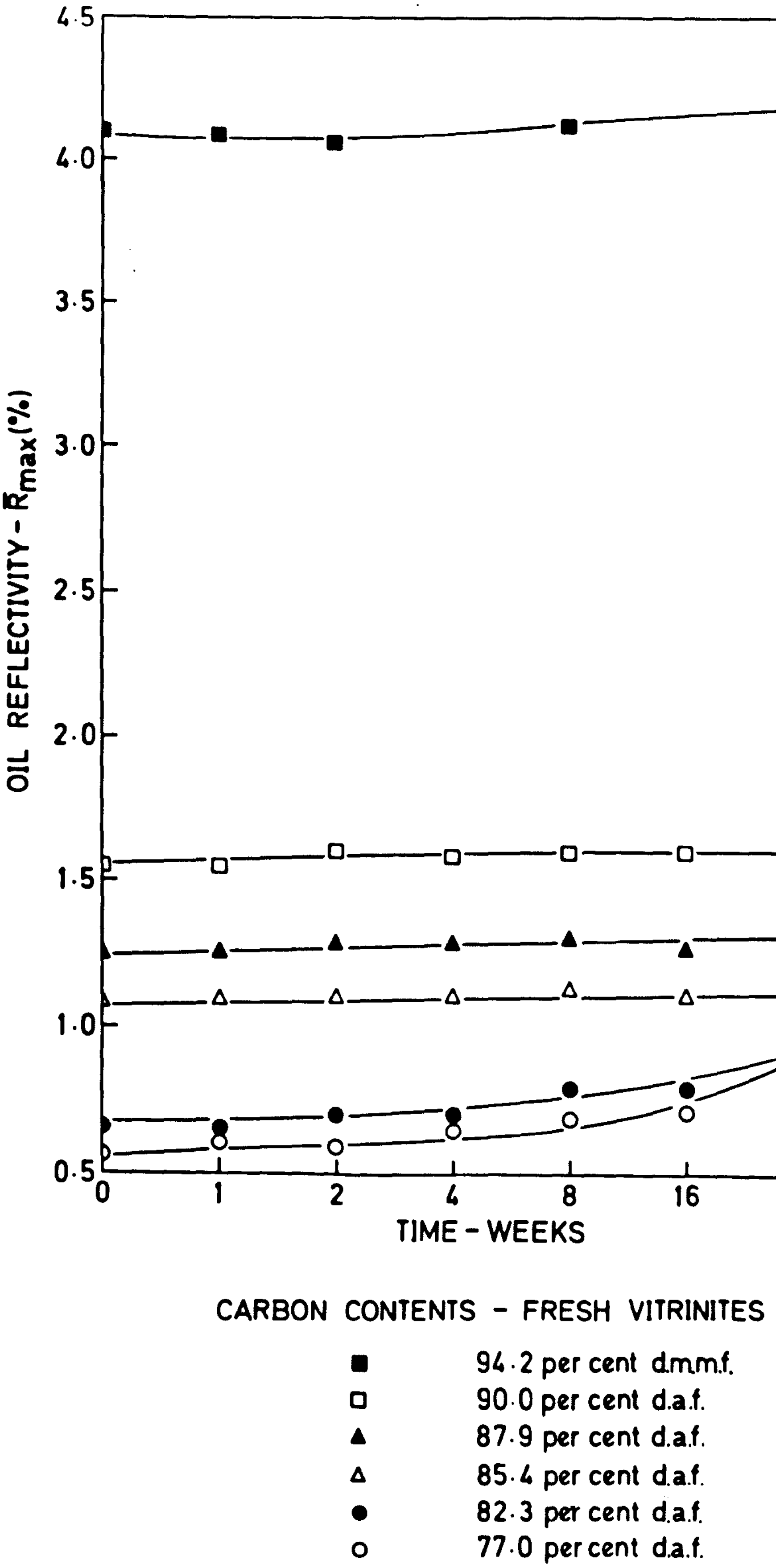

15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94·2 per cent d.m.m.f.
□ 90·0 per cent d.a.f.
▲ 87·9 per cent d.a.f.
△ 85·4 per cent d.a.f.
● 82·3 per cent d.a.f.
○ 77·0 per cent d.a.f.

Fig 77 Variation of reflectivity in oil of different ranks of vitrinite heated for different periods of time at 150°C.


4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
OIL REFLECTIVITY - $\bar{R}_{max}$(%)
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94.2 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.
● 82.3 per cent d.a.f.
○ 77.0 per cent d.a.f.

(ii) Refractive Index (Fig 78)

The curves of the refractive indices against time for the sub-bituminous and low-rank bituminous vitrinites show the greatest modification, although the change in pattern is irregular, the refractive index of the sub-bituminous-rank vitrinite starting to rise after four weeks, but the low-rank bituminous vitrinite showing a continuous increase of refractive index with time. The refractive index time curves for the caking and two coking vitrinites increase slowly with length of heating time, but show less change than do the lower-rank vitrinites. The refractive indices of the anthracitic vitrinite remain practically unchanged with time.

(iii) Absorptive Index (Fig 79)

The absorptive index time curves of vitrinites are not as reliable as the reflectivity or refractive index time curves because the absorptive index is the least accurately determined of the optical parameters. Several of the curves show a slight decrease of the index with time, which would not be expected if the molecular structure is developing. The absorptive index curve of the low-rank and anthracitic vitrinites shows reasonable trends.

(b) Variation at 350°C

(i) Reflectivity (Figs 80 and 81)

The reflectivity-time curves of the sub-bituminous and

Fig 78 Variation of refractive index of different ranks of vitrinite heated for different periods of time at 150°C.

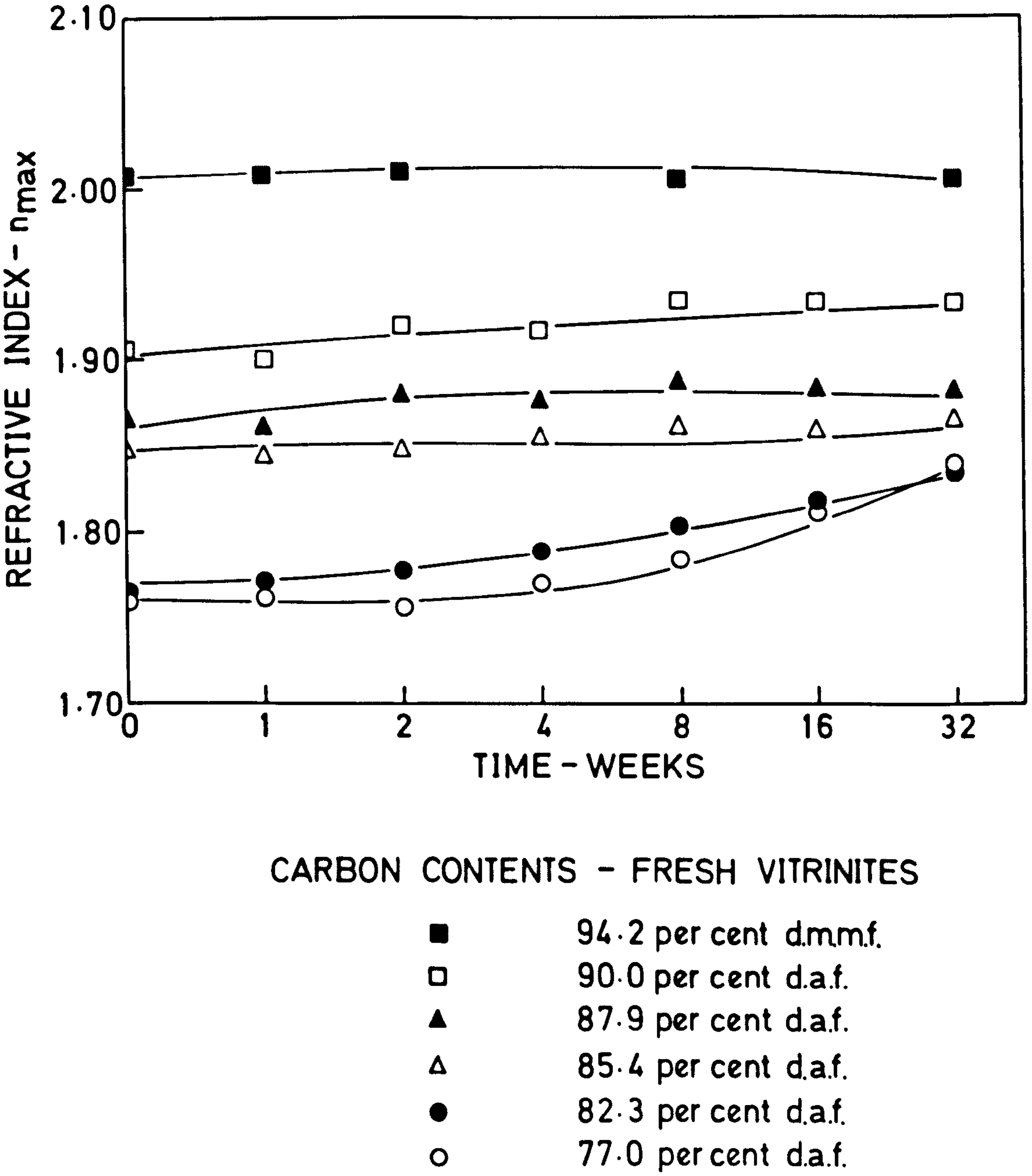

2·10
2·00
1·90
1·80
1·70
REFRACTIVE INDEX - n_{max}
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94·2 per cent d.m.m.f.
□ 90·0 per cent d.a.f.
▲ 87·9 per cent d.a.f.
△ 85·4 per cent d.a.f.
● 82·3 per cent d.a.f.
○ 77·0 per cent d.a.f.

Fig 79 Variations of absorptive index of different ranks of vitrinite heated for different periods of time at 150°C.

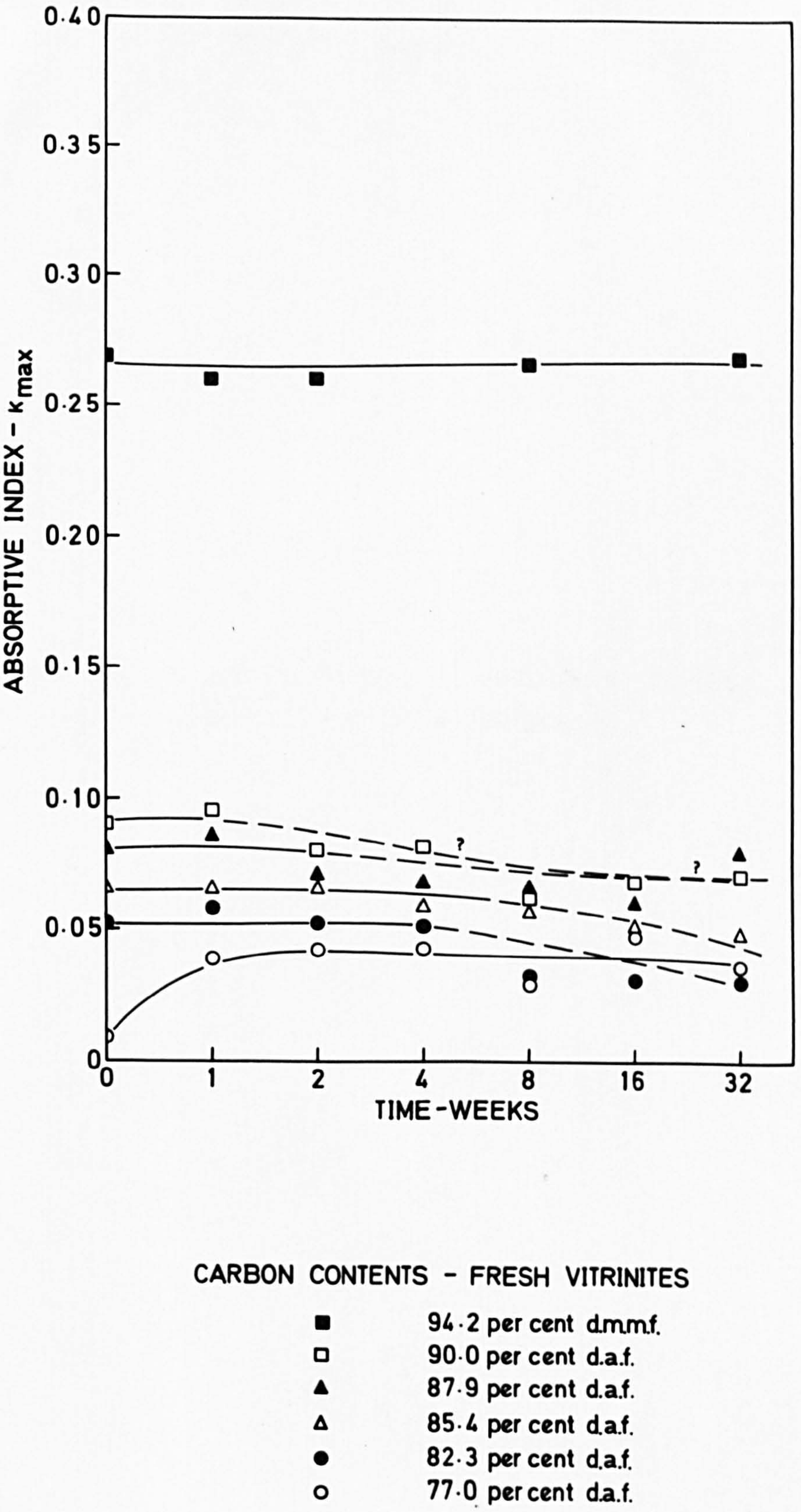

0·40
0·35
0·30
0·25
0·20
0·15
0·10
0·05
0
ABSORPTIVE INDEX - k_{max}
0
1
2
4
8
16
32
TIME-WEEKS
?
?
CARBON CONTENTS - FRESH VITRINITES
■ 94·2 per cent d.m.m.f.
□ 90·0 per cent d.a.f.
▲ 87·9 per cent d.a.f.
△ 85·4 per cent d.a.f.
● 82·3 per cent d.a.f.
○ 77·0 per cent d.a.f.

Fig 80 Variation of reflectivity in air of different ranks of vitrinite heated for different periods of time at 350°C.

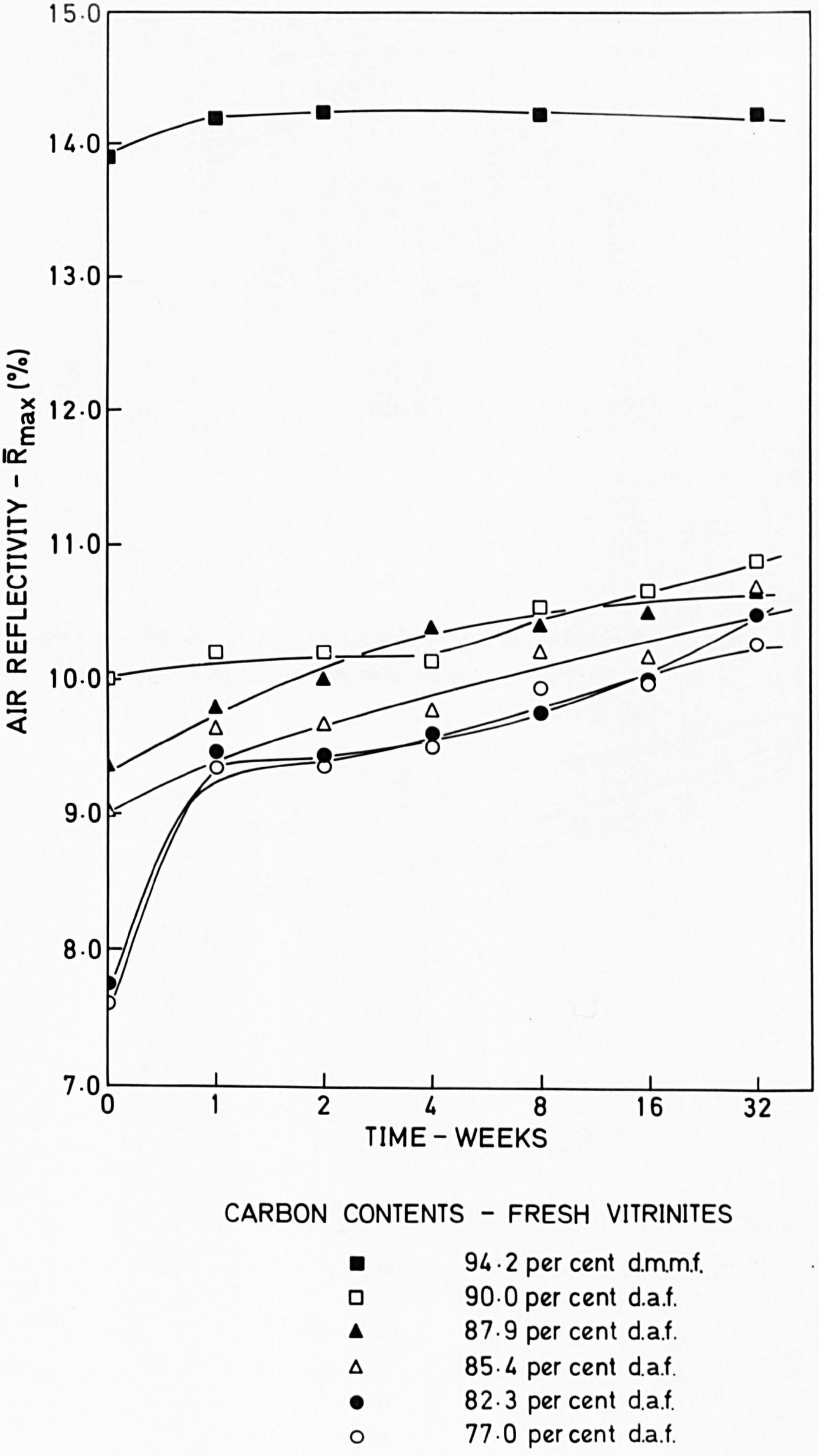
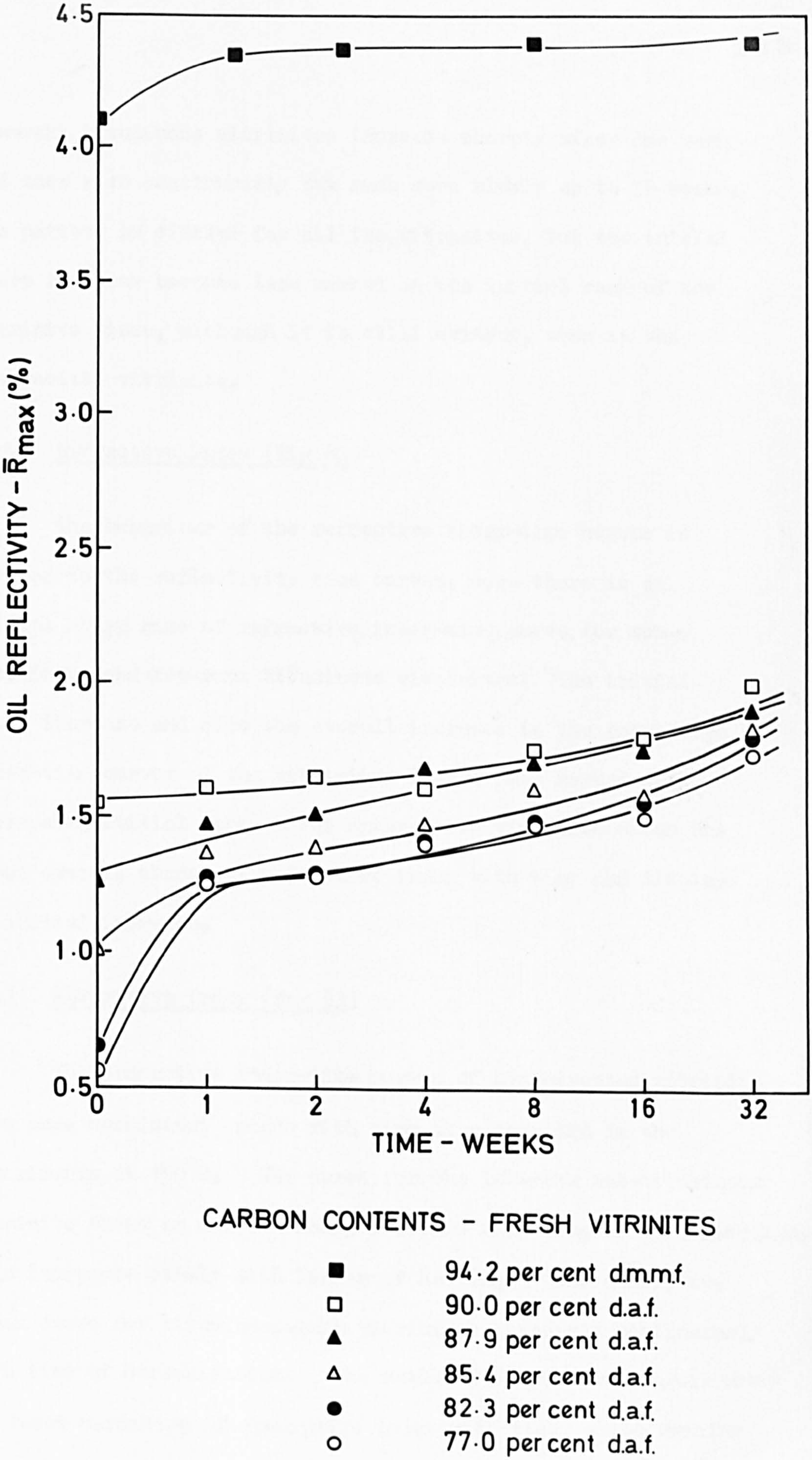

AIR REFLECTIVITY - $\bar{R}_{max}$ (%)
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94.2 per cent d.m.m.f.
□ 90.0 per cent d.a.f.
▲ 87.9 per cent d.a.f.
△ 85.4 per cent d.a.f.
● 82.3 per cent d.a.f.
○ 77.0 per cent d.a.f.

Fig 81 Variation of reflectivity in oil of different ranks of vitrinite heated for different periods of time at 350°C.


OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94.2 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.
● 82.3 per cent d.a.f.
○ 77.0 per cent d.a.f.

low-rank bituminous vitrinites increase sharply after one week and then rise continuously but much more slowly up to 32 weeks. The pattern is similar for all the vitrinites, but the initial sharp increase becomes less marked as the initial rank of the vitrinite rises, although it is still evident, even in the anthracitic vitrinite.

(ii) Refractive Index (Fig 82)

The behaviour of the refractive index-time curves is similar to the reflectivity time curves, e.g. there is an initial sharp rise of refractive index-time curve for sub-bituminous and low-rank bituminous vitrinites. The initial sharp increase and also the overall increase in the refractive index time curves of the vitrinites become less marked with increasing initial rank. The anthracitic vitrinite shows the least overall change of refractive index with time and displays no initial increase.

(iii) Absorptive Index (Fig 83)

The absorptive index-time curves of heat-treated vitrinite show more consistent trends with time than they did in the experiments at 150°C. The curve for the low-rank sub-bituminous vitrinite shows an initial sharp increase with time of carbonisation, then increases slowly with length of heating. The absorptive index curve for bituminous-rank vitrinites increases continuously with time of carbonisation. The anthracitic vitrinite again shows the least variation of absorptive index with time, which remains practically the same as fresh vitrinite up to 32 weeks.

Fig 82 Variation of refractive index of different ranks of vitrinite heated for different periods of time at 350°C.

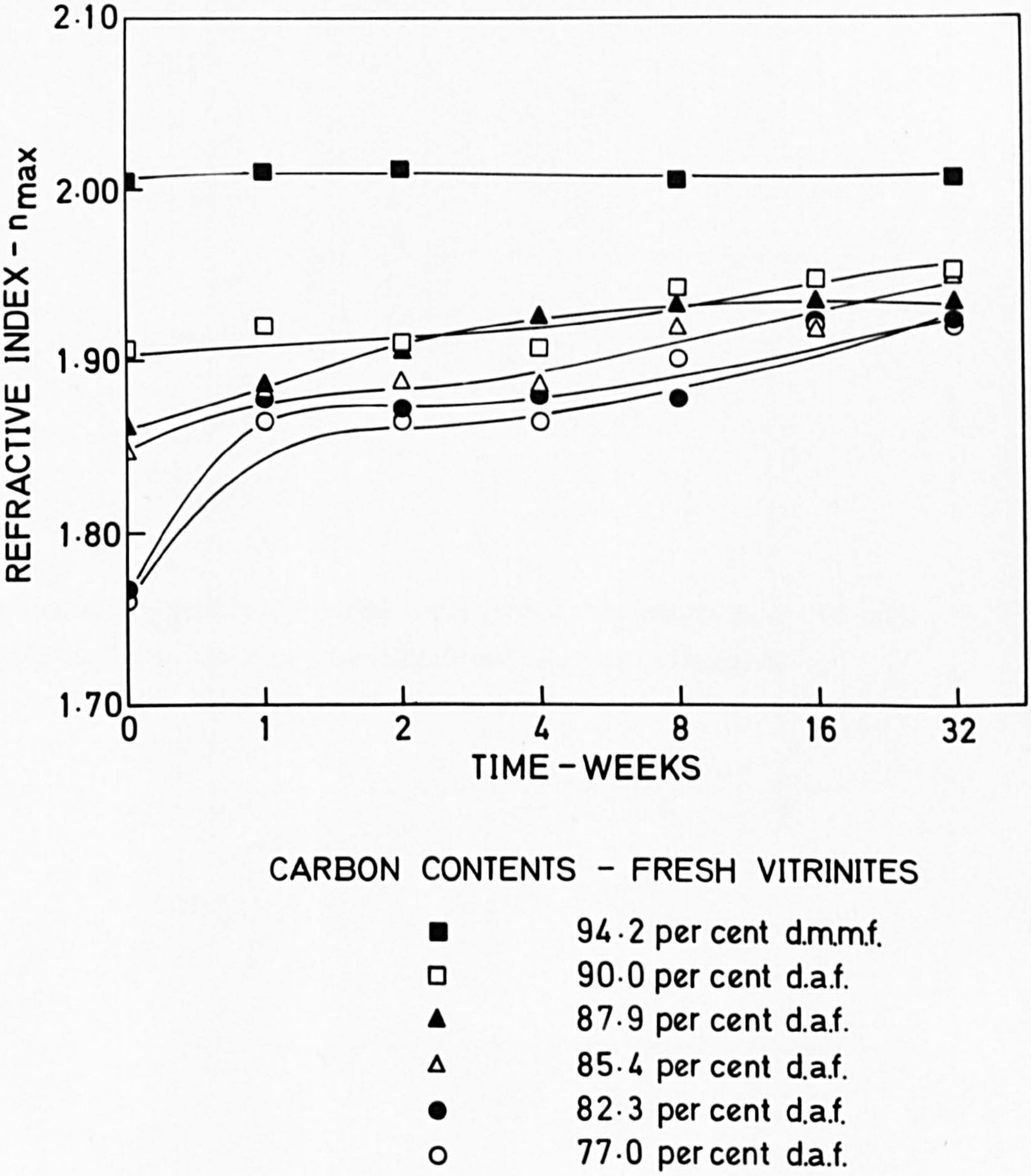
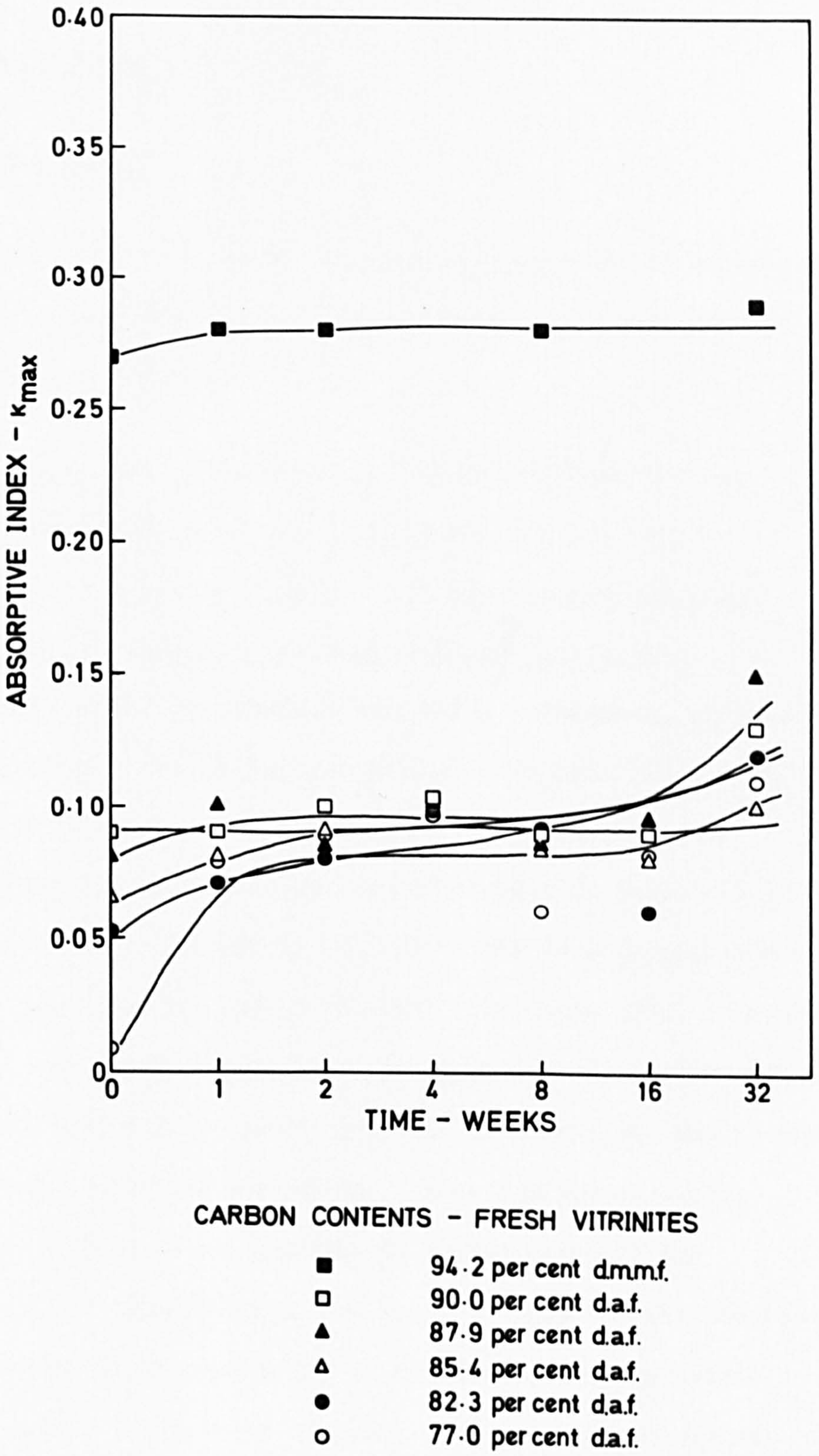

2·10
2·00
1·90
1·80
1·70
REFRACTIVE INDEX - n$_{max}$
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94·2 per cent d.m.m.f.
□ 90·0 per cent d.a.f.
▲ 87·9 per cent d.a.f.
△ 85·4 per cent d.a.f.
● 82·3 per cent d.a.f.
○ 77·0 per cent d.a.f.

Fig 83 Variations of absorptive index of different ranks of vitrinite heated for different periods of time at 350°C.


ABSORPTIVE INDEX - κ_{max}
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
0
1
2
4
8
16
32
TIME - WEEKS
CARBON CONTENTS - FRESH VITRINITES
■ 94.2 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.
● 82.3 per cent d.a.f.
○ 77.0 per cent d.a.f.

D. Discussion

1. Morphology

The above work indicates that the influence of holding time and temperature level is more striking the lower is the rank of the vitrinite.

(a) 150°C: the sub-bituminous vitrinite (Plate 61) and the low-rank bituminous vitrinite (Plate 63) show the greatest morphological changes, e.g. microspores disappear at the maximum length of holding time and the mottled appearance, which is related to cellular structures, becomes more visible. The caking and coking vitrinites (Plates 65, 67 and 69) develop a number of small vesicles and cracks which suggests incipient plastic deformation in these vitrinites. The sporinite in the caking coal vitrinite is depolymerised and becomes brighter, and completely disappears after 32 weeks' holding time in the coking coal vitrinites. The anthracitic vitrinite (Plate 71) remains practically unchanged, due to the more stable molecular structure. What the above results indicate is that it is possible to produce some of the morphological changes which are normally observed with short-term heating in the range 375° - 425°C (e.g. disappearance of sporinite, development of cracks and small vesicles) at much lower temperatures, if the holding time is sufficiently long.

350°C: the development of vesicles in sub-bituminous and low-rank bituminous vitrinites and also the complete disappearance of sporinite (Plates 62 and 64) with increase in the length of time indicates 'active decomposition' of this vitrinite (see Berkowitz 1967; Goodarzi 1971 and Melvin 1974), which is normally only observed in laboratory-treated coals at temperatures over 400°C. Development of vesicles, gradual brightening of the sporinite and its eventual disappearance in the caking and coking coal vitrinites (Plates 66, 68 and 70 a-d) with progressive increase of holding time and finally the development of a mosaic structure in the coking coal vitrinites (Plates 68 and 70) is indicative of gradual decomposition of these vitrinites at a temperature which is substantially below the 'normal' temperatures of 'active decomposition', e.g. 400°C as cited by Berkowitz 1967.

It is interesting to observe the development of a granular mosaic structure in the coking coal vitrinites, which does not normally occur in laboratory-carbonised softening vitrinites (Plates 68 and 70) until a temperature of about 425°C is reached (see for example Goodarzi 1971). Results are also presented in Part III which show that even the true softening vitrinites do not develop mosaic structures at 400°C, even at a slow heating rate. Melvin (1974) also anticipated the development of mosaic structure in thermally metamorphosed coals at temperatures of about 150°C ± 15. Taylor (1961) also suggests the possibility of the formation of mesophase and/or mosaic structure by prolonged heating at temperatures lower than 450° - 460°C.

2. Optical Properties

(a) Variation at 150°C

(i) Reflectivity (Figs 76 and 77)

At 150°C the progressive increase of the reflectivity of the sub-bituminous and low-rank bituminous vitrinites, the slight changes in the level of reflectivity of the caking and coking vitrinites and finally the practically unchanged level of reflectivity of anthracite (Figs 76 and 77) with increase in the length of heating time at a temperature of 150°C reflects the initial basic differences in molecular structure between these vitrinites. The molecular structural changes at this temperature level compared with the fresh material are not severe, and, according to Berkowitz (1968), are limited to the release of physically occluded and/or absorbed moisture and gases such as CH_4 and CO_2. However, the findings of Harrison (1965) show that the reflectivity of certain low-rank vitrinites increases with decrease of moisture content, so the increase in the reflectivity level with length of time of the above vitrinites can possibly be related to some extent to loss of moisture. It is also known that the proportion of amorphous material (aliphatic and/or alicyclic hydrocarbons) decreases with rise of rank (Cartz and Hirsch 1960) and that during carbonisation the amorphous materials begin to devolatilise at temperatures of about 300°C

(Diamond and Hirsch 1958 and Diamond 1960), resulting in condensation of the aromatic structures and hence an increase in reflectivity. But, considering the substantial length of time of carbonisation in the present project, and the results of van Krevelen *et al.* (1956) which show that decomposition reactions at constant and low temperatures are continuous with time, until the maximum level of decomposition is achieved, then surely some degree of decomposition at 150°C must have taken place. Although the decomposition is not severe, it is continuous, leading to slow degasification of amorphous material and subsequent condensation of aromatic structures at temperatures lower than 300°C. The slight increase in the level of reflectivity of the caking and coking vitrinite with length of time is probably attributable to the stability of the structure of these vitrinites, which consists of lesser proportions of amorphous material and more aromatic material, thus requiring a greater level of thermal treatment to produce molecular changes by decomposition reactions.

Finally, anthracitic vitrinite which may have a temperature of formation of 200°C (Cook *et al.* 1972) would not be generally expected to show reflectivity changes with length of time, because of its relatively stable structure.

(ii) Refractive Index (Fig 78)

The refractive index of vitrinites up to high-rank bituminous (carbon = 90.0% daf) increases with length of heating (Fig 78), which indicates molecular changes, such as an increase in crystallite height and/or improvement in packing of the aromatic lamellae (see Part III). The results of Honda et al (1970) and Sanada et al (1973) show a continuous increase of crystallite height with length of holding time at a temperature of about 390°C. While the temperature level of 150°C in the present work is considerably lower than the temperature used by Honda et al. and Sanada et al. the length of time in the earlier studies was only a matter of hours, while in the present study is based on weeks. In addition, the findings of Goodarzi (1971) and Goodarzi and Murchison (1972) show the refractive index of low-rank vitrinite on heating increases at a greater rate than does higher-rank vitrinite. The present study supports the above findings since the greater is the increase of the refractive index, the lower is the rank of the vitrinite.

The sub-bituminous and low-rank bituminous vitrinites, after carbonisation for 32 weeks, develop a level of refractive index similar to the initial refractive index of a caking coal vitrinite, which probably indicates that structurally these two vitrinites have developed similar molecular structures. The difference in molecular structures of the caking and coking vitrinites is apparent from the behaviour of their refractive index-time curves which show that, even after 32 week's continuous carbonisation, changes in molecular structure are much less intense than in lower-rank vitrinites.

At a heating temperature of 150°C, only 32 week's holding time appears to be sufficient to promote the level of the optical properties of sub-bituminous and low-rank bituminous vitrinite up to those of caking vitrinite, only atmospheric pressure being involved. The temperature of 150°C is very close to the temperature of natural maturation (80° - 144°C) of bituminous coal which was quoted by M. Teichmüller and R. Teichmüller (1968). These temperatures of 'metamorphism are lower than the temperature used in those studies, but the length of holding time in the present study was only 32 weeks, whereas geological time may be immense. In order to achieve the same effect as natural metamorphism over a shorter length of time, a temperature increase would be required. The effects of pressure would also have to overcome in the crust, lengthening the time necessary at these relatively low temperatures.

(iii) Absorptive Index (Fig 79)

The behaviour of the absorptive index-time curves of vitrinites of different rank level suggests that the changes in layer diameter (L_a) in the lowest-rank vitrinite are very slight after an initial sharp increase with time of carbonisation.

(b) Variation at 350°C

(i) Reflectivity (Figs 80 and 81)

According to van Krevelen et al. (1956), the initial rate of decomposition is sharp and the initial sharp rise of the reflectivity of all six vitrinites of different rank level after a holding time of one week, must be related to initial degasification and decomposition. The initial sharp rise of reflectivity with holding time agrees with the findings of Ghosh (1968) and de Vries et al. (1968) at temperatures higher than the decomposition point. However, the extent of the initial increase of the level of reflectivity with holding time decreases from the low-rank to the anthracitic vitrinite indicating that the condensation of aromatic structures due to degasification is greater the lower is the rank of the vitrinite. Berkowitz (1967) recognises that carbonisation up to 350°C results in limited devolatilisation, which again, is the greater the lower is the rank of the coal, and the findings of Brooks and Maher (1957) also indicate that thermal stability increases with rising carbon content or decrease of oxygen content. It would then be expected that the overall change in reflectivity with holding time would be reduced with rise of rank, as the present results show (Figs 80 and 81). Condensation of aromatic structures in bituminous-rank vitrinite is continuous with increase in length of holding time (de Vries et al. 1968), so progressive increase in the level of reflectivity curves with holding time of such vitrinites indicates progressive condensation of aromatic structures.

(ii) Refractive Index (Fig 82)

The initial sharp rise of the refractive indices of the lower-rank vitrinites with holding time is due again to modification of their molecular structures caused by degasification increasing in crystallite height or improvement of the packing of layers. (see Honda et al. 1970 and Sanada et al. 1973). In contrast to 150°C the initial increase of refractive indices is greater the lower is the rank of vitrinite, due to the severe molecular structural alteration which is proportionally higher in the lower-rank vitrinites. If the level of refractive index can be taken as an indication of the degree of development of the molecular structure, it is evident from Fig 82 that a low-rank bituminous vitrinite, even after prolonged heating, has still not developed its molecular structure to a level that is equivalent to that of a coking vitrinite at this temperature. The anthracitic vitrinite shows the least increase in its refractive index-time curve which can be expected because of the more stable molecular structure of the anthracites. The anthracitic vitrinite clearly requires an even higher starting temperature to reorganise its initial molecular structure over a heating period as short as 32 weeks.

(iii) Absorptive Index (Fig 83)

The behaviour of the absorptive index-time curves for sub-bituminous and bituminous-rank vitrinites indicates that the aromatic layer diameters increase rapidly in the initial week of heating. This initial increase is more pronounced for sub-bituminous vitrinites than for bituminous-rank vitrinites, because the layer diameter of the lowest-rank vitrinite begins to increase slowly at about 300°C (see Diamond and Hirsch 1958; Diamond 1960), whereas the layer diameters of the bituminous-rank vitrinites only begin to increase at higher temperatures.

Of the absorptive index-time curves for anthracitic vitrinite, little needs to be said because, according to the results of Diamond (1960), increase in the aromatic-layer diameter of anthracite only begins at about 600°C. At the level of temperature (350°C) used here, even after prolonged periods of time, the sizes of aromatic layers in anthracitic vitrinite is not affected.

E. Conclusion

1. the morphological changes with holding time in non-softening vitrinite are greater the lower is the rank,

2. the anisotropy of softening vitrinites (observed with the microscope) increases with holding time

3. truly softening vitrinites develop mosaic structures with prolonged holding times at temperatures much lower than normal softening temperatures,

4. when heated at temperatures below natural decomposition temperatures, the optical properties of low-rank vitrinites are most sensitive to holding time, anthracitic vitrinites the least,

5. the influence of holding time on optical properties becomes more evident the higher is the level of heat-treatment temperature,

6. the effect of holding time on optical properties appears only if the temperature of formation of the vitrinite is lower than the heat-treatment temperature, and

7. low-rank vitrinites develop a similar level of reflectivity to higher-rank vitrinite in a shorter length of time than the higher-rank vitrinite takes to achieve a higher level of reflectivity.

PART V OPTICAL PROPERTIES OF CARBONISED SPORINITES AND CARBONISED MIXTURES OF SPORINITES AND VITRINITES OF DIFFERENT RANK.

Contents Page

1. OPTICAL PROPERTIES OF CARBONISED SPORINITES

A. General Introduction

The purpose of this **Part** is to report on the variation of the optical properties of low and medium-rank sporinites and their mixtures with vitrinite of the same coal over a range of carbonisation temperatures. The behaviour of sporinite, and particularly its possible influence on the properties of vitrinite during the carbonisation process may be important in the preparation of industrial coke, particularly when dealing with swelling, coherency and hardness of the resulting products. To the Writer's knowledge, there has not been a previous systematic study of this nature.

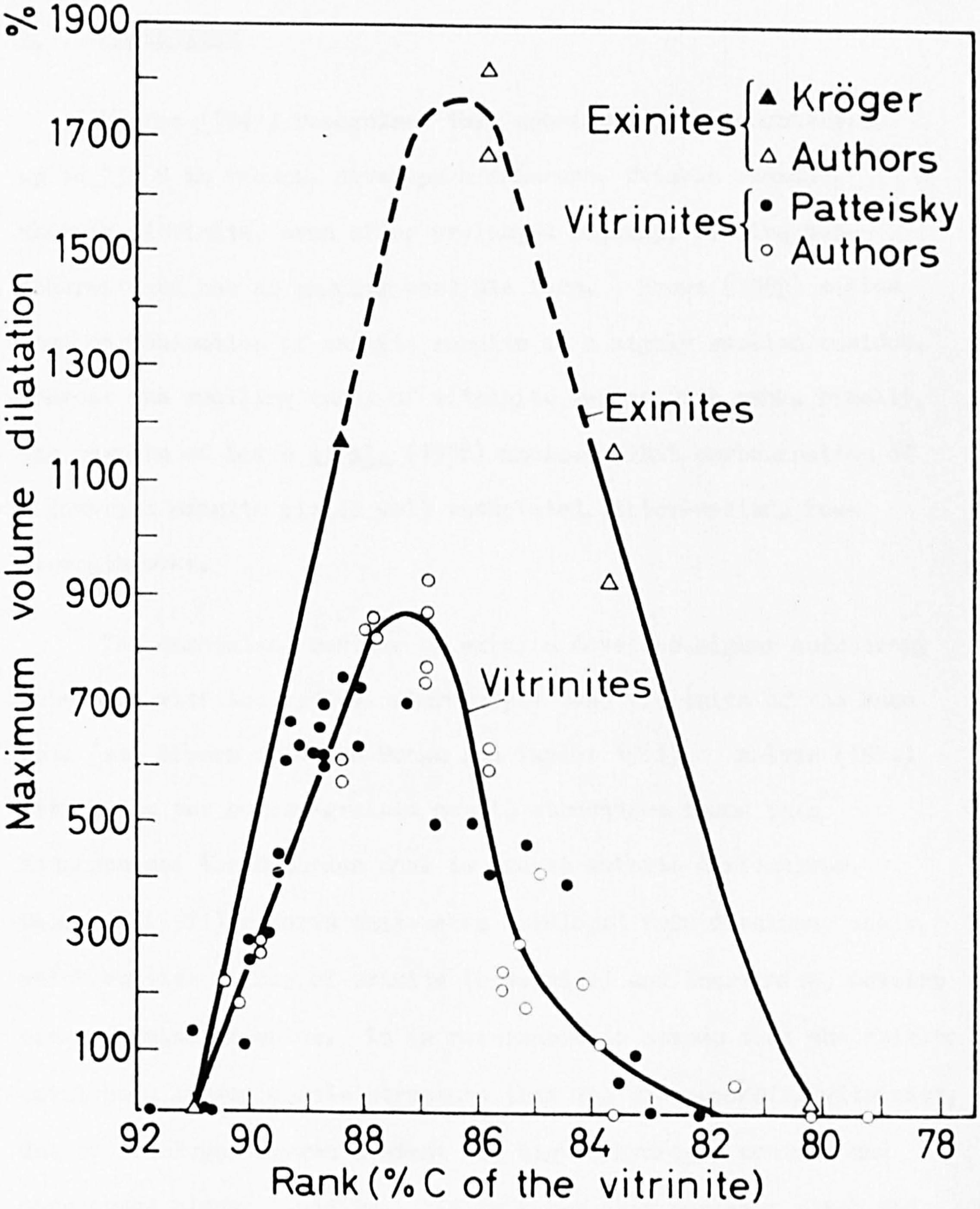
The term 'exinite' is often used in investigations on the properties of sporinite, but strictly the term 'exinite' refers to the exinite group of macerals consisting of sporinite, cutinite, resinite and alginite. The main constituent of the exinite group of macerals in Palaeozoic coals is sporinite and it is the maceral which is dominant in separations.

B. Previous Related Studies

1. Introduction

According to Sprunk et al. (1938); Macrae (1943); Alpern (1956); Kröger and Pohl (1957); Dormans et al. (1957); Nandi (1966) and the International Handbook of Coal Petrography (1971), exinite undergoes an extensive devolatilisation during carbonisation, resulting in a very high yield of tar and high volatile-matter content. Alpern (1956) states that about 40% of exinite substance is devolatilised on thermal treatment. Kröger and Pohl (1957) find that exinite has a higher level of weight loss at about 420°C than does vitrinite, that the rate of decomposition of exinite is higher than that of vitrinite and that exinite decomposes over a shorter temperature range than vitrinite, but the differences between the decomposition behaviour of exinite and vitrinite decrease with increase of rank. The results of Ergun et al. (1959) indicate that on heating (between 450° and 500°C) at a fixed rate, exinite fuses and resolidifies abruptly over a wide temperature range. The duration of the reaction decreases with increase of temperature, but vitrinite fuses at a relatively high temperature and decomposes rapidly. Dormans et al. (1957) indicate that pure exinite produces an abnormal dilatation curve due to its fluido-plastic behaviour and extensive evolution of volatile-matter at the same time. Van Krevelen et al. (1959) recognises that the fluidity of exinite during carbonisation is much greater than that of the vitrinite (Fig 84). Finally, Nandi (cited by Mackowsky and Wolff 1966) recognised, that exinite has a low softening point, becoming very fluid and is highly volatile.

Fig 84 Variation of dilatation with rank of exinite and vitrinite (after van Krevelen *et al.* 1959).



%
1900
1700
1500
1300
1100
900
700
500
300
100
Maximum volume dilatation
Exinites { ▲ Kröger
△ Authors
Vitrinites { ● Patteisky
○ Authors
Exinites
Vitrinites
92
90
88
86
84
82
80
78
Rank (% C of the vitrinite)

2. Morphology

Macrae (1943) recognises that sporinite, on carbonisation up to 350°C in vacuum, develops a coherent, friable residue, whereas vitrinite, even after prolonged heating, remains non-coherent and has an angular particle form. Brown (1959) states that carbonisation of exinite results in a highly swollen residue, whereas the swelling index of vitrinite varies with rank. Finally, the results of Ladem *et al.* (1958) indicate that carbonisation of a low-rank exinite yields well vacuolated, thick-walled, low-strength coke.

The carbonised residue of exinite develops higher anisotropy (observed with the optical microscope) than vitrinite of the same coal (see Alpern 1956 and Brown and Taylor 1961). Melvin (1974) attributes the coarse-grained mosaic structures found in a metmorphosed Northumbrian coal is due to exinite derivatives. Goldring (1971) reports that cokes developed from durainous coals, which consist mainly of exinite (sporinite) and inertinite, develop coarse-grained mosaics. It is reasonable to assume that the exinite develops a larger mosaic structure than the corresponding vitrinite, due to its lower oxygen content and higher hydrogen content and consequent higher fluidity. It is known that coal-tar pitch and carbonaceous material, with a high content of hydrogen in relation to elements other than carbon, develop a larger mosaic structure (see Alpern 1956; Brooks and Taylor 1965 and Marsh *et al.* (1973).

3. Optical Properties

Carbonised residues of exinite, thermally metamorphosed or laboratory carbonised, develop a higher level of reflectivity and bireflectance than the corresponding carbonised vitrinites (see Alpern 1956; Brown and Taylor 1961 and Kisch 1966). Alpern (1956) recognises that the anisotropy of carbonised residues of exinite concentrates is higher than coke made of vitrinite of the same coal(V.M. = 34%) and that the presence of exinite in coal-maceral mixtures promotes the anisotropy of resulting carbonised residues. Brown and Taylor (1961), examining some metamorphosed Antarctic coals, recognise small areas elongated parallel to the bedding, which show stronger anisotropy than the vitrinite, and believe that these areas represent heat-affected exinite. Finally, Kisch (1966) considers that the streaks of highly anisotropic material (Figs 3 and 4, pp 1054-1055) in some heat-affected coals, which also show higher reflectivity than the corresponding vitrinite, are metamorphosed residues of exinite. More recently the results of Khavari (1975) indicate that the reflectivity, bireflectance and absorptive index of carbonised residues of gilsonite pitch increase with rise of temperature and also that the refracrive index curve for the residues follows a similar trend to that of vitrinite of a similar degree of carbonisation when carbonised under similar conditions. Since exinite has a similar compositional relationship to pitch (higher hydrogen and low oxygen content), the optical properties of carbonised exinite may behave similarly to gilsonite pitch.

4. X-Ray diffraction

Carbonised residues of exinite develop better ordering of their molecular structure than vitrinite of corresponding rank. This is indicated by the findings of Durif (1956) show shows that exinites (V.M. = 21.3% - 38.0% daf) graphitise between 1880° and 1990°C, showing better ordering of molecular structure. (apparent from the intensity of 002 band) than the vitrinite of the same rank level. The formation of better graphitic structures in4 carbonised residues of exinite than in the associated vitrinite is probably due to the lower oxygen content of exinite than vitrinite. Further Ladem *et al.* (1958, also show that a low-rank exinite carbonised up to 1000°C develops a better graphitic structure than vitrinite. The findings of Franklin (1951) indicate that the graphitisability of carbonaceous material is directly dependent on its oxygen content and the molecular structure of the semi-coke developed at temperatures ranging between 400° and 500°C. Exinite, having a higher hydrogen and lower oxygen content, probably develops aromatic layers which are more loosely cross-linked than the corresponding vitrinite; so as the temperature increases, exinite probably develops larger and better ordered aromatic lamellae.

5. Summary

To summarise, exinite during carbonisation develops a better molecular structure than the associated vitrinite, due to the basic molecular differences between these two macerals. The results of Alpern (1956); Brown and Taylor (1961) and Kisch (1966) indicate that carbonised residues of exinite show a higher level of anisotropy than vitrinite, while the results of Durif (1956) and Ladam (1958) show a higher level of molecular ordering in carbonised exinites than in the associated carbonised vitrinites. Finally it is not unreasonable to expect that exinite will develop better defined mosaic textures than the associated vitrinite and also that the trends of optical properties of carbonised exinite will differ from those of carbonised vitrinites of similar rank.

C. Results. Description

1. Introduction

The optical properties of low and medium-rank sporinites (carbon = 83.0 and 87.1% daf) carbonised at temperatures ranging from 300° to 950°C were studied. The similar experimental optical data of the carbonised residues of the low and medium-rank sporinites are grouped together (Figs 85 to 89) and also more generalised curves for the same optical data are shown in Figs 90 to 94, together with curves for the equivalent associated vitrinites.

2. Morphology (Plates 73 to 80)

The carbonised residues of both sporinites (sporinite: carbon = 83.0 and 87.1% daf) become coherent (b, c Plates 73 and 77) at about 400°C and develop devolatilisation vacuoles.

The size of vacuoles varies but generally increases with rise of temperature. The residues of both sporinites are almost isotropic at 400°C but become anisotropic at about 450°C (c Plates 73 and 77). The carbonised residues of low-rank sporinite develop a fine-grained mosaic texture (Plates 74 to 76), whereas the medium-rank sporinite develops fine to coarse-grained mosaic on carbonisation. The coarse-grained mosaic mainly develops in areas free of inertinite (bPlate 78). The size of the mosaic structure increases with rising temperature and the mosaic units develop common orientation. Complete details of the morphological changes are given in Appendix III of Volume III.

3. Optical Properties

(a) Reflectivity (Figs 85, 86, 90, 91)

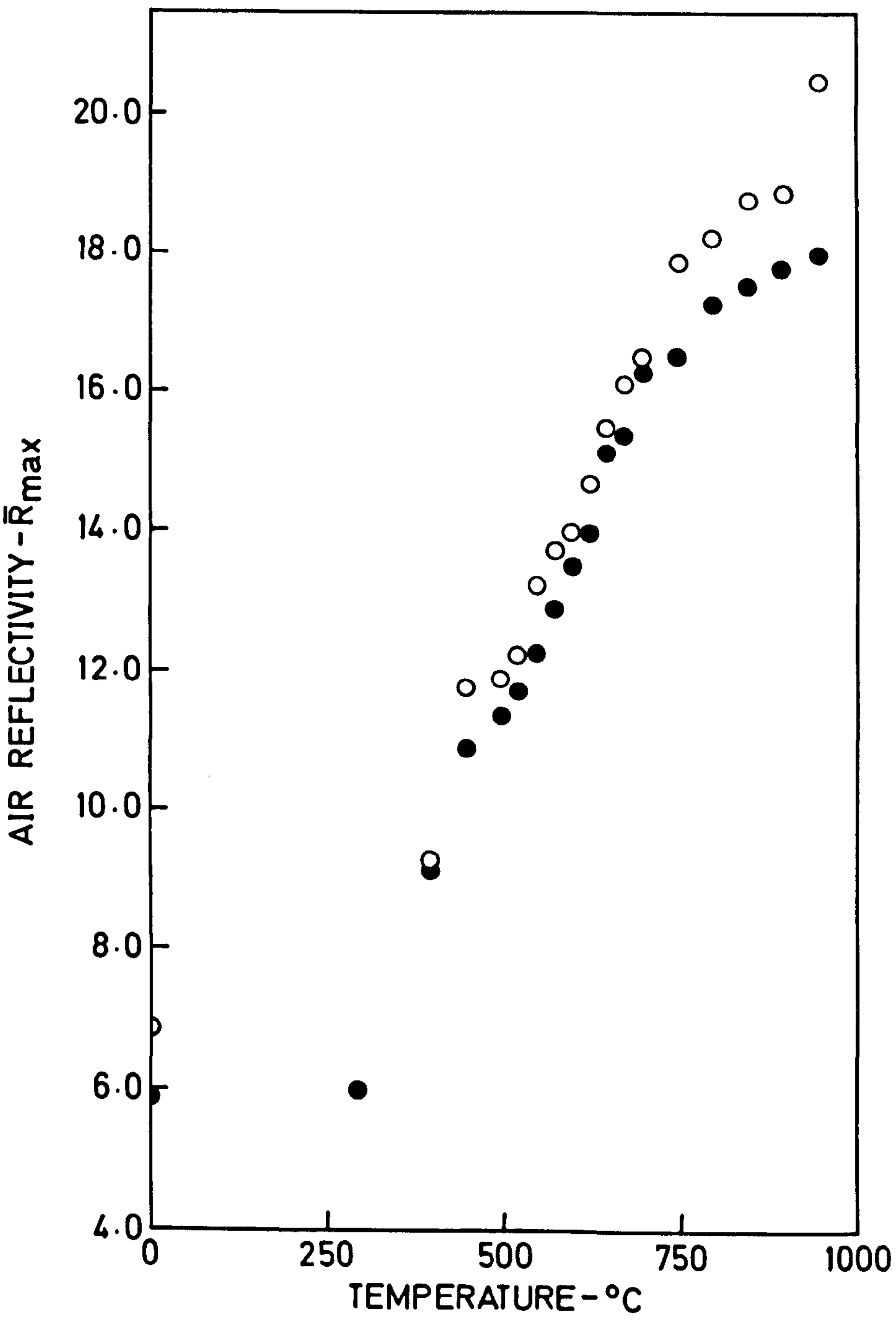
The air and oil reflectivity-temperature curves are described together because of the similarity in their trends.

The reflectivity-temperature curves of the carbonised residues of sporinites follow similar rising trends, the upper curve being for the higher-rank sporinite (Figs 85, 86) The differences between the two curves become more pronounced at temperatures above 650°C, the onset of molecular reorganisation in the solid state. The corresponding vitrinite curves only differ slightly from the sporinites over most of the temperature range (see Figs 90 and 91).

(b) Bireflectance (Figs 87, 92)

The bireflectance-temperature curves of carbonised

Fig 85 Variation with temperature of air reflectivity of low-rank and medium-rank sporinites carbonised up to 950°C.



SPORINITE
● %Carbon 83·0 (d.a.f.)
○ %Carbon 87·1 (d.a.f.)

Fig 86 Variation with temperature of oil reflectivity of low-rank and medium-rank sporinites carbonised up to 950°C.

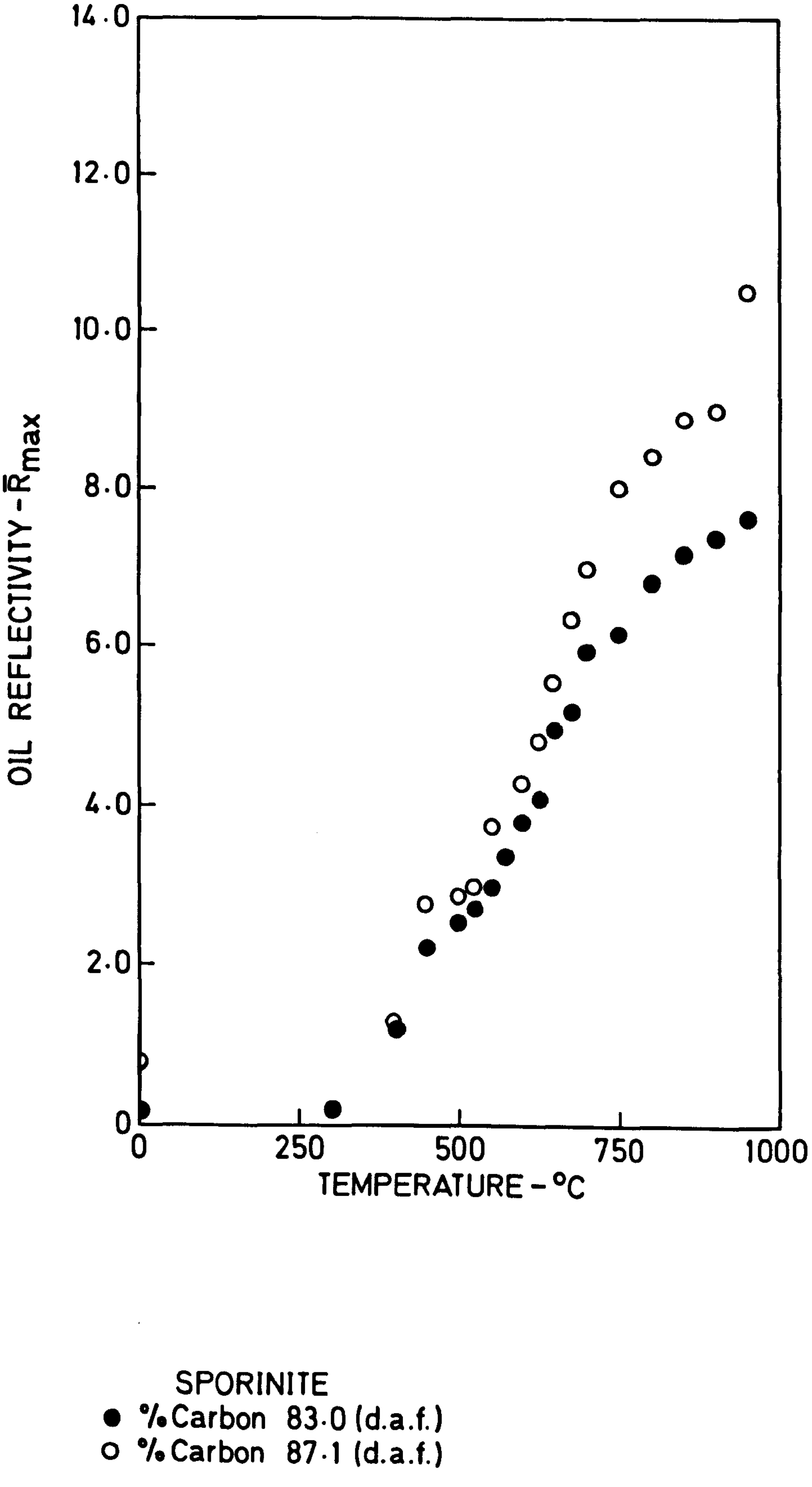
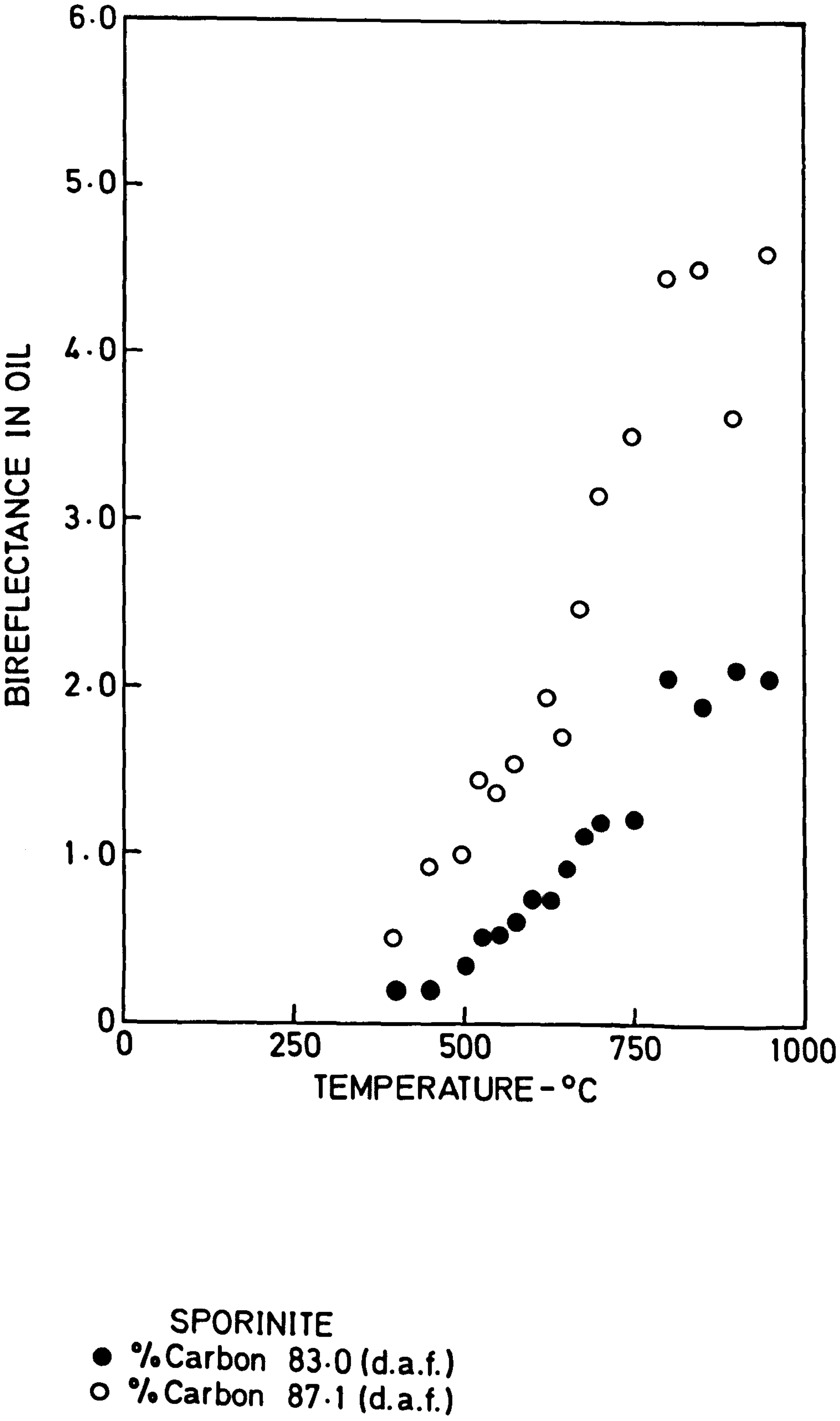

OIL REFLECTIVITY - $\bar{R}_{max}$
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
0
250
500
750
1000
TEMPERATURE - °C
SPORINITE
● %Carbon 83.0 (d.a.f.)
○ %Carbon 87.1 (d.a.f.)

Fig 87 Variation with temperature of oil bireflectance of low-rank and medium-rank sporinites carbonised up to 950°C.

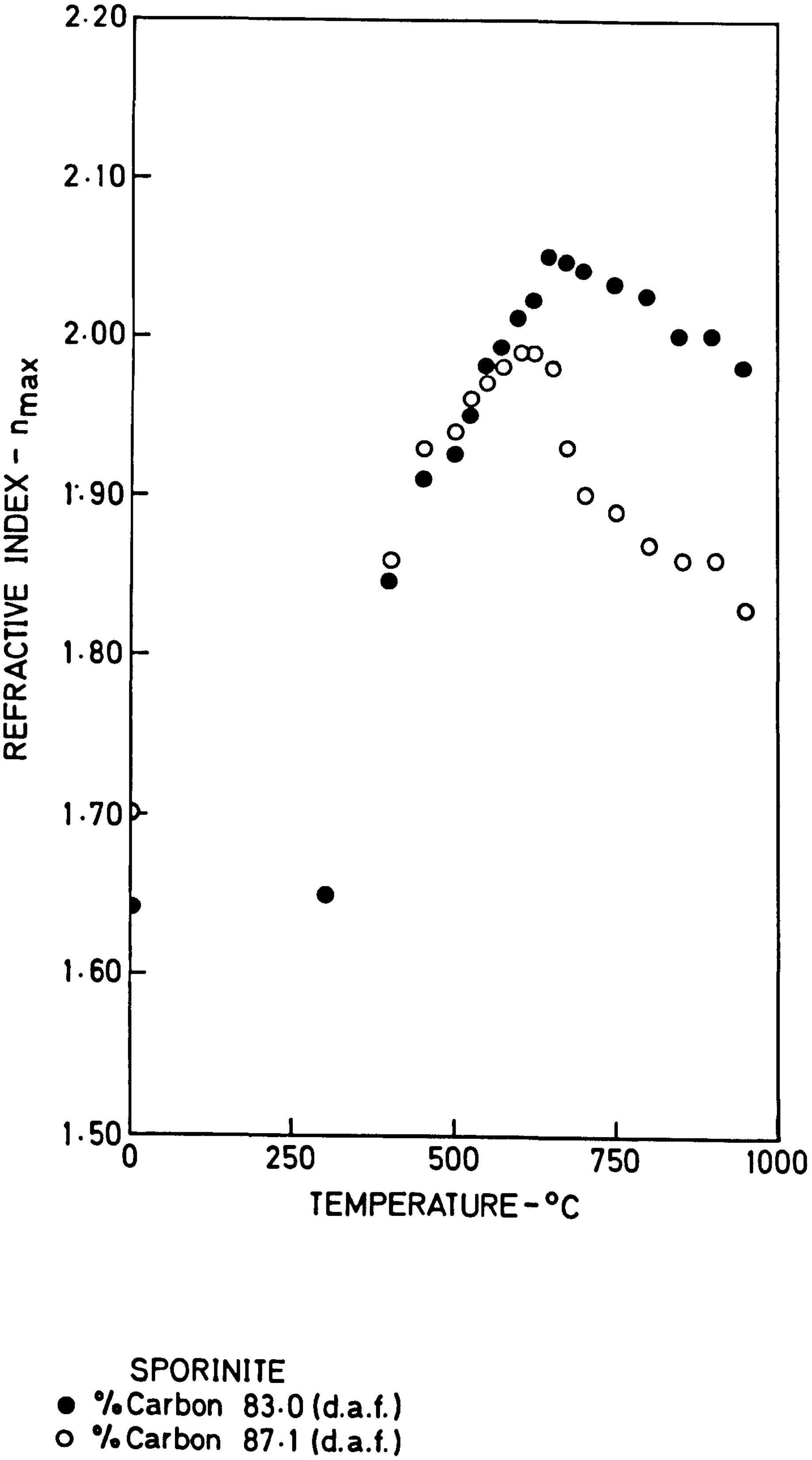

6·0
5·0
4·0
3·0
2·0
1·0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
SPORINITE
● %Carbon 83·0 (d.a.f.)
○ %Carbon 87·1 (d.a.f.)

sporinites again follow a rising trend, with the plot for the medium-rank sporinite at the higher level. Bireflectance rises slowly to about 500°C, then much more sharply to approximately 800°C, after which the rate of increase slows up to the highest temperature employed. There is a much greater contrast between the plots for the bireflectance of sporinites and vitrinites from the same coal than between the reflectivity plots, particularly at temperatures above 500°C (see Fig 92).

(c) Refractive Index (Figs 88 and 93)

The carbonised residues of the low-rank sporinite show a similar trend to the refractive index-temperature curves of non-graphitising vitrinites (Fig 13) (Goodarzi 1971; Goodarzi and Murchison 1972 and Part I of this Thesis.) The refractive index increases sharply between 300°C and 650°C and then decreases slowly with further rise of temperature to 950°C. The trend of the refractive index-temperature curve for the carbonised residue of the higher-rank sporinite also increases sharply to a maximum between 600° and 625°C, but does not reach the same level as the refractive index of the lower-rank sporinite; it then decreases more rapidly than the other sporinite curve with further increase of temperature to 950°C. The form of the refractive index-curve for the carbonised higher-rank sporinite is similar to the curve for graphitising vitrinites (see Goodarzi 1971; Goodarzi and Murchison 1972 and Fig 13). The refractive index curve of higher-rank sporinite also corresponds closely to the curve for vitrinite from the same coal.

Fig 88 Variation with temperature of refractive index of low-rank and medium-rank sporinites carbonised up to 950°C.


2·20
2·10
2·00
1·90
1·80
1·70
1·60
1·50
REFRACTIVE INDEX - n_{max}
0
250
500
750
1000
TEMPERATURE - °C
SPORINITE
● %Carbon 83·0 (d.a.f.)
○ %Carbon 87·1 (d.a.f.)

(d) Absorptive index (Figs 89 to 94)

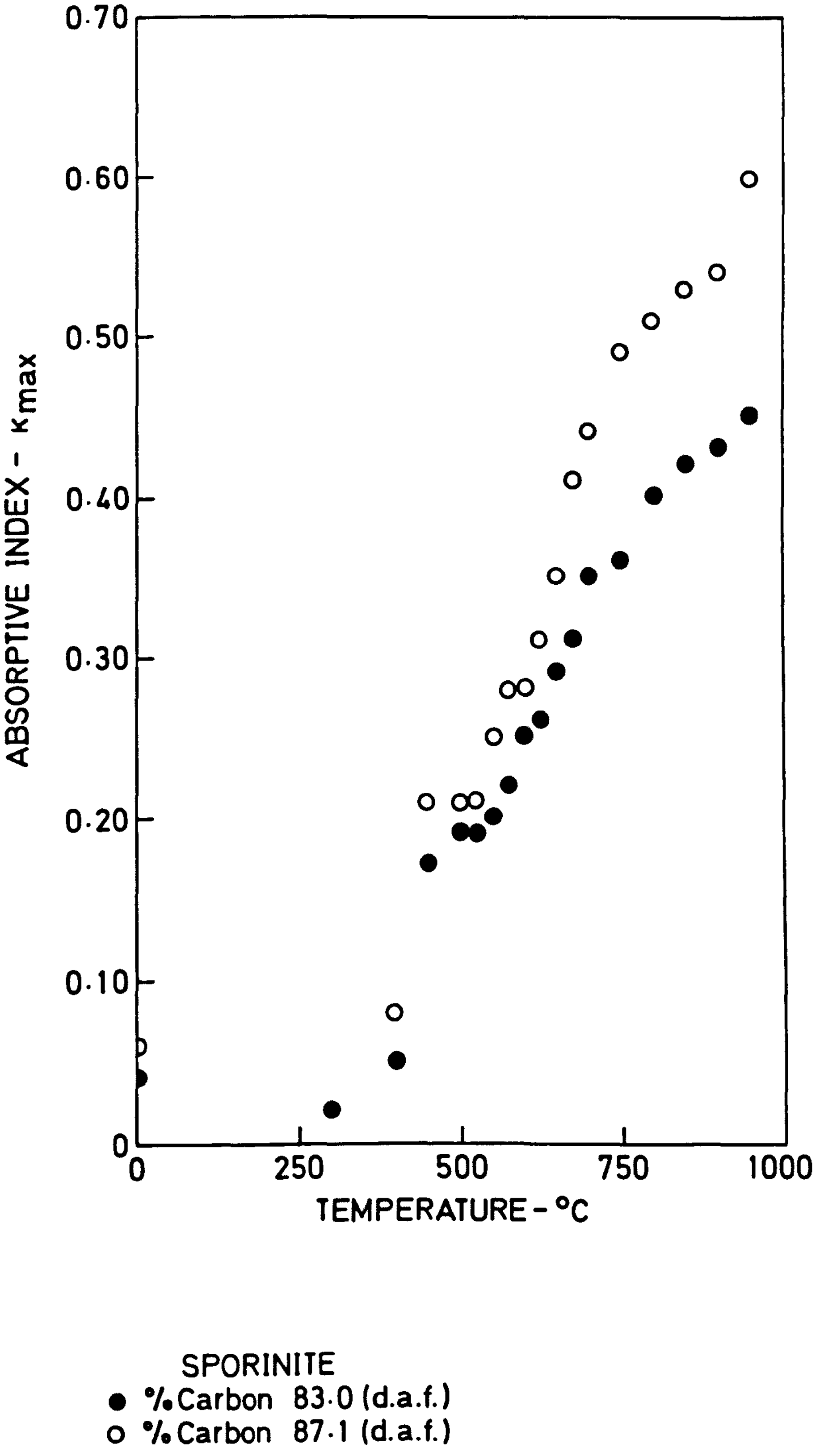
The absorptive index-temperature curves of carbonised residues of sporinites show similar variations to those of the reflectivity-temperature curves.

D. Discussion

1. Morphology (Plates 73 to 80)

The development of a fine-grained mosaic texture with random orientation of the mosaic units in the carbonised residues of the low-rank sporinite indicates that the plasticity of this sporinite is not high enough to promote the regular orientation of the mosaic units, which is normally observed with increase of carbonisation temperature in truly softening vitrinites (see for example Marshall and Murchison 1971 and Part III of this Thesis). In contrast, the high-rank sporinite develops a fine to coarse-grained mosaic texture and also a regular orientation of the granular mosaic units with increase of temperature, reflecting the higher level of plasticity of this sporinite. One interesting feature of the medium-rank sporinite is the development of large areas of very coarse-grained mosaic texture (Plates 76 - 78), which may be due to the melting and migration of isotropic sporinitic pitch and the development and growth of the mosaic texture in areas free of the inertinite that is present in small amounts in the carbonised residues of the sporinite. The influence of inert material on mosaic

Fig 89 Variation with temperature of absorptive index of low-rank and medium-rank sporinites carbonised up to 950°C.


0·70
0·60
0·50
0·40
0·30
0·20
0·10
0
ABSORPTIVE INDEX - κmax
0
250
500
750
1000
TEMPERATURE - °C
SPORINITE
● % Carbon 83·0 (d.a.f.)
○ % Carbon 87·1 (d.a.f.)

structure is to restrict the growth of the mesophase and hence to limit the size of the resulting mosaic structure (see for example Brown _et al._ 1964; Brooks and Taylor 1965 and Marsh _et al._ 1973).

The development of a larger granular mosaic with increase of sporinite rank is, according to the results of Goldring (1971), who reports the development of coarse-grained mosaic in durainous coal, probably also due to decrease of oxygen content and to increase in aromaticity (see also Sanada 1973). This observation further supports the results of Melvin (1974) who attributed the coarse-grained mosaics found in thermally metamorphosed Northumbrian coal to exinitic material.

2. Optical Properties

(a) Reflectivity (Figs 85, 86, 90 and 91)

Dormans _et al._ (1957) and van Krevelen (1961) found that the reflectivity of fresh sporinites increases with rank, generally in the same way as the vitrinite reflectivity increases with rise of rank. Since rise of vitrinite reflectivity during coalification and/or carbonisation is directly related to increase in aromaticity of the vitrinite and/or carbonised residues, then presumably the increase in reflectivity of sporinites during carbonisation can also be related to rise of aromaticity. Recent results of Khavari (1975) show that the reflectivity of carbonised gilsonite pitch increases sharply

Fig 90 Generalised curves for variation with temperature of air reflectivity of carbonised sporinite and vitrinite in low and medium-rank bituminous coals.

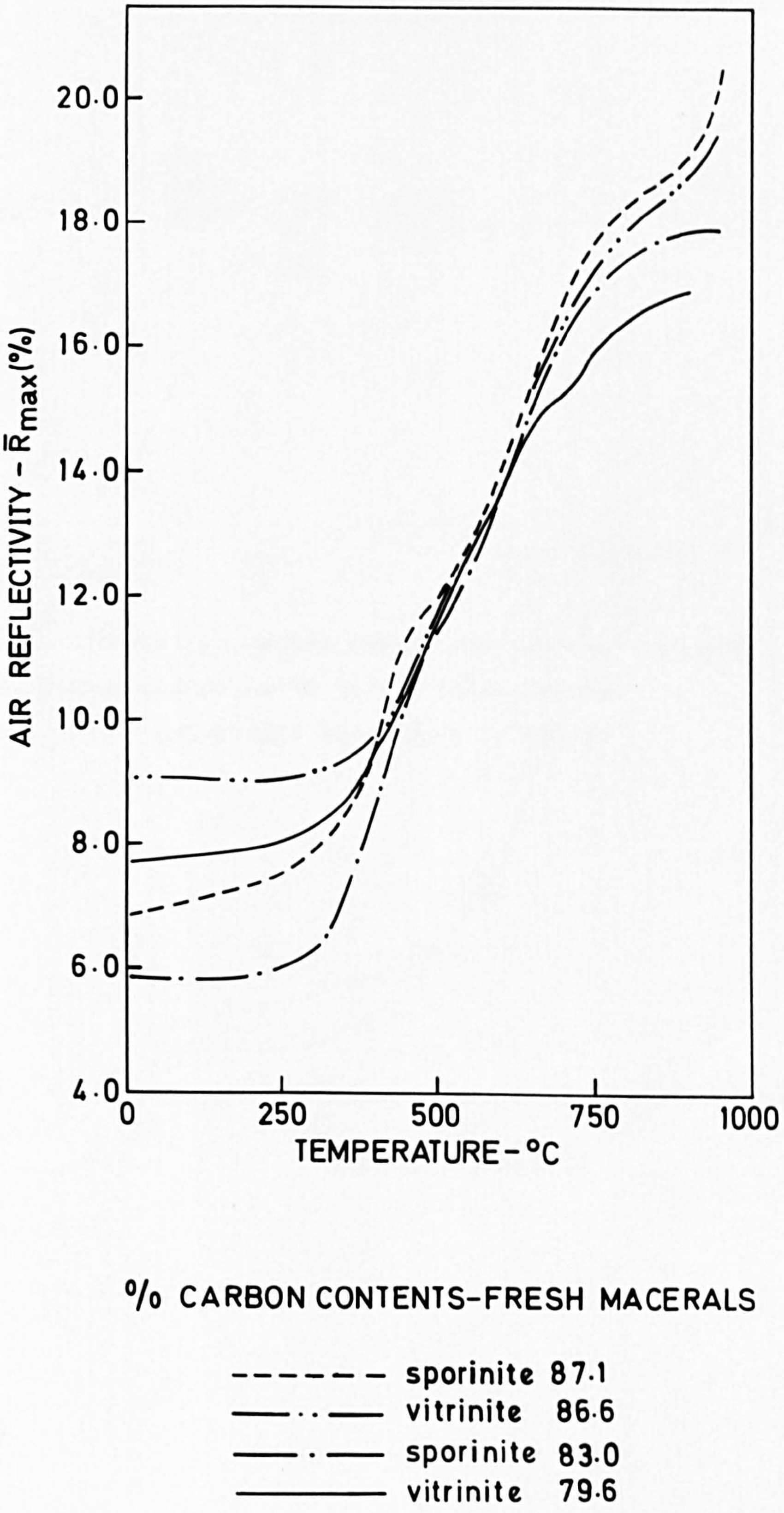
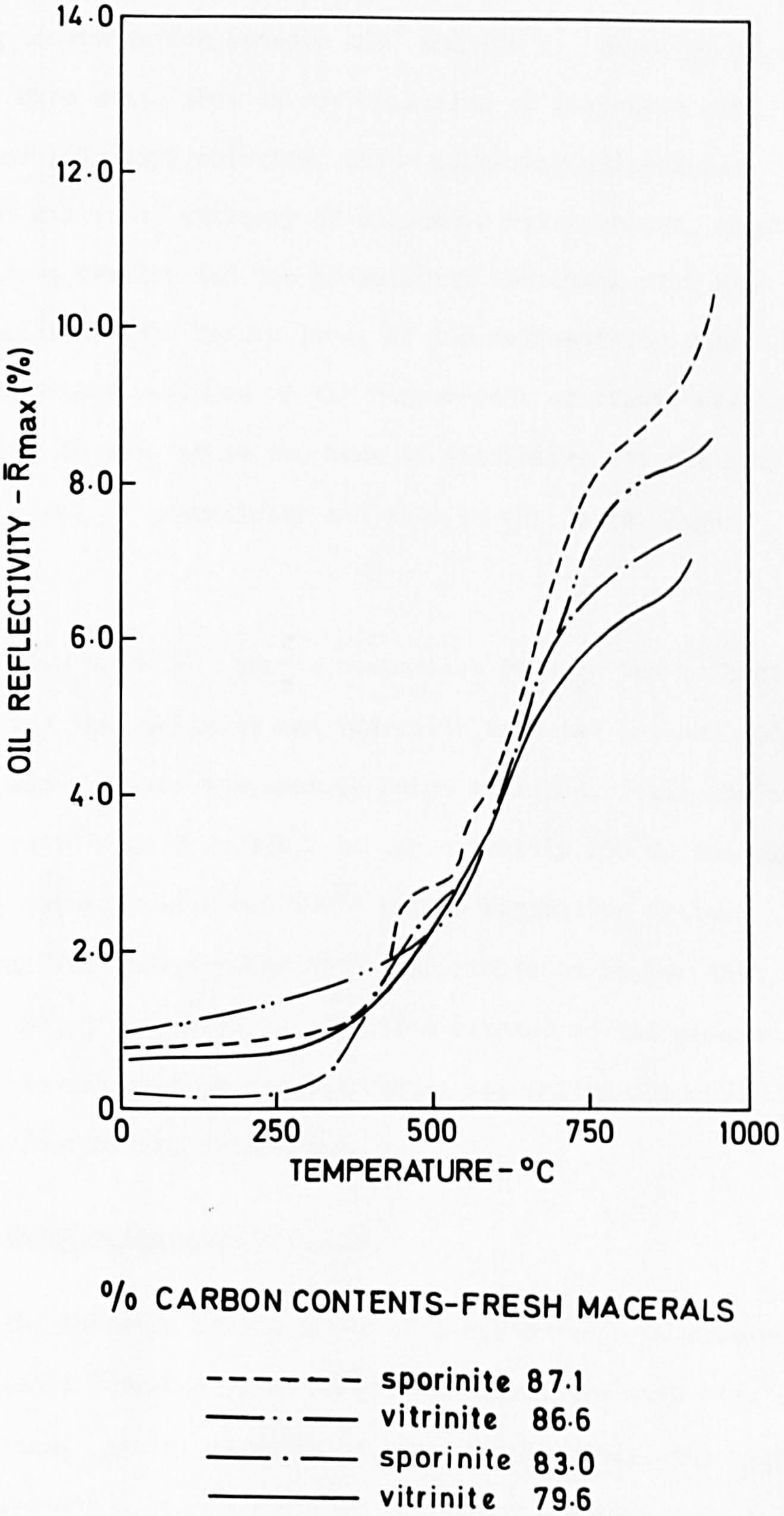

AIR REFLECTIVITY - $\bar{R}_{max}$(%)
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
0
250
500
750
1000
TEMPERATURE - °C
% CARBON CONTENTS-FRESH MACERALS
sporinite 87.1
vitrinite 86.6
sporinite 83.0
vitrinite 79.6

Fig 91 Generalised curves for variations with temperature of oil reflectivity of carbonised sporinite and vitrinite in low and medium-rank bituminous coals.


14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
OIL REFLECTIVITY - $\bar{R}_{max}$ (%)
0
250
500
750
1000
TEMPERATURE - °C
% CARBON CONTENTS-FRESH MACERALS
sporinite 87.1
vitrinite 86.6
sporinite 83.0
vitrinite 79.6

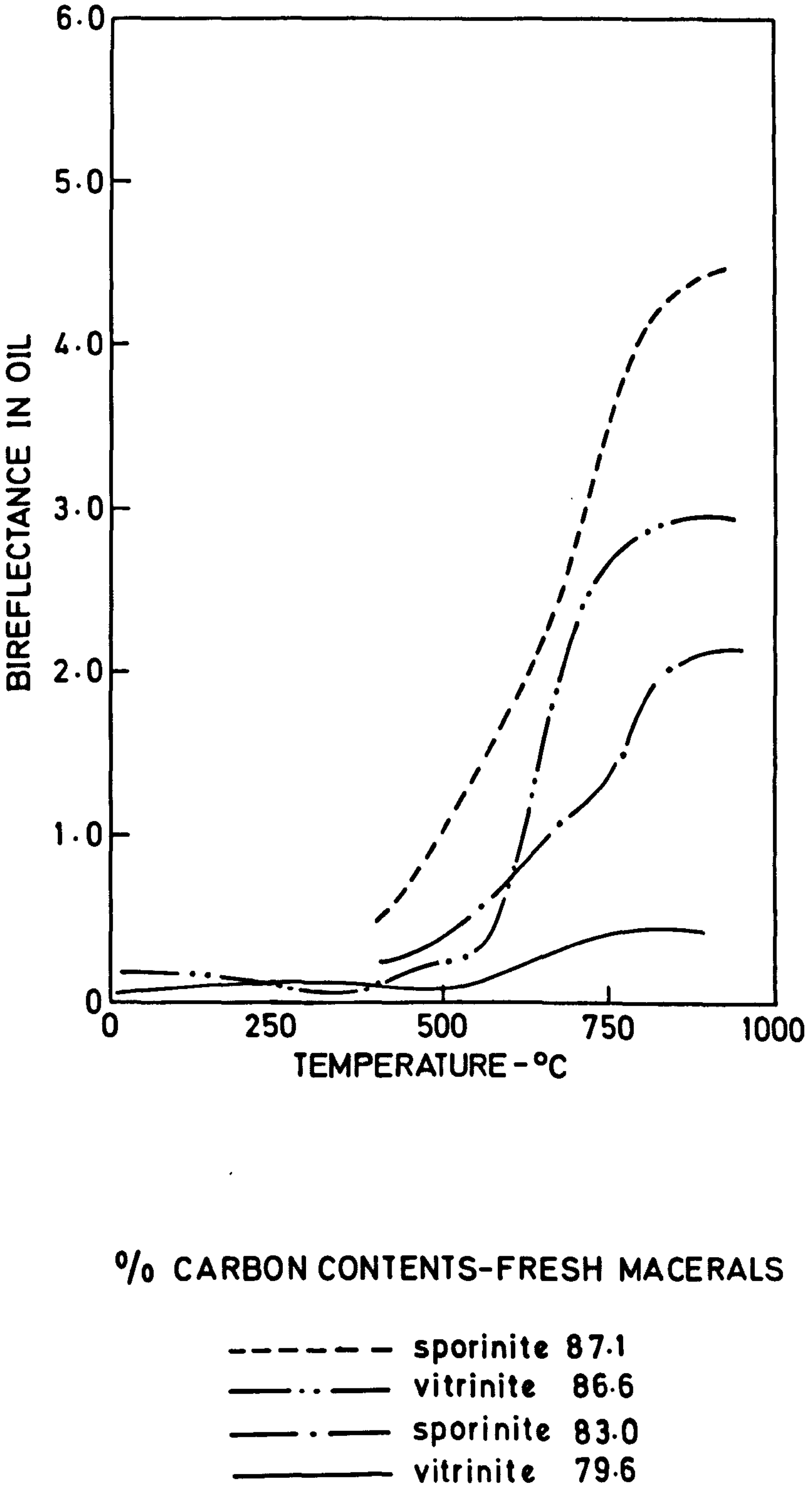
during carbonisation between 400° and 900°C. Marsh et al. (1971) also state that on carbonisation of gilsonite with pitch or polyvinyl chloride, whose molecular structures consist mainly or entirely of aliphatic hydrocarbons, aromatic structures develop and the aromaticity increases with rise of temperature. The higher level of the reflectivity curve for the carbonised residues of the higher-rank sporinite will almost certainly be due, as in the case of vitrinites, to the initial higher level of aromaticity and also to the larger layer diameter.

Figs 90 and 91 show a comparison between the reflectivity curves for the sporinite and vitrinite from the low and medium-rank coals over the temperature range employed. All the curves show a rapid rise from 500°C to approximately 950°C, the curves running together to about 600°C before separating again. For each coal the reflectivity of the sporinite is higher than the corresponding vitrinite, a situation related to the greater plasticity achieved by the individual sporinites compared with their corresponding vitrinites.

(b) Bireflectance (Figs 87, 92)

The increase in the level of bireflectance is related to increased ordering of the molecular structure with rise of temperature. Again, as with carbonised vitrinites, the higher-rank sporinite displays a higher degree of ordering than the lower-rank sporinite at any temperature level with the bireflectance

Fig 92 Generalised curves for variation with temperature of oil bireflectance of carbonised sporinite and vitrinite in low and medium-rank bituminous coals.


6·0
5·0
4·0
3·0
2·0
1·0
0
BIREFLECTANCE IN OIL
0
250
500
750
1000
TEMPERATURE - °C
% CARBON CONTENTS-FRESH MACERALS
------ sporinite 87·1
——··—— vitrinite 86·6
——·—— sporinite 83·0
———— vitrinite 79·6

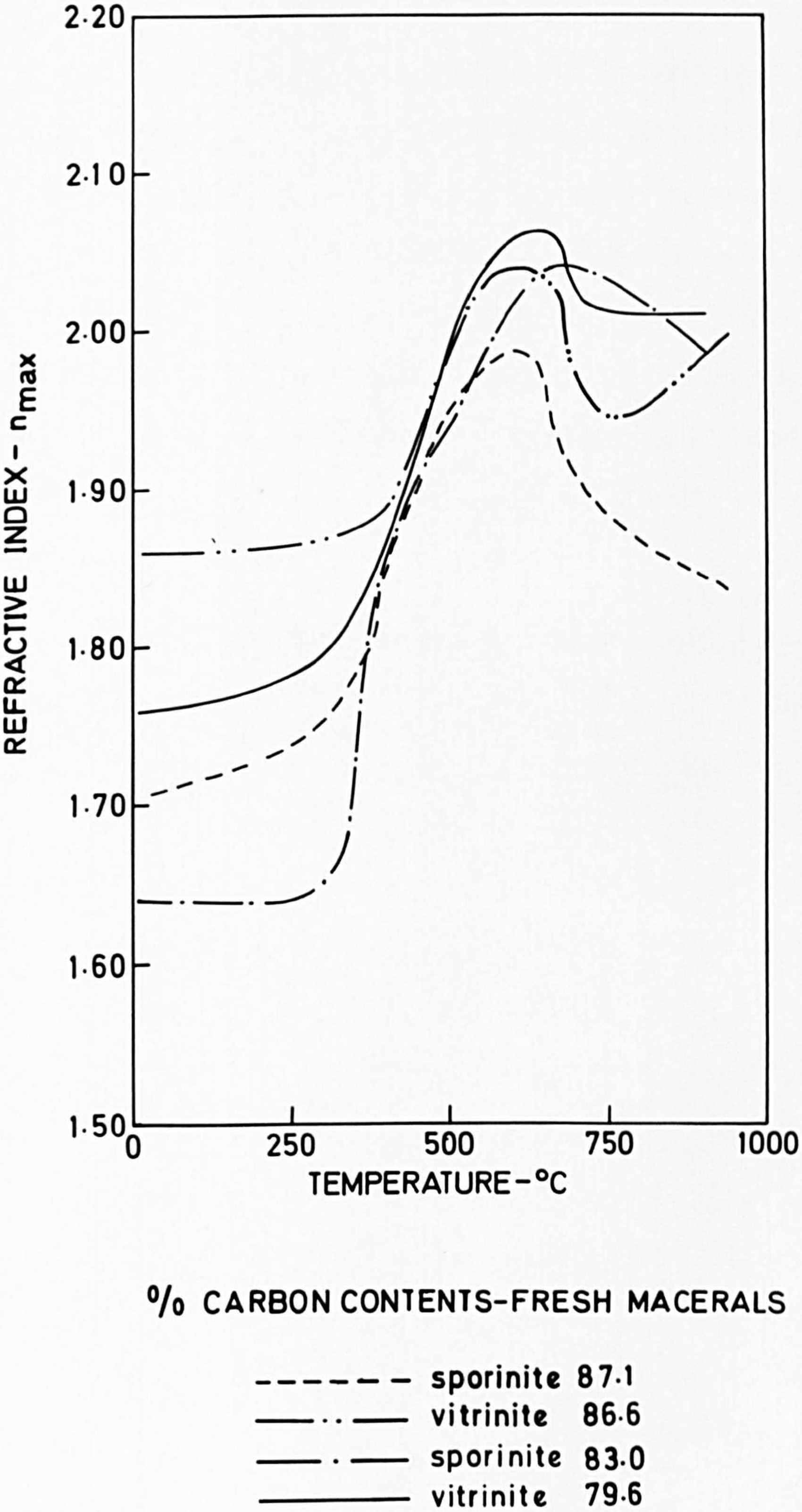
difference progressively increasing. Although in terms of a quantitative measurement of bireflectance the higher-rank sporinite is essentially isotropic when fresh, the higher bireflectance at all temperatures suggests a higher degree of initial ordering than in the low-rank sporinite, as well as a higher initial plasticity.

The same relationships as exist between the reflectivity-temperature curves for sporinites and their corresponding vitrinites are much more obvious between the bireflectance curves for the carbonised residues (see Fig 92). Although sporinite from the low-rank coal (vitrinite: carbon = 79.6% daf) develops considerable bireflectance, the level attained still does not approach that of the relatively highly softening vitrinite (carbon = 86.6% daf) from the caking coal. What is clear, however, is that for any coal and for the same carbonisation conditions, the bireflectance of sporinite will be higher than that of the associated vitrinite. The higher level of bireflectance of sporinite than its corresponding vitrinite is in agreement with the findings of Alpern (1956) who states that on carbonisation the anisotropy of sporinite (exinite) will be higher than vitrinite.

(c) Refractive index (Figs 88, 93)

Goodarzi and Murchison (1972) established that the behaviour of the refractive index-temperature curve of vitrinites

Fig 93 Generalised curves for variation with temperature of refractive index of carbonised sporinite and vitrinite in low and medium-rank bituminous coals.


2·20
2·10
2·00
1·90
1·80
1·70
1·60
1·50
REFRACTIVE INDEX - n_{max}
0
250
500
750
1000
TEMPERATURE - °C
% CARBON CONTENTS-FRESH MACERALS
sporinite 87·1
vitrinite 86·6
sporinite 83·0
vitrinite 79·6

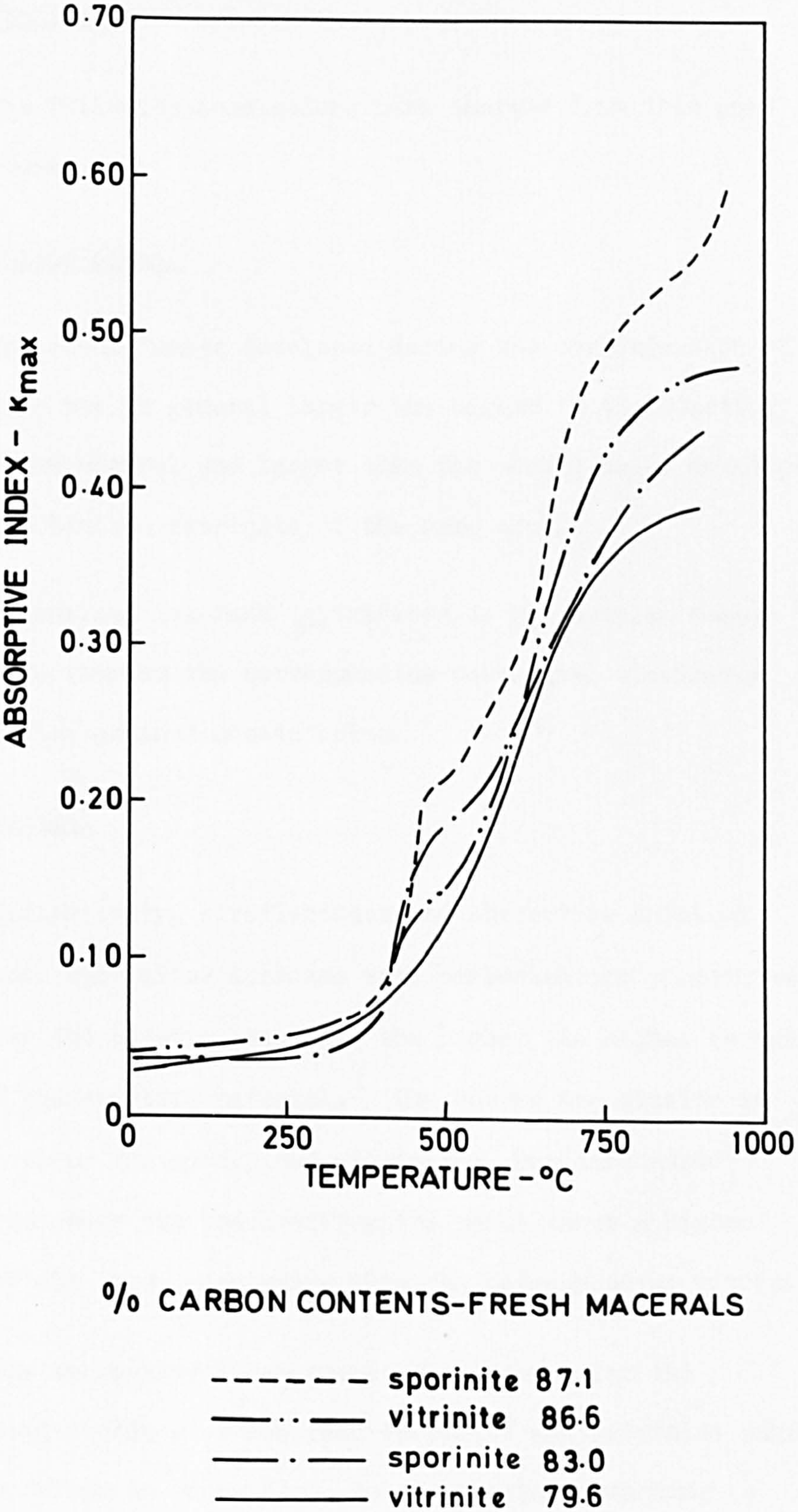
on carbonisation is related to changes in molecular structure, especially to the crystallite height and to the packing of the aromatic lamellae. The results of Cartz and Hirsch (1956) suggest that the molecular structure of exinite (sporinite) is basically similar to that of vitrinite, although exinite is les well-ordered, having smaller aromatic layers and more amorphous material than vitrinite. Thus it is not surprising that the refractive index-temperature curve for carbonised sporinite in general follows a similar trend to that of carbonised vitrinite.

The trend of the refractive index curve of the medium-rank sporinite on carbonisation indicates similar molecular structural changes to those undergone by a softening vitrinite, while the trends of the refractive-index curve of the carbonised low-rank sporinite follows a similar path to that of a non-softening vitrinite. During carbonisation a non-softening vitrinite develops a high level of crystallite height (apparent from the higher level of refractive index) while the subsequent breakdown of the molecular structure with further rise of temperature is not as rapid as for the softening vitrinite. The present work indicates that the carbonised sporinite residues display similar molecular changes to the carbonised vitrinite residues of appropriate rank. Indeed, the recent work of Khavari (1975) shows that carbonaceous materials of quite different origin from coal, such as gilsonite pitch, shungite, etc. behave, during carbonisation, similarly to vitrinites of appropriate rank. Fig 93 compares curves for carbonised sporinites with those for the corresponding vitrinite. The relative degree of softening of these macerals can be deduced from (a) the breadth of the curves, (b) their heights, and (c) their shapes. The refractive index curves support the interpretations based on bireflectance, namely that at this particular rate of heating (5°C/min), the medium-rank sporinite is the most fluid, followed by the medium-rank vitrinite, then the two low-rank macerals.

(d) Absorptive Index (Figs 89 and 94)

Changes in the absorptive index-temperature curves are due to increase in the aromatic-layer diameters (Hirsch 1954). On this basis the results indicate that the sporinite of higher initial rank has a larger layer diameter at any temperature level than the carbonised low-rank sporinite and that the difference between these layer diameters becomes greater with temperature rise. Fig 94 indicates that if the layer diameter is directly correlated with absorptive index, then the layer diameters of the sporinites and vitrinites, which appear to be approximately the same at the start of carbonisation, gradually separate from one another with rising temperature, so that the medium-rank sporinite at 950°C has the largest diameter at 950°C.

Fig 94 Generalised curves for variation with temperature of absorptive index of carbonised sporinite and vitrinite in low and medium-rank bituminous coals.


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 MACERALS
sporinite 87.1
vitrinite 86.6
sporinite 83.0
vitrinite 79.6

E. Conclusion

The following conclusions have emerged from this part of the work:

1. Morphological

(a) The mosaic units developed during the carbonisation of sporinites are in general larger the higher is the starting rank of the maceral and larger than the mosaic units developed by the carbonised vitrinite of the same coal.

(b) Carbonised low-rank vitrinites do not develop mosaic structure, whereas the corresponding carbonised sporinites develop fine-grained mosaic units.

2. Optical

(a) Reflectivity, bireflectance and absorptive index of carbonised sporinites increase with carbonisation temperature and after the plastic stage are the higher the higher is the rank of the starting material. The curves are similar in form to those for carbonised vitrinites, but carbonised sporinite above the resolidification point shows a higher level of all these parameters than the corresponding vitrinite.

(b) The refractive index-temperature curves for the carbonised residues of low-rank sporinite and vitrinite exhibit similar trends to those for a non-graphitising carbon, in contrast to the refractive index curves for carbonised high-rank sporinite and vitrinite which behave similarly to thoseof a graphitising carbon.

2. OPTICAL PROPERTIES OF SPORINITES IN A VITRINITE AND SPORINITE MIXTURE

A. Introduction

In the previous section contrasts were drawn between the molecular structures of the carbonised residues of sporinite and vitrinite of the same coals based on variation of optical properties. For the same carbonisation conditions, carbonised residues of sporinite eventually develop better ordered molecular structures than do carbonised vitrinites from the same coal, due to the greater level of plasticity of sporinite than vitrinite. It is unlikely, however, that in the study of metallurgical cokes, for example, that discrete mosaics developed from individual macerals can be studied, so in this next section there is description and discussion of the morphology and optical properties of mixtures of equal parts of sporinite and vitrinite from the same coal carbonised under the same conditions as for the sporinites and vitrinites separately.

B. Previous Related Studies

Interactions between coal macerals have been studied by Alpern (1956); van Krevelen *et al.* (1959); Brown *et al.* (1964); Mackowsky (1967) and Jukes and Wilmers (1973).

Alpern (1956) examined the anisotropy developed in different ranks of coal (V.M. = 18 to 41%) in mixtures when carbonised and concluded that the blending of softening (anisotropic) and non-softening (isotropic) coals produces a transition zone, resulting in a reduction of anisotropy of the softening coal in the transition zone. The transition zone between two softening coals of different rank is wider and the reaction between them is more extensive than the reactions between the non-softening and softening coals, but the anisotropy is still reduced in the transition zone. The decrease in anisotropy is thought to be due to the 'diffusion of solution phenomena' between the two coals at their contacts, not due to the effect of evolution of volatiles, because when volatile matter, that is released by separately carbonising non-softening coal (V.M. = 41%), passes through a carbonising softening coal (V.M. = 28%) no reduction in anisotropy of the softening coal takes place. However, this experiment by Alpern is not the same as carbonising an intimate mixture of the two coals together, where the individual particles are in direct contact with one another. Considering the swelling and internal pressure developed by a non-softening coal, its volatile matter, and particularly the composition of the volatiles which diffuse, must have some effect on the immediately surrounding particles.

Van Krevelen et al. (1959) reported that exinite in an exinite/vitrinite mixture of the same rank has an additive effect on the dilatation of the resulting residues (Fig 84). The effect of inertinite is to reduce the dilatation of exinite when in an inertinite/exinite mixture. The results of Brown et al. (1964) show that the size of mosaic unit developed by vitrinite diminish at boundaries with inertinite. Mackowsky (1967), examining the plastic behaviour of exinites and vitrinite in coal during carbonisation, shows that exinite reduces the viscosity of vitrinite, whereas exinite disappears when associated with inertinite, leaving a porous texture. Finally, Jukes and Wilmers (1973) state that interaction between blend components exert some effect on the mosaic size, but the authors do not make it clear whether this effect is an increase or decrease of the mosaic size.

The above results indicate that mixtures of macerals result in a decrease of the plasticity of the maceral which is more fluid (e.g. exinite) and an increase of the one which is less fluid (e.g. vitrinite). In Part III of this Thesis the size of mosaic unit developed by vitrinite during carbonisation was related to its degree of plasticity (see also Abramski and Mackowsky 1952); thus decrease in the level of plasticity of sporinite/vitrinite mixtures should result in a smaller mosaic size. Brooks and Taylor (1965) also demonstrate that the growth of spherical mesophase in coal-tar pitch is inhibited by introducing fine carbon black-like residue (insoluble material), resulting in poor graphitisability. In view of this, it can be concluded that the presence of inert or less plastic material, such as inertinite and/or vitrinite of the same coal associated with sporinite will result in a decrease in plasticity. The optical properties, which are influenced by the degree of plasticity should be correspondingly modified.

C. Results. Description

1. Introduction

The curves which relate to the following descriptions arise from measurements on the following materials:-

(a) carbonised residues of sporinites; these are generalised curves from plots of measurements already recorded in Figs 85 to 89 - these curves are only used for comparison in Figs 102 to 106.

(b) areas resulting from carbonisation of sporinite in the sporinite-vitrinite mixtures (see typical area in Plate 90), and

(c) areas which still obviously arise from carbonised vitrinite in the sporinite-vitrinite mixtures (see typical area in Plate 90).

On the text Figures the contraction 'vitrinite-sporinite mix' and 'sporinite-vitrinite mix' have been used to denote measurements taken on areas arising from carbonised vitrinite and sporinite respectively (see also Plate 90).

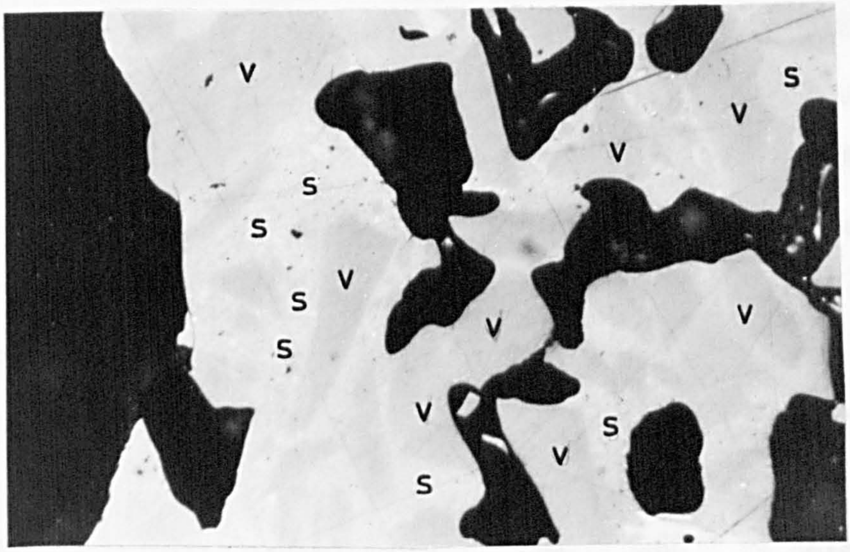


Plate 90 Typical areas resulting from sporinite and vitrinite in a carbonised sporinite and vitrinite mixture

(s) sporinite

(v) vitrinite

2. Morphology

The carbonised residues of both blends of sporinite and vitrinite from low-rank and medium-rank coal become coherent at 400°C (Plates 81b and 85b).

(a) Low-rank blend: the size of the vacuoles varies, but generally increases with rising carbonisation temperature. The sporinite residue in the blend develops fine-grained mosaic textures, whereas the vitrinite residues remain isotropic or become slightly anisotropic with increase of temperature (Plates 81c to 85). The carbonised sporinite develops a finer mosaic pattern at the peripheries of the vitrinite particles. A narrow 'reaction zone' is developed between the carbonised residues of sporinite and vitrinite in the mixture, which is recognisable by the progressive decrease in mosaic size at the peripheries of vitrinite particles. The intensity of anisotropy of both carbonised macerals in the blend increases with rise of temperature.

(b) Medium-rank blend: the size of vacuoles varies but again generally increases with rise of carbonisation temperature. The residues develop a more homogeneous morphology in comparison with the low-rank blend and generally the coke wall is thicker than in the low-rank blend. The carbonised residues of both macerals develop a mosaic structure at 450°C, but the vitrinitic residues develop only a very fine-grained mosaic, whereas the sporinitic residues show a fine- to medium-grained mosaic

(Plate 85c). A wider 'reaction zone' is developed between the carbonised residues of sporinite and vitrinite in the blend, which is recognisable by the progressive decrease in mosaic size from the carbonised sporinite towards the vitrinitic residues (see Plates 86 to 89). The intensity of anisotropy of carbonised residues of both macerals increases with rise of carbonisation temperature.

3. Optical Properties

(a) Reflectivity (Figs 95 to 98; 102 and 103)

The pattern for air reflectivity is not as distinct as for oil reflectivity.

(i) Low-rank Blend (vitrinite: carbon = 79.6% daf)(Figs 95; 96; 102; 103)

The reflectivity-temperatures curves for the carbonised residues of the vitrinite in the mixture follow an upward and almost similar trend to that of the carbonised sporinite in the mixture up to 700°C, when differentiation between the two curves becomes distinct up to higher temperatures. The reflectivity trend of the sporinite carbonised separately follows a similar path to the residue of the sporinite in the mixture up to 750°C, when the reflectivity paths divide, with the separately carbonised sporinite being higher up to 900°C.

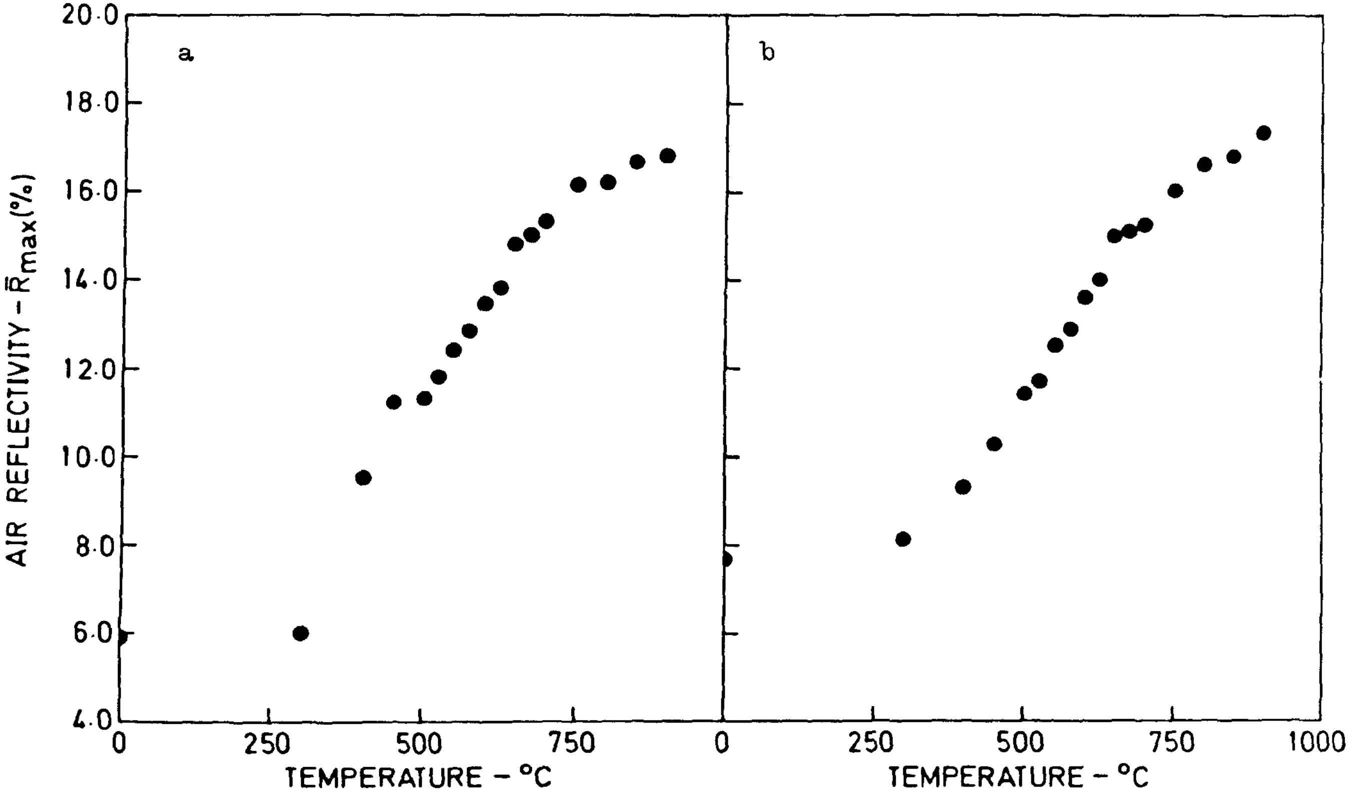
(ii) Medium-rank Blend (vitrinite: carbon = 86.6% daf) (Figs 87, 98 and b102, 103)

Virtually the same trends as for the low-rank sporinite and vitrinite are displayed here, but separation of the sporinite curves from the vitrinite begins much earlier (500°C) and the two sporinite tracks separate at approximately 700°C. Again the pattern for air reflectivity is not as distinct as for oil reflectivity.

Fig 95 Variation with temperature of air reflectivity of carbonised sporinite and vitrinite from a low-rank bituminous coal

(a) sporinite

(b) vitrinite



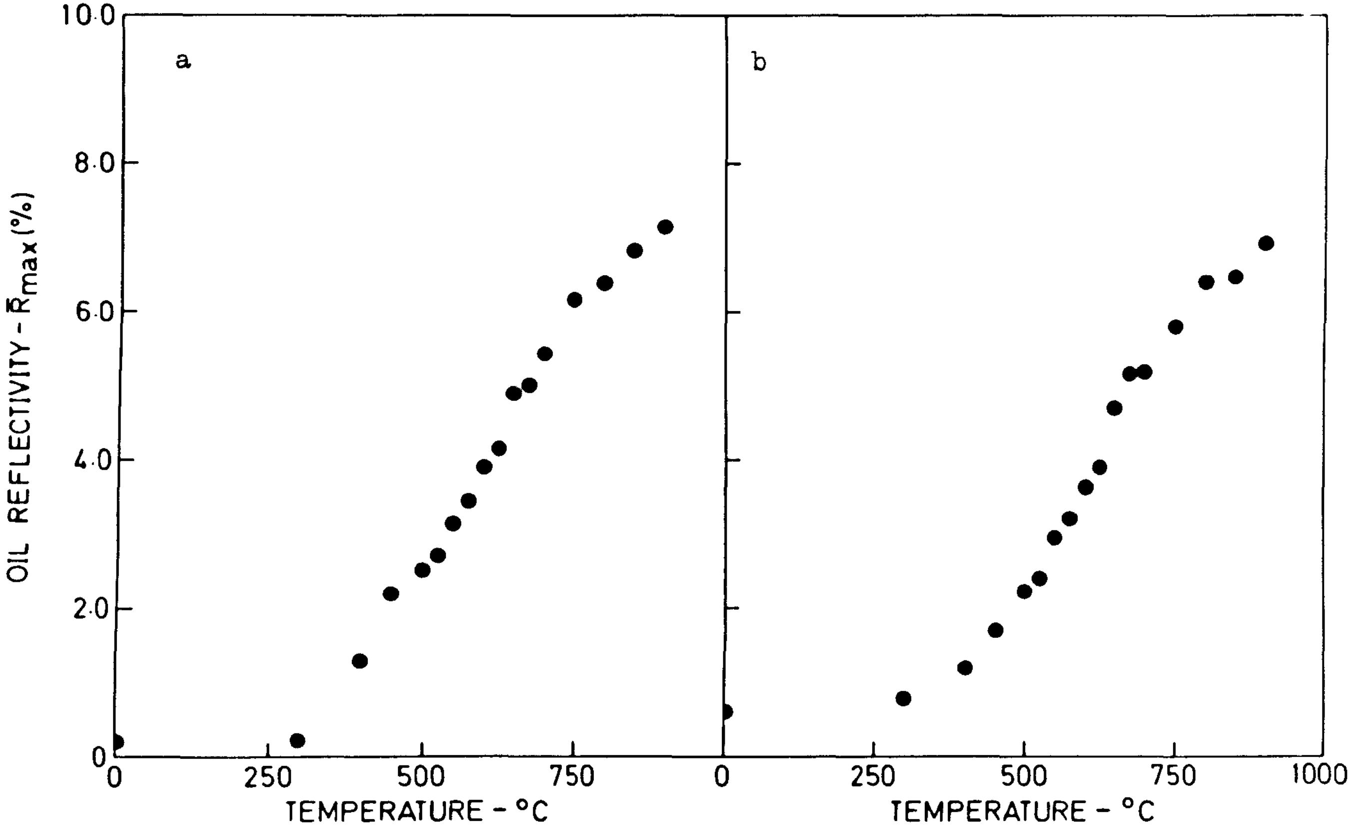
LOW RANK COAL

sporinite % carbon 83·0 (d.a.f)

vitrinite % carbon 79·6 (d.a.f)

Fig 96 Variation with temperature of oil reflectivity of carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from a low-rank bituminous coal

(a) sporinite
(b) vitrinite



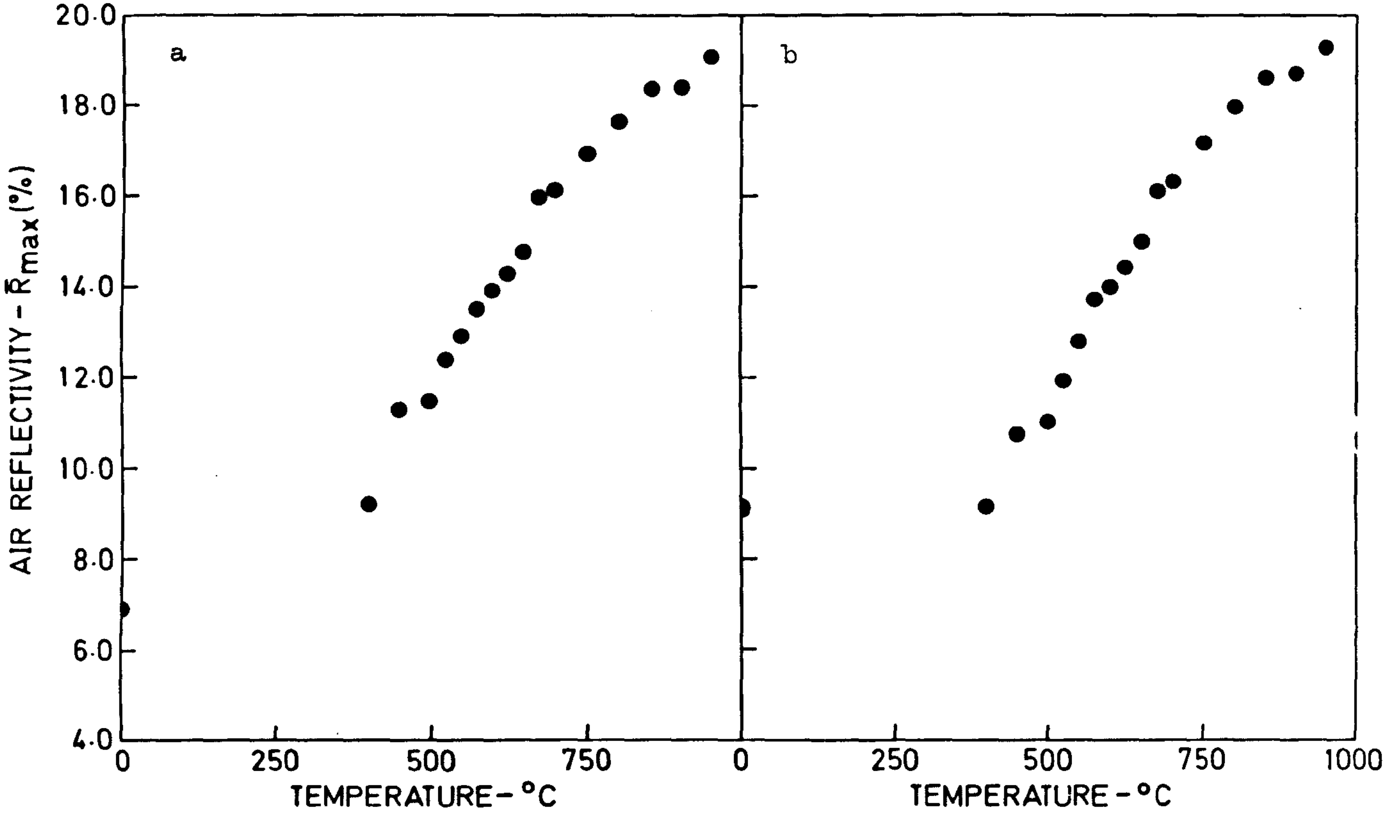
LOW RANK COAL

sporinite % carbon 83.0 (d.a.f)

vitrinite % carbon 79.6 (d.a.f)

Fig 97 Variation with temperature of air reflectivity of carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from a medium-rank bituminous coal

(a) sporinite
(b) vitrinite



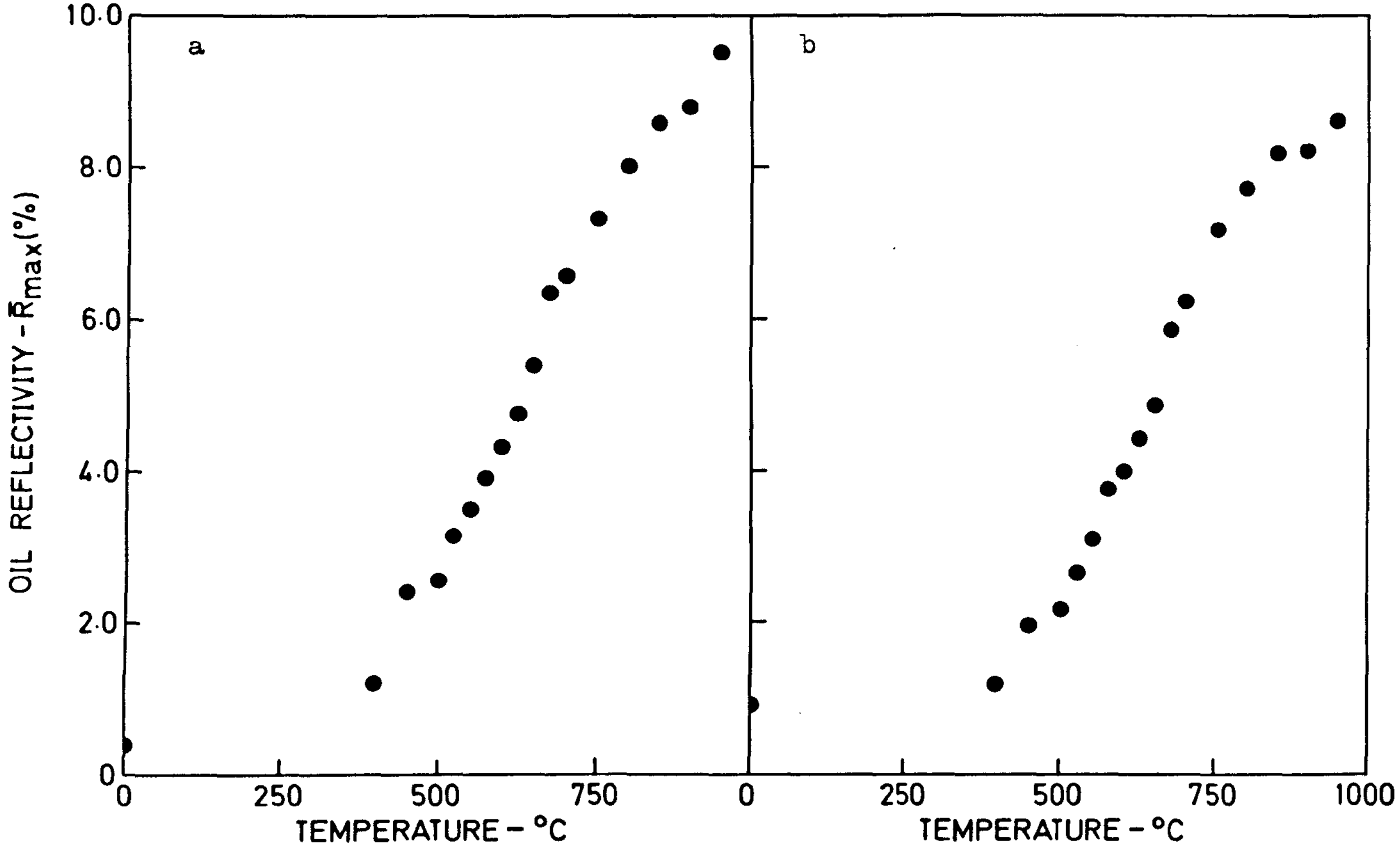
MEDIUM RANK COAL

sporinite%carbon87.1(d.a.f)

vitrinite%carbon 86.6(d.a.f)

Fig 98 Variation with temperature of oil reflectivity of carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from a medium-rank bituminous coal

(a) sporinite
(b) vitrinite



MEDIUM RANK COAL

sporinite%carbon87.1(d.a.f)

vitrinite%carbon 86.6(d.a.f)

(b) Bireflectance (Figs a and b 99: 104)

(i) Low-rank coal (Figs a99: 104)

The bireflectance-temperature curves for the separately carbonised sporinite and the sporinite and vitrinite carbonised together follow similar paths up to 450°C. The differences between the three curves increase from this temperature up to 900°C, with the separately carbonised sporinite bireflectance being highest, those for the vitrinite residues being the lowest.

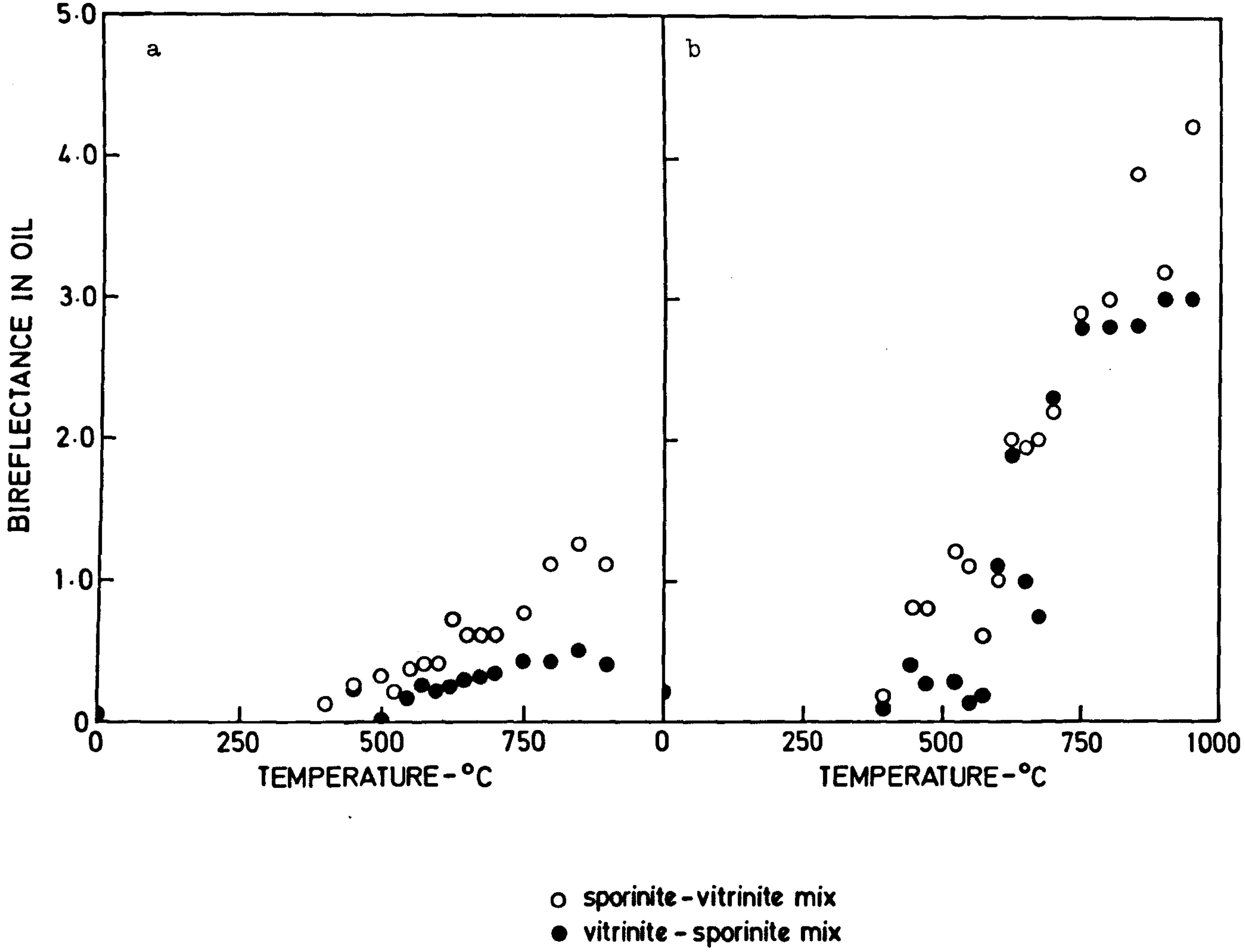
(ii) Medium-rank coal (Figs b99: 104)

A similar pattern applies to the medium-rank coal, but the rate of bireflectance increase for all three tracks is much greater. The individual plots, however, while showing considerable scatter, still allow tracks to be drawn.

Fig 99 Variation with temperature of oil bireflectance of carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous

(b) medium-rank bituminous



vitrinite %carbon 79·6 (d.a.f.)
sporinite %carbon 83·0 (d.a.f.)

vitrinite % carbon 86·6 (d.a.f.)
sporinite %carbon 87·1 (d.a.f.)

(c) Refractive Index (Figs a and b 100: 105)

(i) Low-rank coal (Figs a100 and 105)

The refractiveindex-temperature curves of the carbonised residues of sporinite and the carbonised residues of sporinite and vitrinite in the mixture follow similar trends to that of carbonised non-graphitising vitrinite (Fig. 13). All the curves show the broad shape characteristic of macerals which have not truly softened. It is the curve for sporinite carbonised in the mixture which shows the greatest departure, which, although havings its maximum value at approximately the same temperature as the separately carbonised sporinite, only reaches a level substantially lower than that for the separately carbonised sporinite, or indeed the refractive index of the carbonised vitrinite in the mixture.

(ii) Medium-rank coal (Figs b100 and 105)

The curves here follow trends similar to that for graphitising vitrinite at a low rate of heating (see Part III), then the curves separate, but run roughly parallel to one another up to 950°C. Both show the sharp peak and rapid fall associated with graphitising vitrinite. The curve for the carbonised vitrinite (from a caking coal) shows an intermediate character due to the low rate of heating (5°C/min) (see Part III).

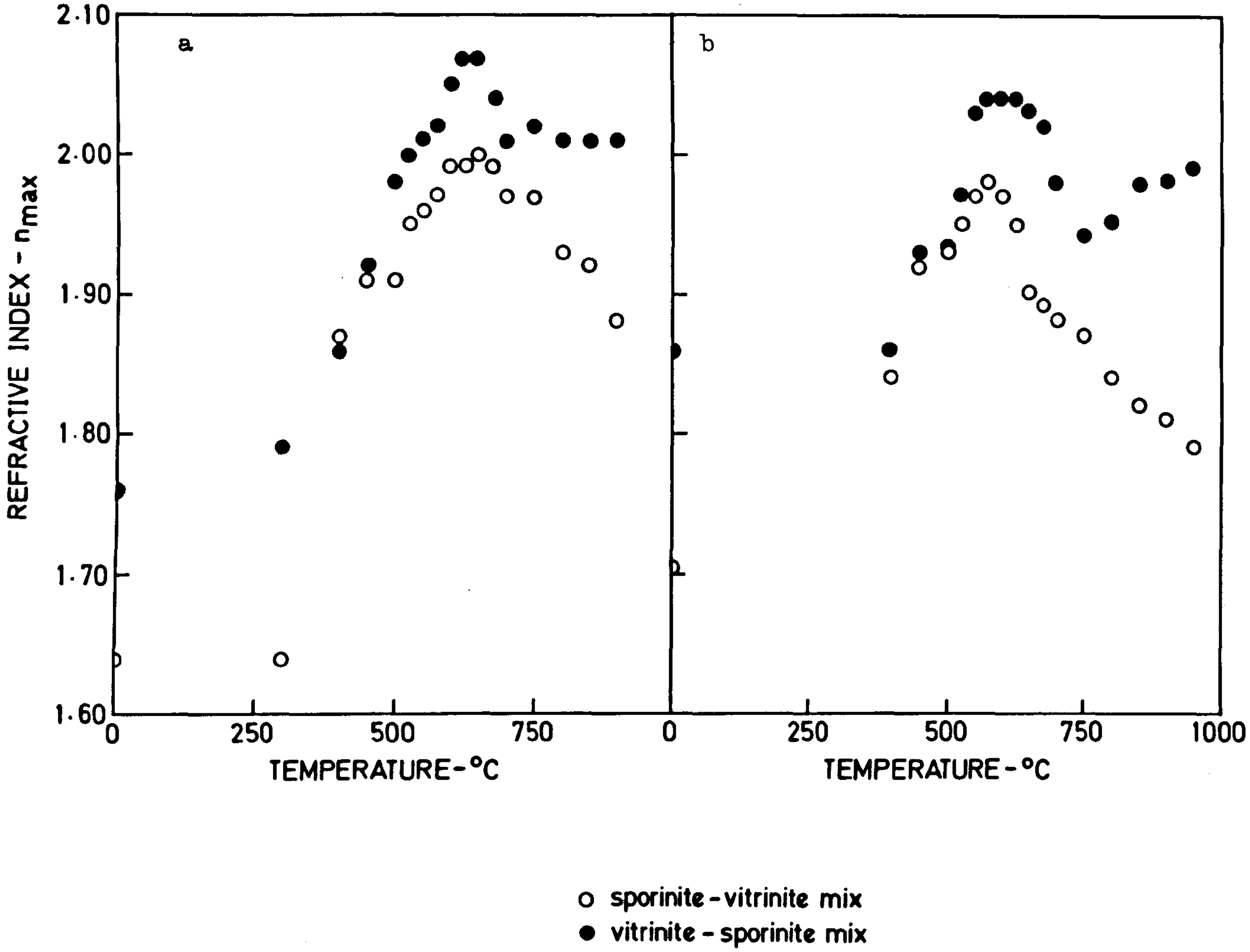
(d) Absorptive Index (Figs a and b 101 and 106)

The absorptive index-temperature curve for the three sets of carbonised residues follow paths similar to the oil reflectivities.

Fig 100 Variation with temperature of refractive index of carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous

(b) medium-rank bituminous

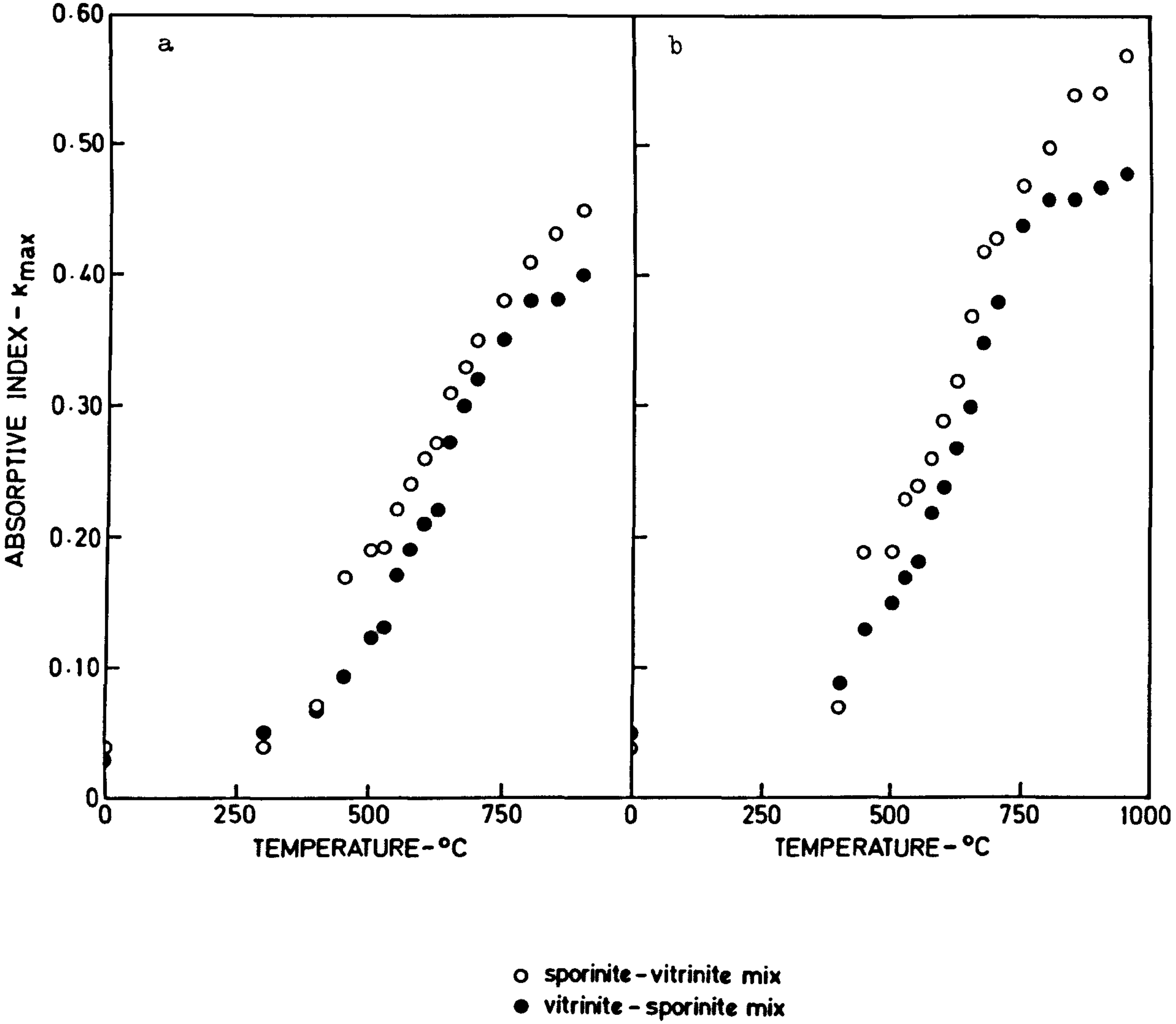


vitrinite %carbon 79·6 (d.a.f.)
sporinite %carbon 83·0 (d.a.f.)

vitrinite %carbon 86·6 (d.a.f.)
sporinite %carbon 87·1 (d.a.f.)

Fig 101 Variation with temperature of absorptive index of carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous
(b) medium-rank bituminous



vitrinite %carbon 79·6 (d.a.f.)
sporinite %carbon 83·0 (d.a.f.)

vitrinite % carbon 86·6 (d.a.f.)
sporinite %carbon 87·1 (d.a.f.)

D. Discussion

1. Morphology

The carbonised residue of sporinite in the low-rank coal (vitrinite: carbon = 79.6% daf) in the blends develops a fine-grained mosaic texture whereas the carbonised residue of vitrinite in the blend does not. The carbonised sporinite of the medium-rank coal (vitrinite: carbon = 86.6% daf) in the blend develops a mosaic texture of fine to coarse-grain, but the carbonised vitrinite in the blend develops only a fine-grained mosaic texture. This contrast clearly indicates the basic structural difference between the two macerals, i.e. the higher oxygen and lower hydrogen contents of the vitrinites compared with the corresponding sporinites. The size of the mosaic units (see Kipling *et al.* 1964 and Sanada *etw al.* 1973) is dependent upon the oxygen content; the higher the oxygen content, the smaller will be the mosaic size. This is due to a reduction in the plasticity of the residue due to the development of rigid cross-linking between the aromatic lamellae during the carbonisation process. The results of Alpern (1956); Brooks and Taylor (1965) and numerous later investigators indicate the influence of the hydrogen content of the carbonaceous material because the enhanced plasticity allows the development of large mosaic units. And so relatively larger mosaic units develop from the sporinite than from the associated vitrinite.

In establishing that carbonised sporinite develops larger mosaic units than does the corresponding vitrinite, it is interesting to note the interaction between the reactive sporinite and the less reactive vitrinite in the medium and low-rank coals. The size of the granular mosaic developed by sporinite decreases when it is mixed and carbonised with the vitrinite of the same coal. This must be due either to the influence of oxygen released during carbonisation of the vitrinite or to the influence of the lower level of plasticity of the vitrinite of the same coal.

The carbonised residues of the mixtures of sporinite and vitrinite of the low-rank coal show a narrow reaction zone between the sporinite (granular anisotropic) and the vitrinite (non-granular: isotropic). The zone is marked by a decrease in the mosaic size from the sporinite towards the vitrinite and the isotropic and/or slightly anisotropic vitrinite develops a high level of anisotropy at the peripheries of the particles which are in contact with the carbonised sporinite. This may be due to the development of a higher level of plasticity of the vitrinite because of an additive plasticity introduced by the sporinite (see van Krevelen <u>et al.</u> 1959).

The reaction zone between the carbonised sporinite and vitrinite mixture from the medium-rank coal is wider than in the low-rank blend because both the sporinite and the vitrinite are more reactive, but the sporinite (larger mosaic size) is still also more reactive than is the vitrinite. The mosaic size decreases from the sporinite towards the vitrinite, which also loses its original angular shape and becomes plastic, but still its original identity is made apparent by the different form of anisotropy, probably because of the different fluidising temperatures for sporinite and vitrinite (see for example Ergun *et al.* 1959). Sporinite becomes plastic, the vitrinite is probably still in a solid state, becoming plastic later. Thus the vitrinite may become plastic only when the sporinite is perhaps at the end of the plastic stage; the reacting vitrinite releases oxygen and influences the final development of the mosaic in the sporinite, so producing the smaller mosaic units of the zone.

2. Optical Properties

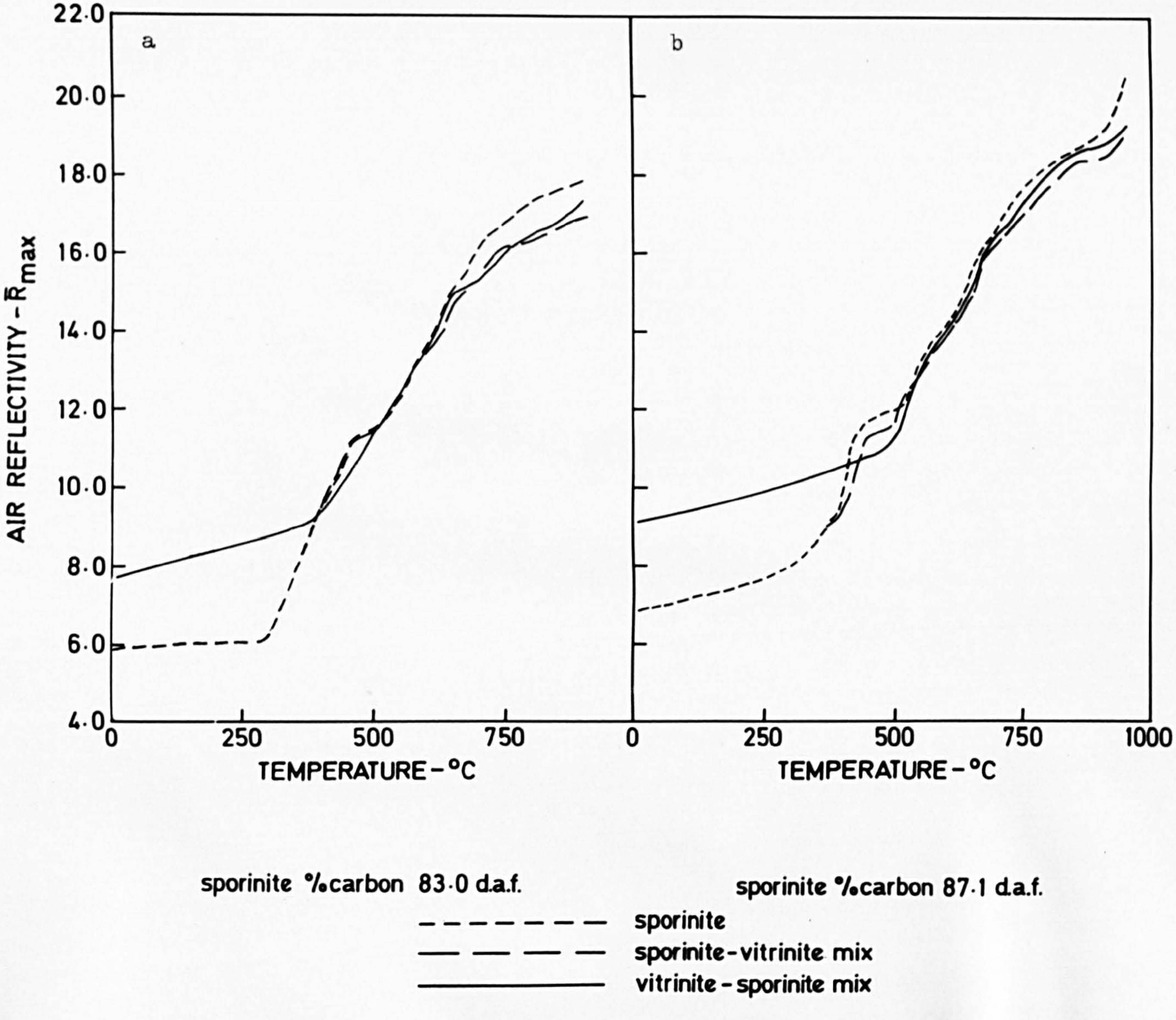
As indicated before, the two principal optical parameters indicating structural change in the carbonised residues are the refractive index and the bireflectance which are also the critical optical parameters displaying the greatest change for any particular alteration of molecular structure. The effect of introducing vitrinite particles with sporinite from the same coal has a substantial effect on the optical properties of areas of the semi-coke which have clearly arisen from sporinite. The level of both parameters is reduced markedly, the bireflectance from approximately a temperature of 500°C onwards and the refractive index from roughly 600°C onwards.

What explanation can be put forward for these noticeable changes indicated in the degree of ordering? It is clear that the plasticity of sporinite/vitrinite mixtures is reduced from that of separately carbonised sporinites. The photomicrographs demonstrate this feature well in showing smaller mosaic structures (compare Plates 78, 79 with 86, and 87). Alpern (1956) made similar qualitative microscopical comparisons when he carbonised two coals of different rank, showing that there was a decrease in the anisotropy of softening coal if it was carbonised with non-softening coal; in other words, plasticity was reduced.

Why should mixtures of vitrinite and sporinite from the same coal reduce the sporinite plasticity? It seems likely

Fig 102 Generalised curves for variation with temperature of air reflectivity of sporinite alone, and carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous
(b) medium-rank bituminous



sporinite %carbon 83.0 d.a.f.

sporinite %carbon 87.1 d.a.f.

Fig 103 Generalised curves for variation with temperature of oil reflectivity of sporinite alone, and carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous
(b) medium-rank bituminous

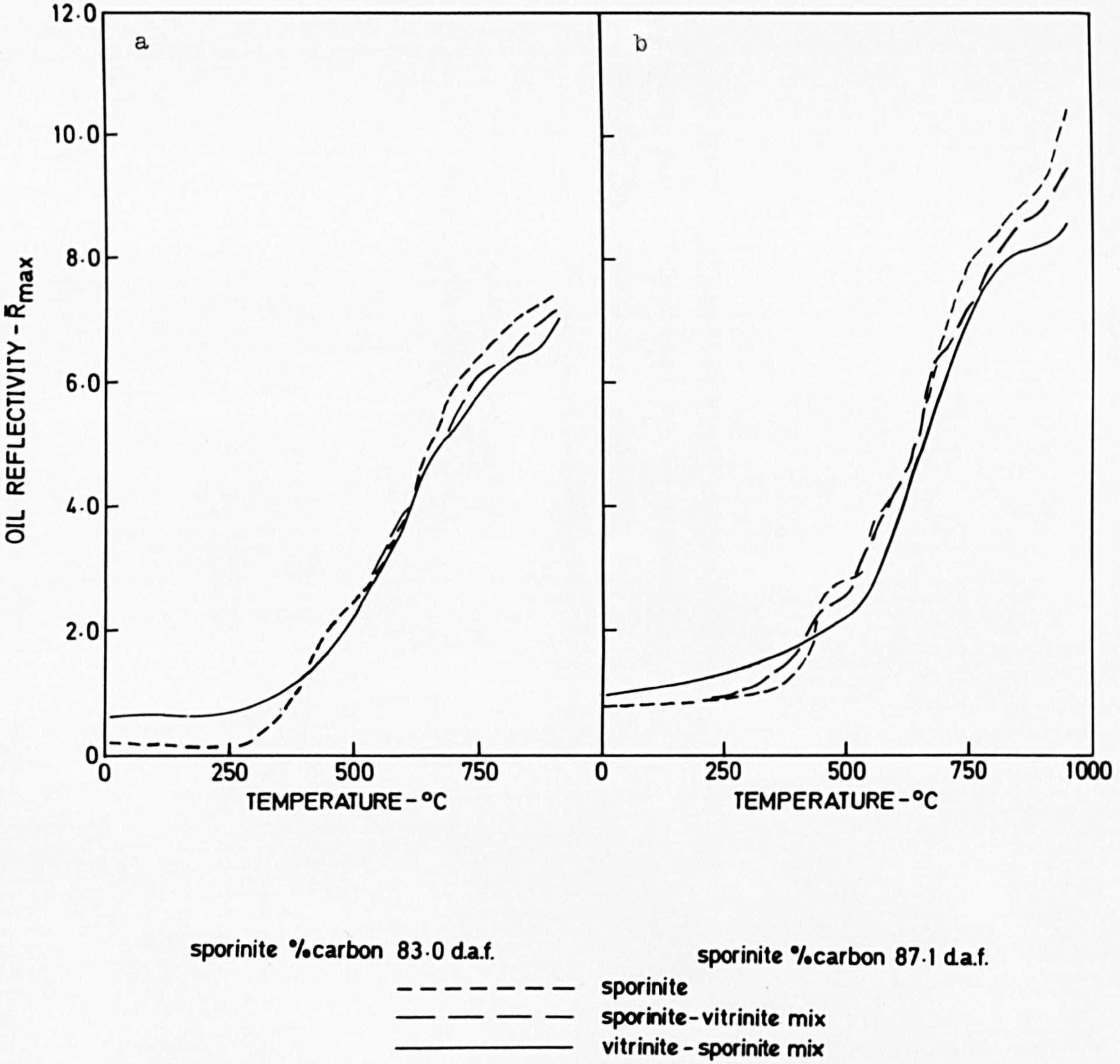
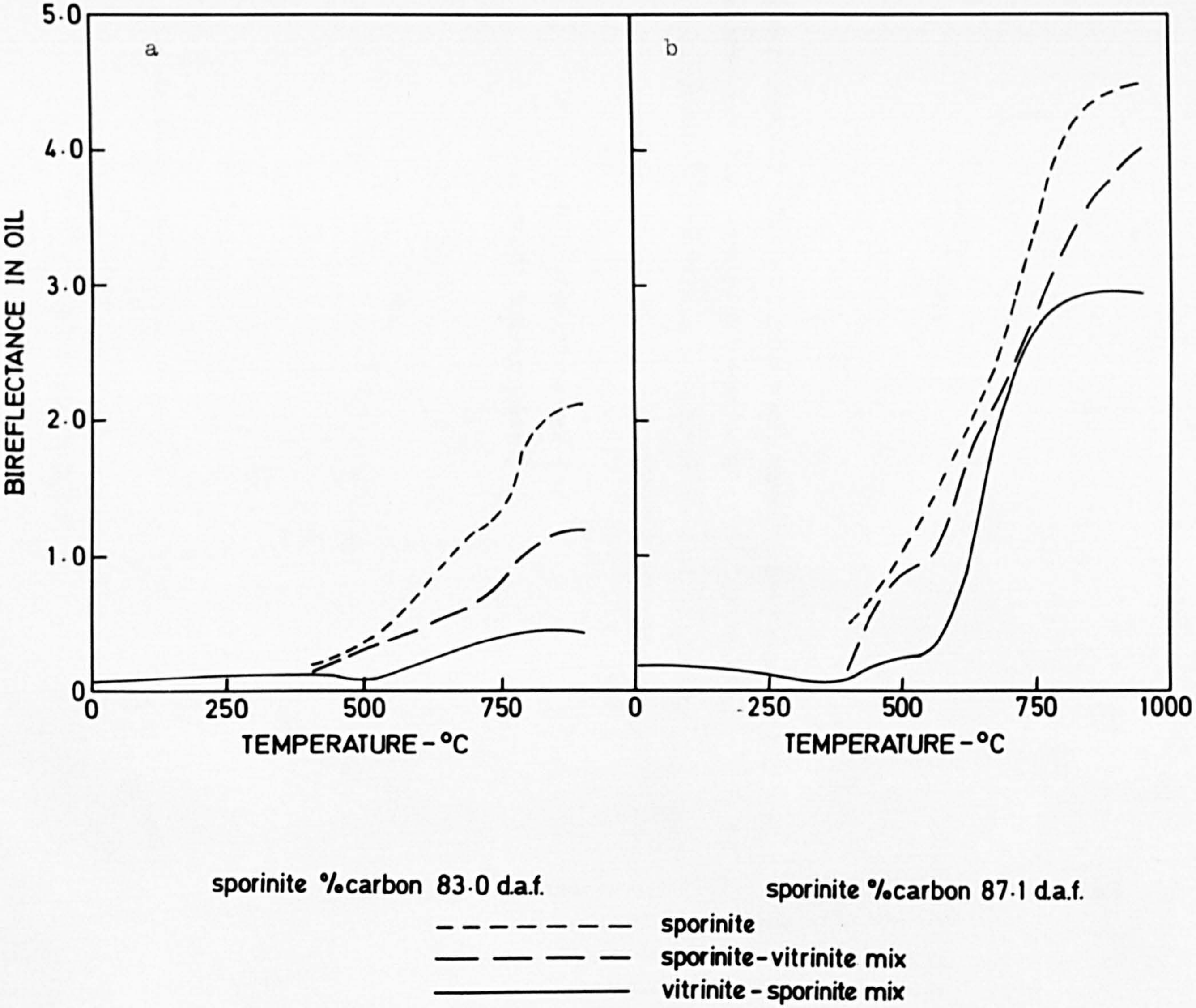

a
b
OIL REFLECTIVITY - R̄max
12.0
10.0
8.0
6.0
4.0
2.0
0
0
250
500
750
0
250
500
750
1000
TEMPERATURE - °C
TEMPERATURE - °C
sporinite %carbon 83.0 d.a.f.
sporinite %carbon 87.1 d.a.f.
sporinite
sporinite-vitrinite mix
vitrinite - sporinite mix

Fig 104 Generalised curves for variation with temperature of oil bireflectance of sporinite alone, and carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous
(b) medium-rank bituminous

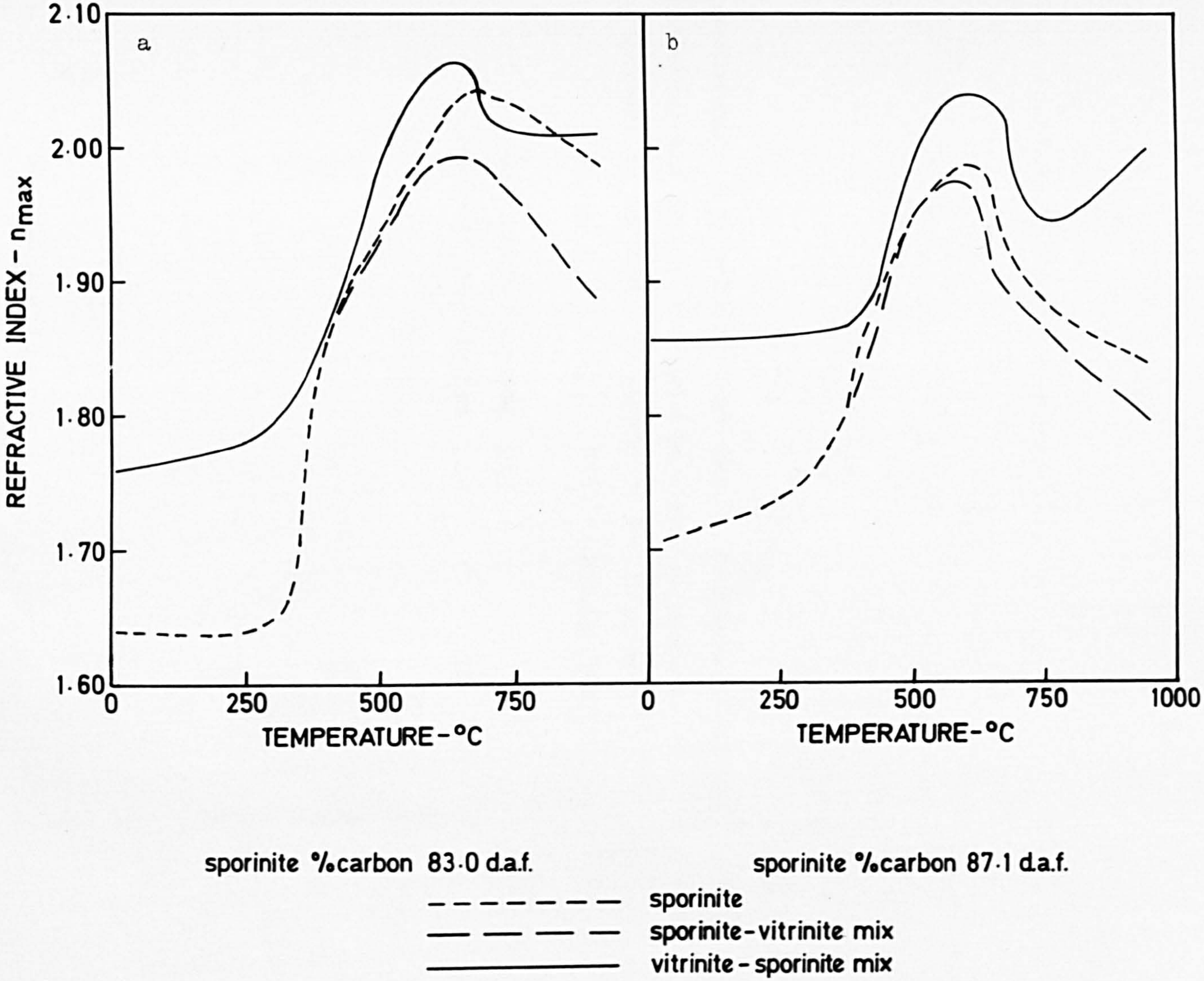


sporinite %carbon 83.0 d.a.f.

sporinite %carbon 87.1 d.a.f.

Fig 105 Generalised curves for variation with temperature of refractive index of sporinite alone, and carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous
(b) medium-rank bituminous

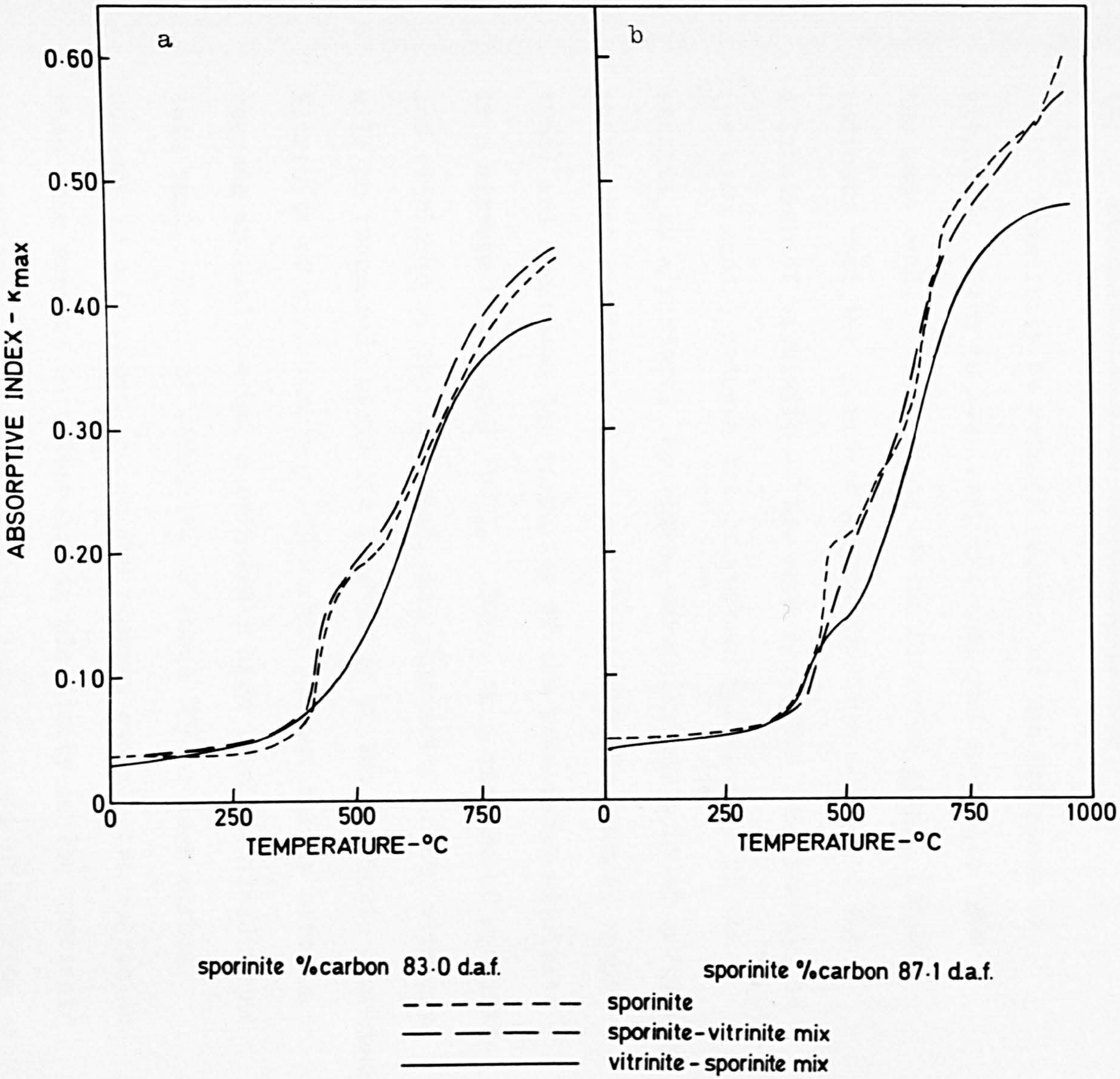


sporinite %carbon 83·0 d.a.f.

sporinite %carbon 87·1 d.a.f.

Fig 106 Generalised curves for variation with temperature of absorptive index of sporinite alone, and carbonised sporinite and vitrinite in a mixture of sporinite and vitrinite from

(a) low-rank bituminous
(b) medium-rank bituminous



sporinite %carbon 83·0 d.a.f.

sporinite %carbon 87·1 d.a.f.

to be due to:-

(a) the effect of less reactive macerals, and/or

(b) the influence of mild oxidation.

(a) The effect of less reactive macerals.

Plasticity is reduced because of the influence of vitrinite, which is less reactive than the sporinite from the same coal. The results of van Krevelen *et al.* (1959) indicate that the sporinite has an additive effect on the dilatation of vitrinite of the same rank, but that inertinite (or even sand!) reduces the dilatation (plasticity) of the exinite in a mixture. Sporinite generally has a lower softening point than vitrinite of the same coal (see for example Nandi 1966) and decreases the viscosity of the associated vitrinite in a mixture (Mackowsky 1967). Thus, in a mixture of sporinite and vitrinite of the same rank, the plasticity of the vitrinite will be increased, while the plasticity of the sporinite decreases. Vitrinite of approximately 80% carbon content hardly softens, whereas sporinite shows a relatively high level of fluidity at this rank. Thus, if vitrinite of about 80% or less carbon content is carbonised (as in the present study) with sporinite, then this results in a decrease in plasticity of the sporinite which softens and probably slightly increases the plasticity of the corresponding vitrinite. This effect is more clearly shown in low-rank than in medium-rank coals, and is particularly well demonstrated by the reduction in the level of the bireflectance curves. Also the above authors note a decrease in plasticity (Plate 29b) when solid material (inerts) are present, but they do not explain precisely why the plasticity should decrease when less reactive and/or inert materials are present. However, Brooks and Taylor (1965) and Marsh et al. (1973b) attempt to give some explanation about the mechanism of the plasticity decrease when a solid phase is present. Brooks and Taylor (1965) state that the presence of inert particles enhances the coalescence of the mesophase, but decreases the growth of individual mesophase units. Marsh et al. (1973b) maintain that the mesophase will flow, then accumulate and grow on the surface of inert particles. However, the decrease in mosaic size of sporinite in sporinite and vitrinite mixtures can only be partially due to the presence of inerts; it must mainly be due to the influence of mild oxidation.

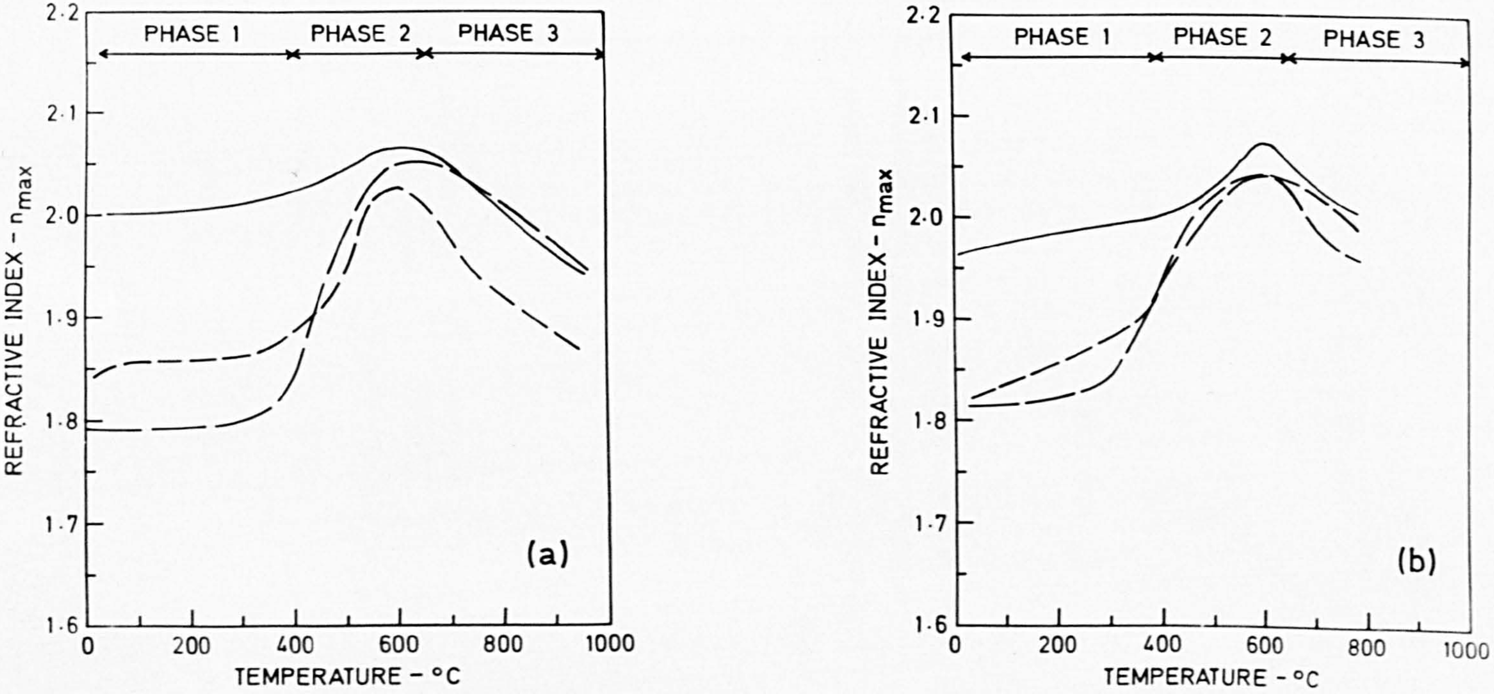
(b) The Influence of Mild Oxidation

Carbonaceous material with a high ratio of hydrogen to other non-carbon elements are the truly softening (graphitising) carbons (see for example Brooks and Taylor 1965). Such materials develop large mosaic structures, for example, medium-rank sporinites (see the section on morphology in this part and Appendix IV). Further, as has been earlier shown, the size of the mosaic units is related to the degree of plasticity of the constituents (Abramski and Mackowsky 1952; Patrick 1973 and results presented in PartIII of this Thesis). The results of Kipling et al. (1964) and Kipling and Shooter (1966) indicate that the size of the mosaic units (plasticity) will decrease with oxidation. Also de Vries et al. (1968) indicate that the anisotropy of vitrinite decreases when it is pre-oxidised before being carbonised (see also Goodarzi 1971). So one explanation for the decrease in the mosaic size (and bireflectance) of sporinite in the mixture may lie in the influence of volatile matter released during carbonisation from the vitrinite in the mixture. Alpern (1956), however, states that the volatile matter of low-rank coal (V.M. = approximately 41.8%) during carbonisation has no effect on the anisotropy of coking coal (V.M. = approximately 28%). However, considering the molecular structure of sporinite, which has a higher percentage of hydrogen and/or 'amorphous' groups than vitrinite of the same rank, the sporinite can be more readily oxidised in this situation, because it is known that vitrinite has a higher oxygen content that the corresponding exinite (sporinite) (see Dormans et al. (1957) and Given et al. 1960). Therefore devolatilisation of oxygen groupings of vitrinite in the mixture during carbonisation (Berkowitz 1968) probably results mild oxidation of sporinite in the mixture. This appears to be not unreasonable, because of the more drastic increase in bireflectance and refractive index of the sporinite in the low-rank mixture (aFigs 104 and 105), which, owing to the higher oxygen content of the associated vitrinite (carbon = 79.6% daf) is probably relatively more oxidised than the sporinite in the higher-rank mixture and so is probably less oxidised (see bFigs 104 and 105). The results of Goodarzi and Murchison (1973) indicate that the level of the refractive index of the low-rank vitrinite when pre-oxidised decreases on carbonisation (Figs 107 and 108). The pre-oxidation carried out by Goodarzi and Murchison was extensive and cannot be compared in detail with the probable mild oxidation taking place during carbonisation of sporinite/vitrinite mixtures. At these temperatures materials are reactive.

Now, after establishing that reduction in plasticity of carbonised residue of sporinite mixture is related to the above two factors, it is interesting to see which factor has the more pronounced effect.

In a sporinite/vitrinite mixture of the low-rank coal, it appears that both factors are influencing the plasticity of the sporinite, because first, the low-rank vitrinite (carbon = 79.6% daf) is far less reactive than the corresponding sporinite and does not become plastic, behaving similarly to an inert substance in the sporinite/vitrinite mixture at this heating rate. Secondly, the percentage of volatilised oxygen groupings is relatively higher in low-rank coal, so the combination of the above two factors results in a much reduced level of plasticity of the carbonised sporinite in the mixture which is apparent by the much reduced levels of the bireflectance and refractive index curves of sporinite in the mixture to that of separately carbonised sporinite. The influence of the two factors is better demonstrated in medium-rank coal because of the wider reaction

Fig 107 After Goodarzi and Murchison (1973).



Comparison of generalized curves of refractive index (546nm) with temperature for three vitrinites

(a) carbonized

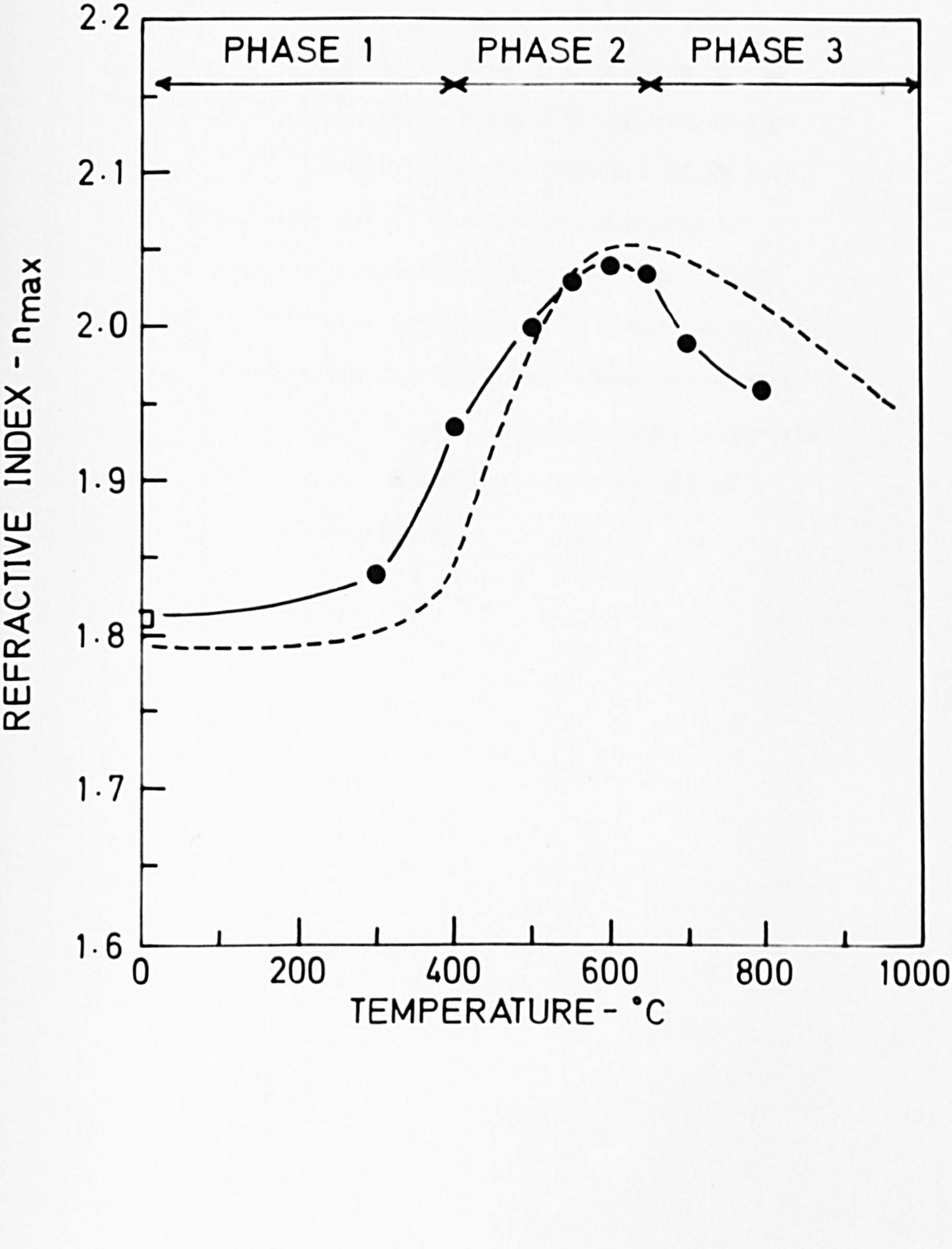
(b) pre-oxidized and carbonized

——————— (d.a.f. carbon content 93·1%)

– – – – – – (d.a.f. carbon content 88·0%)

— — — — (d.a.f. carbon content 82·5%)

Fig 108 Generalised curves for variation with temperature of refractive index of low-rank bituminous vitrinite (carbon = 82.5% daf) (after Goodarzi and Murchison 1973).


PHASE 1
PHASE 2
PHASE 3
2·2
2·1
2·0
1·9
1·8
1·7
1·6
0
200
400
600
800
1000
REFRACTIVE INDEX - n_{max}
TEMPERATURE - °C

zone between the sporinite and corresponding vitrinite. The effect of mild oxidation at this rank level is not as pronounced as in low-rank coal, because of the relatively low oxygen content of fresh vitrinite (carbon = 86.6% daf), but still it is sufficient to reduce the plasticity of sporinite in mixtures of sporinite and vitrinite. The reduction of plasticity, apparent from the reduction in mosaic size (see Appendix IV) and bireflectance curve must primarily be due to the influence of less reactive vitrinite (see Figs a and b 104) which results in a reduction of plasticity of sporinite mixture.

E. Conclusion

1. Morphological

(a) Carbonised sporinite in the mixture develops a smaller mosaic structure than separately carbonised sporinite of equivalent rank, due to a decrease in the plasticity brought about because of the presence of less reactive vitrinite and its oxygen content.

(b) The mosaic units developed by carbonised sporinite in the mixture are larger than those in the corresponding carbonised vitrinite. A transition zone can be observed at boundaries between carbonised sporinite and vitrinite in the mixture. The zone is wider the higher is the initial rank of the coal, ast least in the bituminous rank range.

2. Optical

(a) The reflectivity, bireflectance and refractive and absorptive index-temperature curves of carbonised sporinite in sporinite/vitrinite mixtures are lower than for the same curves for separately carbonised sporinite.

(b) The refractive index-temperature curves for carbonised sporinite in the mixtures behave either as graphitising or non-graphitising carbon, depending on the rank of starting sporinite, but the refractive index curve of the carbonised vitrinite follows a higher trend than does the corresponding carbonised sporinite in the mixture.

PART VI OPTICAL PROPERTIES OF VITRINITES CARBONISED AT DIFFERENT PRESSURES OVER A RANGE OF TEMPERATURES

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Contents(contd) Page

D. DISCUSSION (contd) ... ...

A. General Introduction

A further factor which has received relatively little attention is the effect of pressure on macerals that are being carbonised. The studies here report the changes in optical properties observed in a high-rank bituminous vitrinite carbonised under varying pressures over temperatures ranging from 350° to 600°C at 50°C intervals. Due to the existence of a temperature gradient within the sample capsule, only samples from the centre part of the capsule were used, so that any variation due to temperature within single samples has been, as far as possible, eliminated. It is thus possible to consider solely the influence of pressure level on the optical properties of the carbonised residues of this vitrinite. Due to the small amounts of samples available from the gold capsules, only about 25 individual reflectivity measurements could be made on each carbonised sample.

A brief description of the apparatus used for carbonisation under pressure was given earlier in the Thesis (Part II). In general, with rising temperature, pressure in the bomb rises continuously and almost linearly. However, at low pressures ($\leq$ 5000 psi), it was possible to control the pressure at particular levels over the temperature range 0 - 600°C. It will be clear that, depending on the starting pressure selected in the bomb, it is possible at any particular temperature to obtain a wide range of pressures. In this work, apart from the relatively low pressures of 3000 and 5000 psi, which were chosen because they would approximate to geological situations with considerable depths of overburden, two higher ranges of pressure, one low and one high, were employed. Fig 109a shows two typical runs over the temperature range 0° - 450°C, one beginning with a low initial pressure, the other much higher. The main difference between the two runs, apart from the pressure levels, is that the course of the higher-pressure track begins to flatten at approximately 400°C, while the lower-pressure track continues to increase with temperature. Virtually the same features are displayed by two equivalent runs over the temperature range 0-600°C (Fig 109b). It is also possible to combine the pressure-temperature relationships that exist in (a) all runs beginning with a low initial pressure (ca. 3000 psi) and (b) high initial pressure (ca. 23000 psi), so developing the relationships displayed in Fig 110 over the entire temperature range - 20° to 650°C.

These relationships might seem superficially to make comparison of both morphology and quantitative optical properties more difficult, but from Fig 110 comparisons within individual pressure-temperature zones are perfectly possible, and, provided there is always awareness of the particular experimental conditions, then comparisons between the zones of Fig 110 are also feasible. Also Fig 109b shows that in the runs with high starting pressures, comparisons from 400°C upwards are virtually being made at a

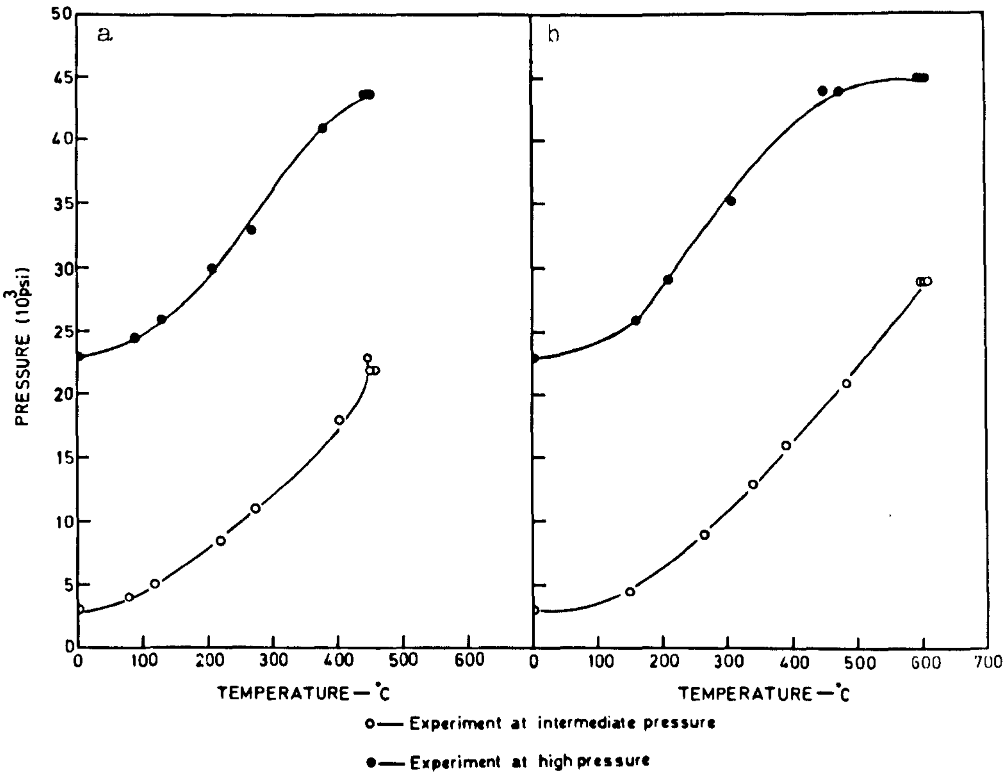


Fig 109 Variation of pressure with temperature for intermediate and high pressure runs in the bombs with maximum temperatures of

(a) 450°C

(b) 600°C

(after Hermon 1974)

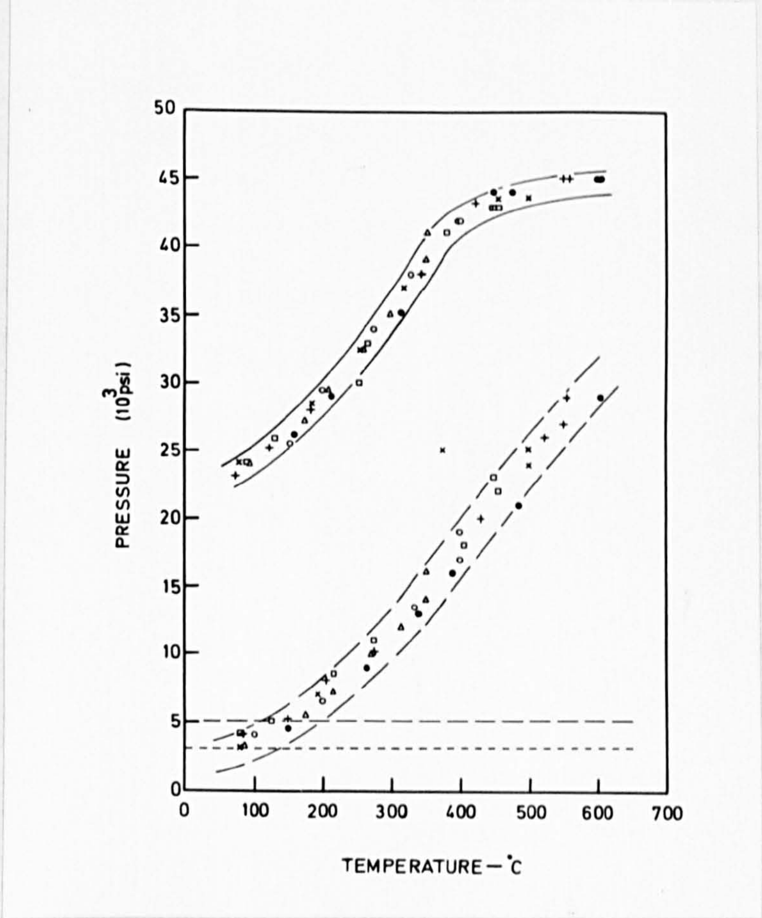


Fig 110 Relationship between pressure and temperature for a number of runs, grouped to give overlaps, at

- - - - - 3000 psi

— — — 5000 psi

═ ═ ═ ═ pressure starting at ca. 3000 psi and rising (intermediate pressure)

══════ pressure starting at ca. 23000 psi (high pressure)

(after Hermon 1974)

constant pressure level (within a range of 1000 psi). After a review of previous work on this field, the changes observed in optical properties will, therefore, be described in the following order:-

(i) low pressure runs, i.e. at 3000 and 5000 psi (low-pressure level),

(ii) runs with a high starting pressure (ca. 23000 psi) and virtually constant pressure at temperatures above 400°C (high-pressure level), and

(iii) runs with a low starting pressure (ca. 3000 psi) and an intermediate final pressure between 16000 and 29000 psi, depending on the final temperature level (intermediate pressure level).

B. Previous Related Studies.

1. Introduction

Carbonisation under pressure enhances the coking of coal particles and increases the swelling index. Blayden *et al.* (1944) state that a caking coal might be made to coke if the carbonisation is carried out under pressure. Hamann (1957) also states that pressure supresses the thermal decomposition of most organic materials; high pressure shifts the decomposition temperature to higher levels and the thermal cracking of hydrocarbons is inhibited at high pressure. Van Krevelen (1961) believes that coal softening is due to the deploymerisation and transformation of the initial coal to a fluid mass or a metaplast, which consists of primary tar (fluid) and a solid residue; the plasticity being caused by dispersion of this liquid (tar) in the solid. The liquid evaporates by a cracking process, resulting in decomposition of the metaplast into semi-coke (solid) and volatile matter which is eliminated from the system. It is also known that compressed gas behaves similarly to liquid and its viscosity increases or decreases with increase of pressure or temperature (see Hamann 1957). Hryckowian *et al.* (1963) indicate that a low-rank anthracite can be fused under pressure at temperatures of

Carbonisation of organic material under pressure in a 'bomb' differs considerably from that of carbonisation at atmospheric pressure, because of the retention of the decomposition products in the system and the contribution of those materials to the structure of carbonised residue. Berkowitz (1968) states that carbonisation under pressure retards the carbonisation process and that the influence of pressure during Phase I of carbonisation (about 120° to 400°C) is negligible, but that the influence of pressure is more important in Phase II (between about 400° and 600°C), because pressure affects the rate of degasification and also the composition of the volatile matter; in Phase III (about 600° to 1000°C) the increase of pressure probably facilitates the rate of degasification of aromatic hydrogen and also the ordering of structural units. Marsh *et al.* (1973) states also that pressure enhances the viscosity of carbonaceous material during carbonisation, stating that when vitrinites of different rank are carbonised under pressure, all the vitrinite components are carbonised due to the closed system and the volatile matter, which under normal carbonisation is eliminated from the system, remains within the system during carbonisation under pressure, contributing to the structure of the carbonised residue. This results in an increase of the anisotropic material in the coke and also an increase in the size and percentage of mosaic units. More recently Bostick (1974) has stated that the influence of pressure is more noticeable in low-rank coals (high-volatile bituminous coal) due to their pore volume, pressure resulting in reduction of this volume and causing an acceleration of the coalification.

The above results indicate clearly that the different stages of the carbonisation process are inhibited during carbonisation under pressure, due to a shift of the thermal-decomposition point to higher temperatures, and also due to an increase in the viscosity of the carbonised coal under pressure, which results in lessening of the plasticity. During carbonisation under pressure the solid, liquid (metaplast) and gases interact with each other. Changes in the physical or chemical state of one will affect the others, e.g.pressure results in an increase of viscosity of the gaseous products, which in turn influences the metaplast and so it can only react for a shorter length of time than under normal carbonisation conditions, because of increase in viscosity in the system due to gas behaving similarly to a liquid.

2. Morphology

The morphology of residues of carbonaceous material carbonised under pressure has been studied by polarised-light microscopy or by Stereoscan microscopy by Mackowsky (1961); Hryckowian et al. (1963); Chandra (1965); Kamiya et al. (1971); Whang (1973) and Marsh et al. (1973).

(a) Optical Microscopy

Mackowsky (1961) relates the plastic deformation of coal under pressure to modification of the structural elements caused by mechanical pressure. From the work of Mackowsky (1961); Hryckowian et al. (1963); Chandra (1965) and Kamiya et al. (1971), it is evident that the anisotropy of carbonaceous material carbonised under pressure increases. Mackowsky (1961) shows with photographs that residues of vitrinite carbonised under pressure exhibit a higher anisotropy than the carbonised products at the same temperature carbonised under atmospheric pressure. The results of Hryckowian et al. (1963) indicate that at constant temperature, anthracite particles carbonised at 600°C lose their original identity with increase of hydrothermal pressure from 5000 to 25000 psi, a compact mass finally being produced. At constant hydrothermal pressure, the fusion of anthracitic particles increases with temperature and the carbonised residues show a high degree of anisotropy. Low-rank anthracite fuses at about 425°C after 4 hours under a pressure of 2000 psi. The carbonised residues under hydrothermal pressure do not form a compact mass if more than 15% water is added to the fresh vitrinite. The samples carbonised under a combination of hydraulic and mechanical pressure do not appear to fuse so greatly as those carbonised under the hydrothermal pressure. This phenomenon is related to uneven distribution of pressure throughout the residues carbonised under combine hydraulic and mechanical pressure. These results indicate that anthracitic vitrinite, which does not produce a fused char during carbonisation in an open boat (Marshall and Murchison 1971 and Goodarzi and Murchison 1973), cakes and produces a compact coke under pressure. This is in accord with the earlier observations of Blayden et al. (1944) on the effect of pressure on weakly caking coal which cokes when carbonised.

The work of Kamiya et al. (1971) shows that angular particles of non-graphitising carbon carbonised under a pressure of 5 Kbar up to about 1600°C can produce strongly anisotropic material at contacts between particles. Whang (1973) also recognises the importance of the level of pressure on the morphology of the pressure-carbonised products of anthracene at 600°C under pressure. At this temperature under 10,000 psi, a mixture of vesicular and spherical semi-coke is produced, but at the same temperature, but under 30,000 psi, a completely spherical semi-coke develops.

The above investigations clearly show that the morphology of carbonised residues under pressure is different to that of residues in normal carbonisation, since non-coking vitrinites, such as anthracite, can be made to fuse under high pressure and even non-graphitising (isotropic) carbons under pressures and high temperatures can yield highly anisotropic carbon.

(b) Electron Microscopy

Marsh *et al.* (1973) examined with an electron scanning microscope a range of vitrinites (carbon 77 to 91% daf) carbonised to 600°C under a pressure of 20,000 psi. They state that the size of the mosaic units increases from 5um to 7um with progressive increase of rank of vitrinite from carbon 83.8% daf, although it is not clear how such precise estimates were reached. Anthracitic vitrinite does not fuse and retains its original anisotropy; low-rank coals do not develop liquid crystals. The same authors emphasise that the anisotropy observed with the polarised-light microscope can be related to the morphology observed with the scanning electron microscope; liquid crystals produced by coking coal are very similar to those formed on carbonisation of pure aromatic compounds such as napthalene. These results of Marsh *et al.* (1973) are directly opposed to the earlier findings of Hryckowian *et al.* (1963), who demonstrated by optical microscopy that the anthracite particles under hydrothermal pressure fuse and produce a compact char. Marsh *et al.* (1973) also claims that carbonisation under pressure is a useful tool for the examination of the individual liquid crystals, because pressure prevents the liquid crystals from coalescing.

3. Optical Properties

The optical properties of vitrinites carbonised under pressure have only been partially and cursorily investigated by several workers, (Hryckowian *et al.* 1963; Huck and Patteisky 1964; Chandra 1965; Melvin 1974 and Bostick 1971 and 1974), who have studied the optical properties, in particular reflectivity and bireflectance.

Hryckowian *et al.* (1963) carbonised three anthracites (Fixed carbon = 74.6% to 92.5%) under hydrothermal and mechanical pressures from 2000 up to 145000 psi at temperatures ranging from approximately 460° to 860°C using holding times from, 7 minutes to about 62 hours. The reflectivity at given levels of pressure increases sharply at about 500° to 700°C (Fig 111). However, the sharp increase of the reflectivity curve between 500° and 700°C is rank dependent and is less sharp the higher is the rank (Fig 111). Bireflectance increases with temperature and level of pressure, but at between 700° and 800°C the bireflectance curves of samples under 10,000 to 20,000 psi decrease (Fig 112). It appears that anthracite, depending on its rank, undergoes a semi-plastic stage similar to bituminous rank vitrinites at an appropriate temperature and this semi-plasticity decreases with the increase of rank in the anthracite range. However, the reflectivity increase with the combined influence of temperature and pressure is not as great as with temperature alone; pressure exerts little effect on the level of reflectivity. Bireflectance increases continuously with rise of pressure and temperature up to 600°C.

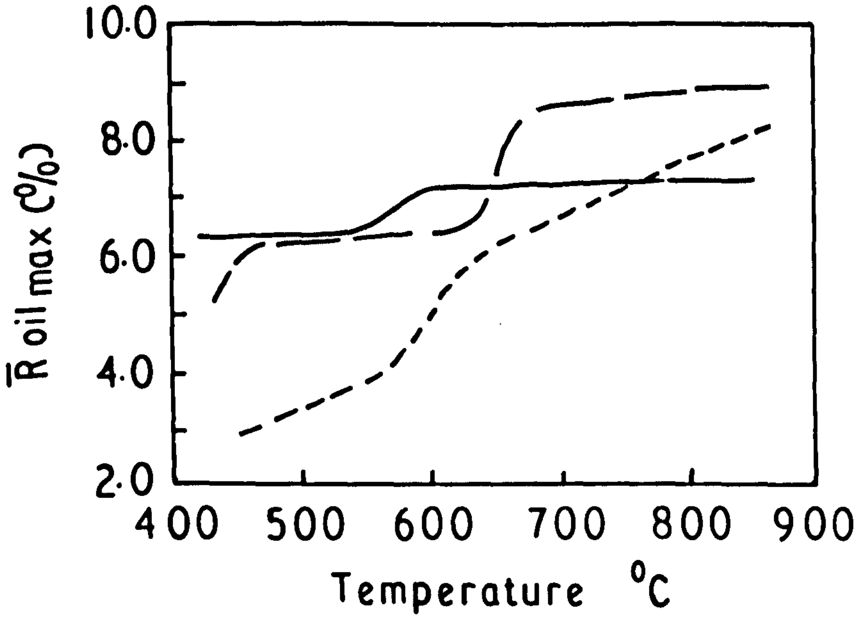
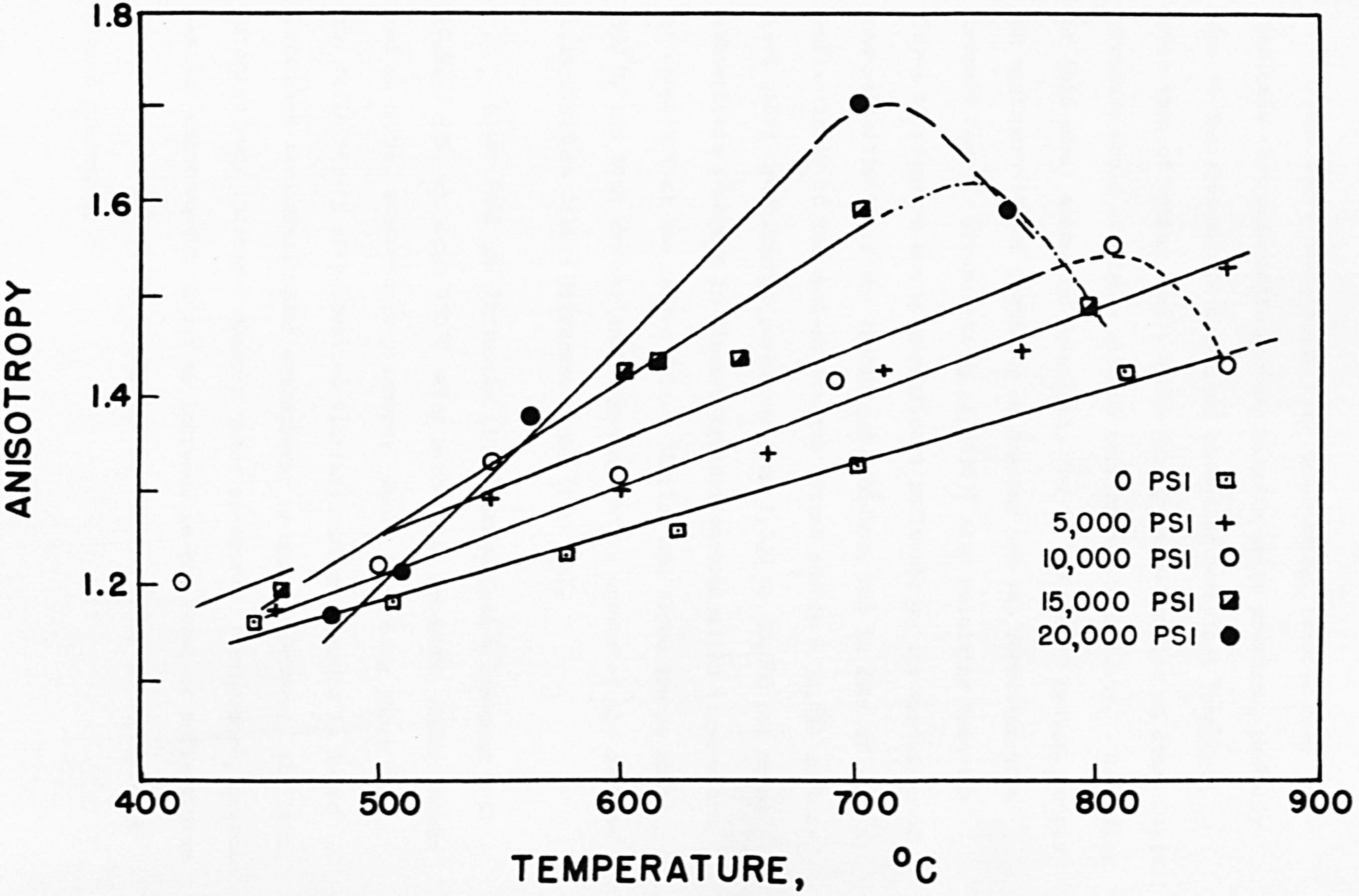


Fig 111 Generalised curves for the variation with temperature of oil reflectivity for semi-anthracitic and anthracitic vitrinite carbonised under pressure of 5000 psi

	Fixed carbon %
———————	92.5
— — —	87.8
- - - - -	74.6

(redrawn after Hryckowian et al. 1963)

Fig 112 Variation of oil bireflectance with temperature for semi-anthracitic vitrinite (fixed carbon = 74.6%) carbonised under pressure (after Hryckowian *et al.* 1963)


1.8
1.6
1.4
1.2
ANISOTROPY
400
500
600
700
800
900
TEMPERATURE, °C
0 PSI ▣
5,000 PSI +
10,000 PSI ○
15,000 PSI ◩
20,000 PSI ●

The above results are very interesting, because they indicate that anthracite becomes plastic under pressure, probably due to the presence of a limited amount of metaplast (compared with that of coking coal), which during carbonisation at atmospheric pressure would evaporate without causing any plasticity. Retention of this small amount of metaplast, due to the closed system, causes an agglomeration of particles on heating and the formation of a compact mass. Hyrckowian et al.(1963) also maintains that the level of pressure has no significant influence on the variation of the reflectivity of the carbonised residues, but in fact if the reflectivity of the semi-anthracite (Fixed carbon = 74.6%) carbonised under hydrothermal pressures from 2,000 to 20,000 psi or at atmospheric pressure is plotted against carbonisation temperature, it appears that the curves follow similar and close trends up to 550°C, but then the reflectivity-temperature curves of the carbonised residues follow different paths (Fig 113).

Later Huck and Patteisky (1964) carbonised a low-rank coal (V.M. = 33%) at about 350°C under mechanical pressure, under vacuum and at normal atmospheric pressure. Table 12 clearly shows that the reflectivity of carbonised vitrinite under pressure is lower than when carbonised under atmospheric pressure. However, the level of anisotropy increases sharply under pressure; furthermore, carbonisation under vacuum causes an increase in the level of reflectivity compared with the reflectivity levels reached under atmospheric or higher pressures.

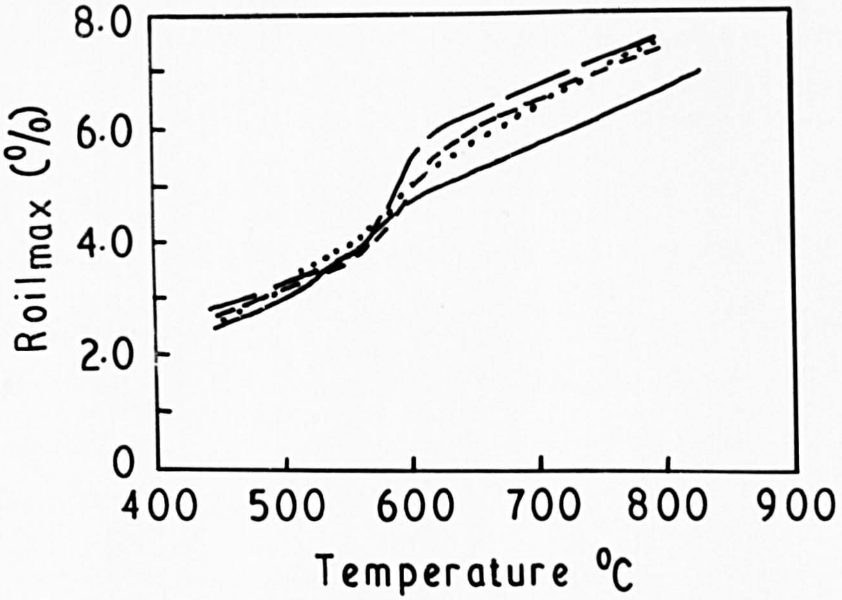


Fig 113 Variation with temperature of oil reflectivity of semi-anthracite (fixed carbon = 74.6%) carbonised at different pressures (redrawn after Hryckowian <u>et al.</u> 1963)

————————	0 psi
— — —	2000 psi
- - - - -	5000 psi
• • • • •	20000 psi

TABLE 12.% REFLECTIVITY IN OIL MEASURED ON FRESH VITRINITE AND CARBONISED RESIDUES AT 350°C (after Huck and Patteisky 1964).

Fresh	0.91
Atmospheric pressure	1.21
Under vacuum	1.51
Pressure of 150 atmosphere	1.01

The above results show that the rate of removal of volatile matter within the carbonisation system influences the level of reflectivity. Chandra (1965) carbonised a caking vitrinite (carbon = 84% daf) at 325° and 350°C under mechanical pressures of 1,000 to 6,000 atmospheres using holding times of between 5 and 25 days (Figs 114 and 115). Reflectivity increased only slightly at 325°C, while the bireflectance remained constant, but at 350°C the reflectivity rose sharply at 2,000 atmospheres, after which it increased continuously with rise of pressure. Chandra relates the high level of reflectivity at 1,000 atmospheres to additional pressure caused by degasification which exceeds the mechanical pressure (Fig 115). However, the bireflectance at 350°C increased continuously with rise in the level of pressure. The reflectivity curves of vitrinites carbonised under pressure, when plotted against carbon content, follow a curve between those of naturally regionally metamorphosed coals and carbonised residues of vitrinites carbonised at atmospheric pressure. The anisotropy of carbonised residues in pressure experiments is higher than those from either naturally regionally metamorphosed or normally carbonised vitrinites.

Fig 114 Variation of oil reflectivity with temperature for caking coal vitrinite (carbon = 84.3% daf), carbonised under pressure (after Chandra 1965).

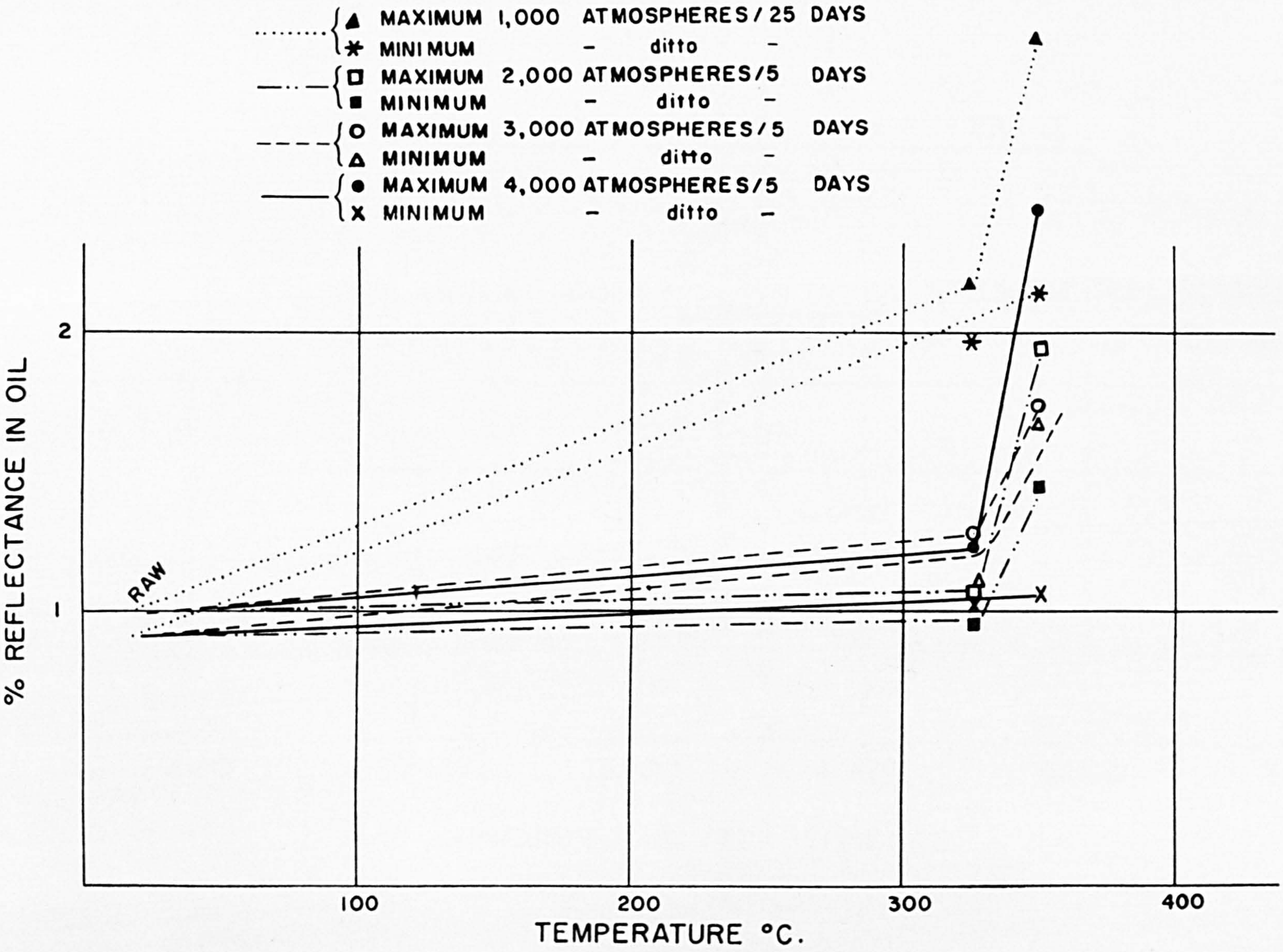
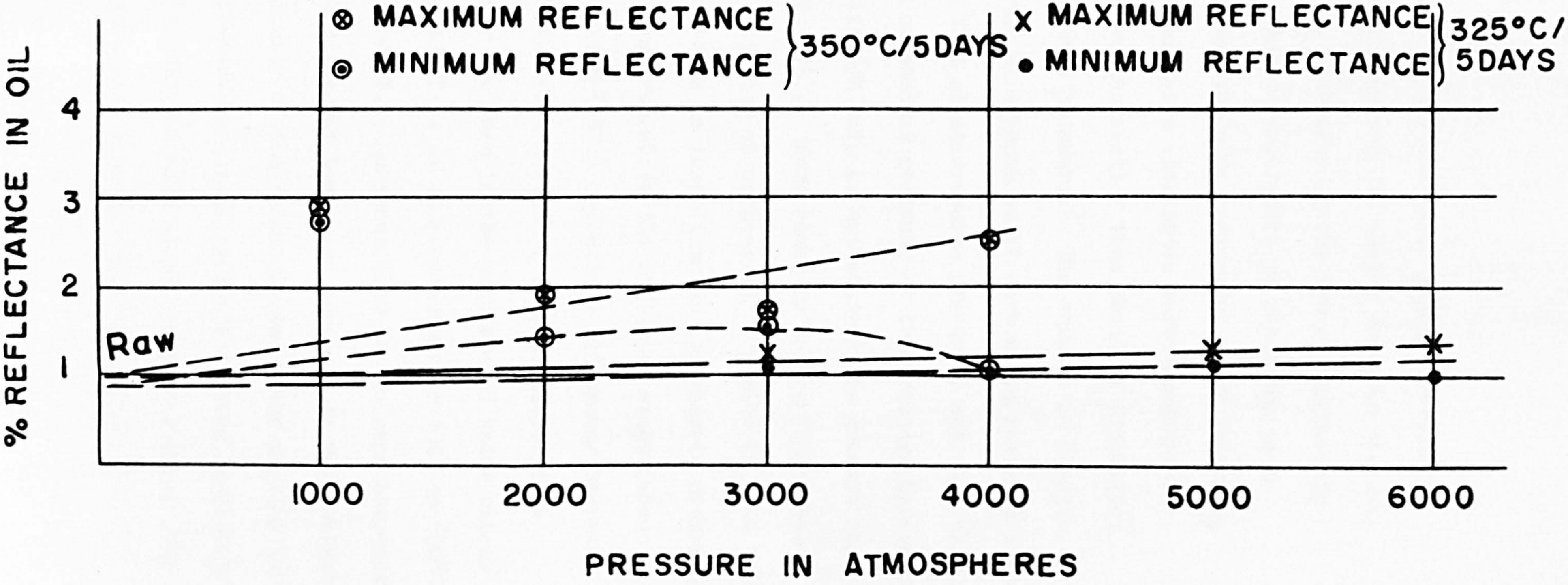

▲ MAXIMUM 1,000 ATMOSPHERES / 25 DAYS
✱ MINIMUM - ditto -
□ MAXIMUM 2,000 ATMOSPHERES / 5 DAYS
■ MINIMUM - ditto -
○ MAXIMUM 3,000 ATMOSPHERES / 5 DAYS
△ MINIMUM - ditto -
● MAXIMUM 4,000 ATMOSPHERES / 5 DAYS
X MINIMUM - ditto -
RAW
% REFLECTANCE IN OIL
2
1
100
200
300
400
TEMPERATURE °C.

Fig 115 Variation of oil reflectivity with pressure for carbonised caking coal vitrinite (carbon = 84.3% daf) (after Chandra 1965).

VARIATION OF REFLECTANCE WITH PRESSURE



Later, Chandra, in another paper (1965) attempts to evaluate the effect of pressure and states that for the same level of reflectivity, vitrinite carbonised at atmospheric pressure requires a higher temperature to reach the same reflectivity as that of vitrinite carbonised under pressure, i.e. for similar temperatures vitrinites carbonised under pressure show higher reflectivities than those of vitrinites carbonised at atmospheric pressure. The results of Chandra also indicate that the bireflectance of carbonised residues under pressure are higher than at atmospheric pressure, and also that the reflectivity of carbonised residues at low pressure, (presumably with confinement, although this is not stated), is greater than at higher pressures (Fig 115). More recently Melvin (1974) has stated that the reflectivity of carbonised vitrinite (R_{oil} = 1% when fresh) under pressure is lower than at atmospheric pressure, particularly at temperatures above the softening stage (about 400°C. Finally, Bostick (1974) reports no difference between the reflectivity of fine coal particles ('phytoclasts')from shale carbonised under pressure in the presence of water vapour between 1 and 1640 atmosphere at temperatures from 100° to 600°C over a period of one month. He shows that at the same temperature the influence of the different levels of pressure is very slight and that the reflectivity of the 'phytoclasts' after heating for one month at the different levels of pressure is very similar to the reflectivity of vitrinites carbonised at one atmosphere for a few hours. The same author suggests that the influence of pressure on the reflectivity of carbonised vitrinite probably retards the carbonisation process, but Bostick also believes the pressure results in a rapid acceleration of the coalification of low-rank coal due to reduction in its pore volume. However, the results of Huck and Patteisky (1964) indicate that the reflectivity of vitrinite carbonised under mechanical pressure is lower than in normal carbonisation at the same temperature. This conclusion is in agreement with the findings of Melvin (1974) for vitrinite carbonised in a bomb, but is contrary to the results of Hryckowian et al. (1963) and Chandra (1965) who find that the reflectivity of vitrinite carbonised under hydrothermal and/or mechanical pressure is higher than for chars prepared by carbonisation at a pressure of 1 atm. (Hryckowian et al 1963). The results of Bostick (1974) do not agree with any of the above authors, because he claims no difference between the level of reflectivities with or without pressure. Chandra (1965) compared the reflectivity of carbonised semi-cokes under pressure for a holding time of approximately 5 days, with products carbonised at approximately the same temperature for only 1 hr. Chandra does not consider the influence of holding time, whereas the effect of holding time appears to be very important (see Mackowsky 1961; Ghosh 1968 and de Vries et al. 1968). On the basis of the work of these authors, a holding time of 5 days will surely result in an increase in the level of reflectivity. The pressure carbonisations by Bostick (1974) were carried out in the presence of water vapour, which may be a possible reason why reflectivities after prolonged carbonisation at different levels of pressure are very similar to one another. However, the lack of agreement between some of the above investigators is probably due to differences in experimental apparatus and conditions.

4. Influence of pressure on molecular structure of carbonised residues

The changes brought about due to carbonisation under pressure on the molecular structure of carbonaceous materials have been studied by Hryckowian et al. (1963) and Kamiya et al. (1971).

Hryckowian et al. (1963) relates the increase in reflectivity with rising carbonisation temperature under pressure to an increase in the carbon content due to degasification of hydrogen and methane, suggesting also that the influence of pressure on reflectivity is not as great as temperature. The increase in the level of bireflectance with pressure (Fig 112) is related to an improvement in the ordering of the structural units and the authors recognise that the higher the pressure, the better will be the structurel ordering of the molecular units. The decrease of bireflectance after 700°C at pressures above 10,000 psi is also believed to be due to softening and breakdown of the molecular ordering of the anthracite in this range of temperature and pressure. The authors believe that at pressures lower than 10,000 psi, temperatures higher than 860°C are required to break down the molecular structure of the anthracite; pressures higher than 10,000 psi partially inhibit the softening due to partial obliteration of the plasticity. X-ray diffraction studies of carbonised anthracitic residues do not show noticeable structural changes, but a bituminous coal carbonised at 500°C under a pressure of 30 Kbar for 10 hours showed a sharpening of the 002 bands, indicating better structural ordering and greater crystallite height. Hryckowian et al. did not make a quantitative

X-ray diffraction study.

Later, Kamiya et al. (1971) studied the behaviour of non-graphitising carbons carbonised under pressure. They stated that the strongly anisotropic domains formed at the boundaries of the isotropic carbon particles are graphite and are formed due to localised graphitisation at the contact of particles due to influence of pressure. The content of graphitic material as determined by X-ray methods rises with increase of anisotropic material.

The above studies show that the ordering of molecular structure is improved with rise of pressure; anthracitic vitrinite, which does not soften at low temperatures (apparent from the bireflectance curve), undergoes a molecular disordering similar to bituminous-rank vitrinite at appropriate levels of pressure and temperature. Isotropic carbon is also able to order its disordered structure under pressure to form a partially graphitic structure.

In summary, in comparison with open boat experiments carbonisation under pressure seemingly retards the carbonisation process, forces the plastic stage to a higher temperature. Progressive increase in the level of pressure probably decreases the length of the plastic stage. Pressure prevents the coalescence of the mosaic structure, whereas in carbonisation under atmospheric pressure, mosaic structures are able to coalesce. However, pressure promotes the ordering of the molecular structure (apparent from the increase in the level of bireflectance) and finally, carbonaceous material, which does not soften during carbonisation at atmospheric pressure, e.g. anthracite, becomes plastic when carbonised under suitable pressure and temperature conditions. It appears from the above studies that the reflectivity of bituminous-rank vitrinite carbonised under hydrothermal or mechanical pressure is lower than the same vitrinite carbonised at atmospheric pressure (Huck and Patteisky 1964 and Melvin 1974), but if factors such as rank (Hryckowian 1963), soaking period (Chandra 1963) and moisture content of the fresh sample (Bostick 1974) are taken into consideration, then the above relationship may not hold.

C. Results. Description

1. Morphology (see Appendix V, VolumeIII)

The carbonised residues at all pressure levels at 350°C are essentially similar to one another, but slightly brighter than fresh vitrinite.

(a) Low pressure runs (3000 and 5000 psi) (Plates 91 to 94)

The most interesting feature of these runs is the long pre-devolatilisation phase, which is the longer the lower is the pressure level (compare Plate 91 with Plate 93). For mosaic structures to develop, a contrast between pressure runs at 3000 psi and 5000 psi is apparent, because the devolatilisation vacuoles occur at 550°C for samples at 3000 psi (Plate 92a) whereas the vacuoles begin before 500°C (Plate 93b) in samples at 5000 psi. There is development of a coarse-grained to flow-type mosaic at 3000 psi (Plate 92) and a coarse-grained mosaic at 5000 psi (Plate 93). The mosaic size is the larger the lower is the pressure. The intensity of anisotropy increases with rise of temperature and pressure.

(b) High pressure runs (runs starting at 23000 psi) (Plates 95 to 97)

At 400°C the residues develop numerous small vacuoles of about 2.5 um diameter and occasionally much larger vacuoles of about 25 um diameter (Plate 95a). There is development of rounded vacuoles of about 50 um diameter at 450°C. The size and shape become irregular and decrease, but their number increases with rise of temperature between 500° and 600°C (Plates 96 and 97). A fine-grained mosaic structure forms at 450°C. and the mosaic size does not alter with rise of temperature. The intensity of anisotropy increases with temperature.

(c) Intermediate pressure runs (runs starting at 3000 psi with rising pressure (Plates 98 to 100)

Rounded vacuoles of about 25 um diameter develop at 400°C. The shape of the vacuoles becomes irregular, but their size increases with rise of temperature up to 550°C, when once again large rounded vacuoles develop. At 450°C a mesophase develops and partially transforms to a fine-grained mosaic structure.

2. Optical Properties

(a) Introduction

The results reported here are presented in two ways; optical changes against temperature at different pressures and a second set of data showing plots of optical properties against pressure for different temperature levels.

(b) Optical Properties - temperature curves

The data are presented in the following manner and the text figures in the appropriate sections relate to the ordering below:-

1. graphs comparing runs at 3000 and 5000 psi (Figs 116 to 119),

2. graphs showing runs at intermediate and high pressures (Figs 120 to 124) because of some variation of the pressure levels at different temperatures, particularly for experiments at intermediate pressures; the pressure level is quoted for each temperature - as stated previously, the high-pressure runs only show relatively slight pressure variations with rise of temperature, mainly at the lower temperatures, and

3. graphs consisting of generalised curves for runs from open boat (atmospheric), 3000, 5000 psi and high pressure (45000 psi), which are all essentially experiments at constant pressures (Figs 125 to 128).

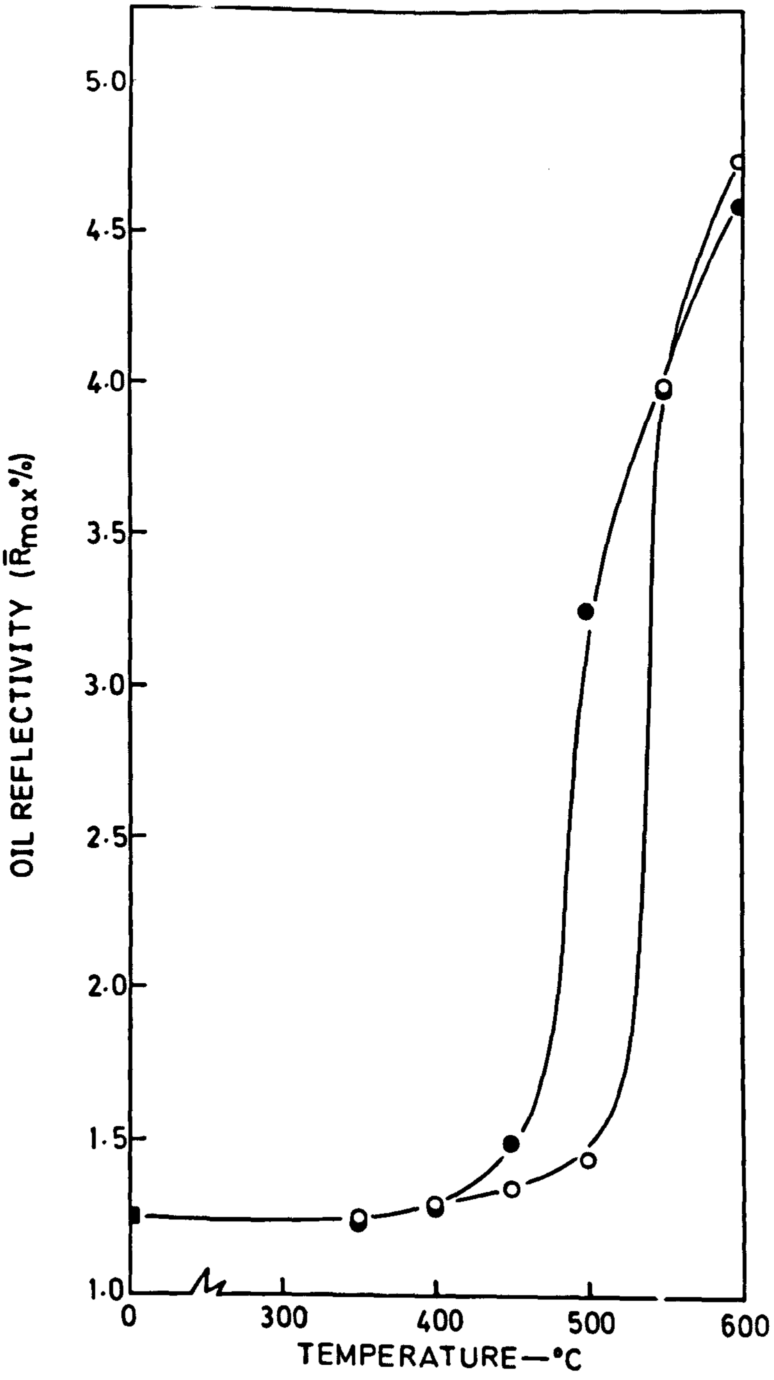
(i) Reflectivity (Figs 116, 120, 121 and 125)

As is usual, because of the similarity between the reflectivity-temperature curves in air and oil, only the oil-reflectivity curves (Figs 116, 120 and 125) are considered.

There are certain sequential patterns in the reflectivity-temperature curves for the different pressure levels. The sharp increase of reflectivity, which normally occurs at the onset of the plastic stage (Goodarzi 1971; Goodarzi and Murchison 1972), is delayed with decreasing pressure level in the bomb. At the lowest pressure (3000 psi), the most pronounced reflectivity jump occurs, between 500° and 550°C (Fig 116), whereas the rise commences between 450° and 500°C for the other low-pressure experiments (5000 psi) (Fig 116). Fig 120 shows the reflectivity-temperature plots for intermediate and high-pressure runs. At high pressure (ca 45000 psi), the initial reflectivity jump occurs at about 400°C. It is evident that the pressure increases continuously with temperature in the intermediate pressure runs and that the reflectivity-temperature plots for the intermediate run at each temperature level maintain a higher level than the high-pressure plots up to 600°C.

Fig 125 shows the groups of reflectivity-temperature curves. The reflectivity-curve at atmospheric pressure follows a higher level than for curves for samples carbonised under pressure over the entire range of the carbonisation temperature used. The reflectivity-temperature curves at other pressures follow similar and very close trends up to 400°C, then the reflectivity curves

Fig 116 Variation with temperature of oil reflectivity of coking coal vitrinite (carbon = 87.9% daf), carbonised at different low temperatures.

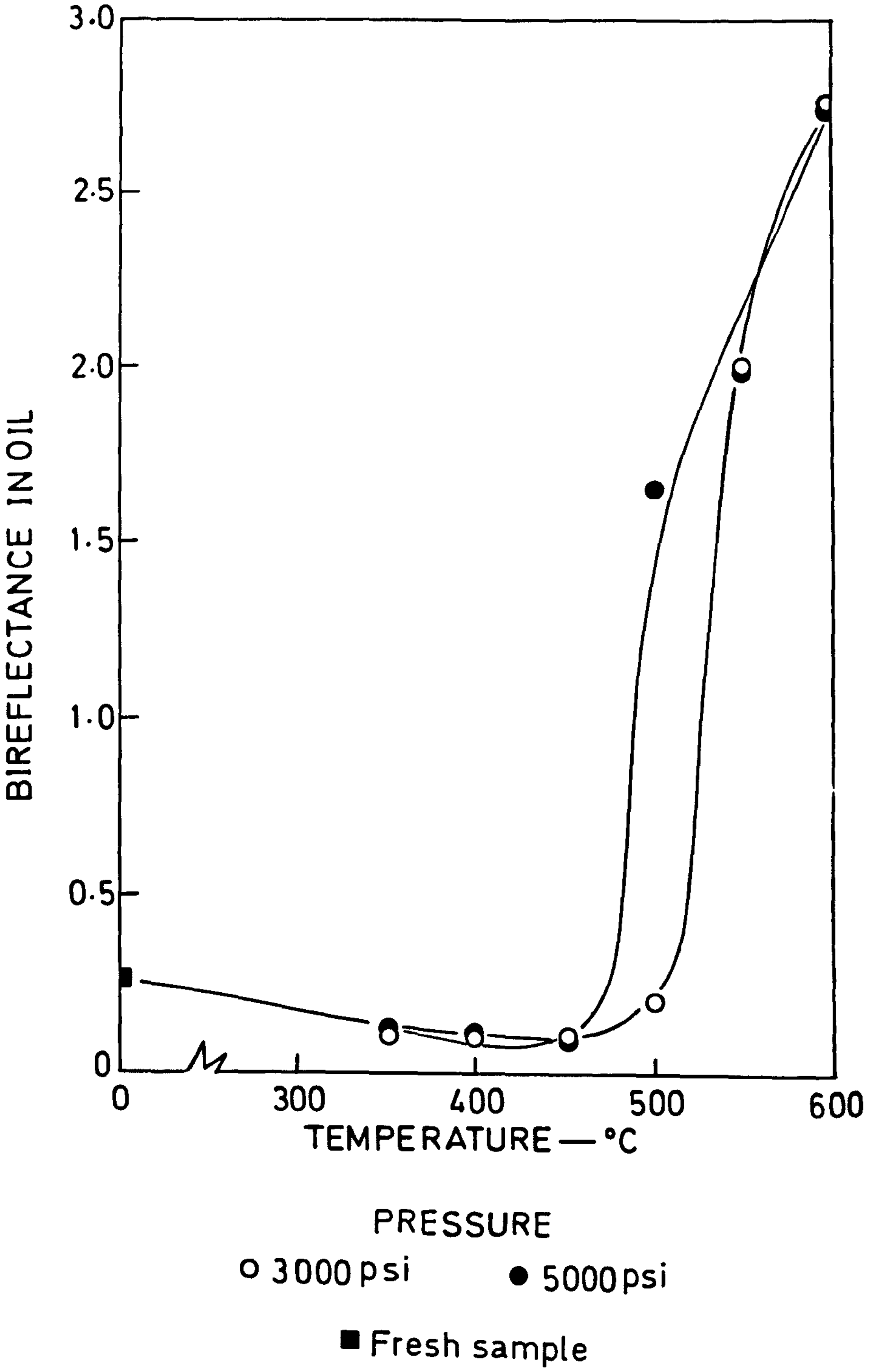


PRESSURE

○ 3000 psi ● 5000 psi

■ Fresh sample

Fig 117 Variation with temperature of bireflectance in oil of coking coal vitrinite (carbon = 8.79% daf) carbonised at different low pressures.



3.0
2.5
2.0
1.5
1.0
0.5
0
BIREFLECTANCE IN OIL
0
300
400
500
600
TEMPERATURE — °C
PRESSURE
○ 3000 psi
● 5000 psi
■ Fresh sample

Fig 118 Variation with temperature of refractive index of coking coal vitrinite (carbon = 87.9% daf), carbonised at different low pressures.

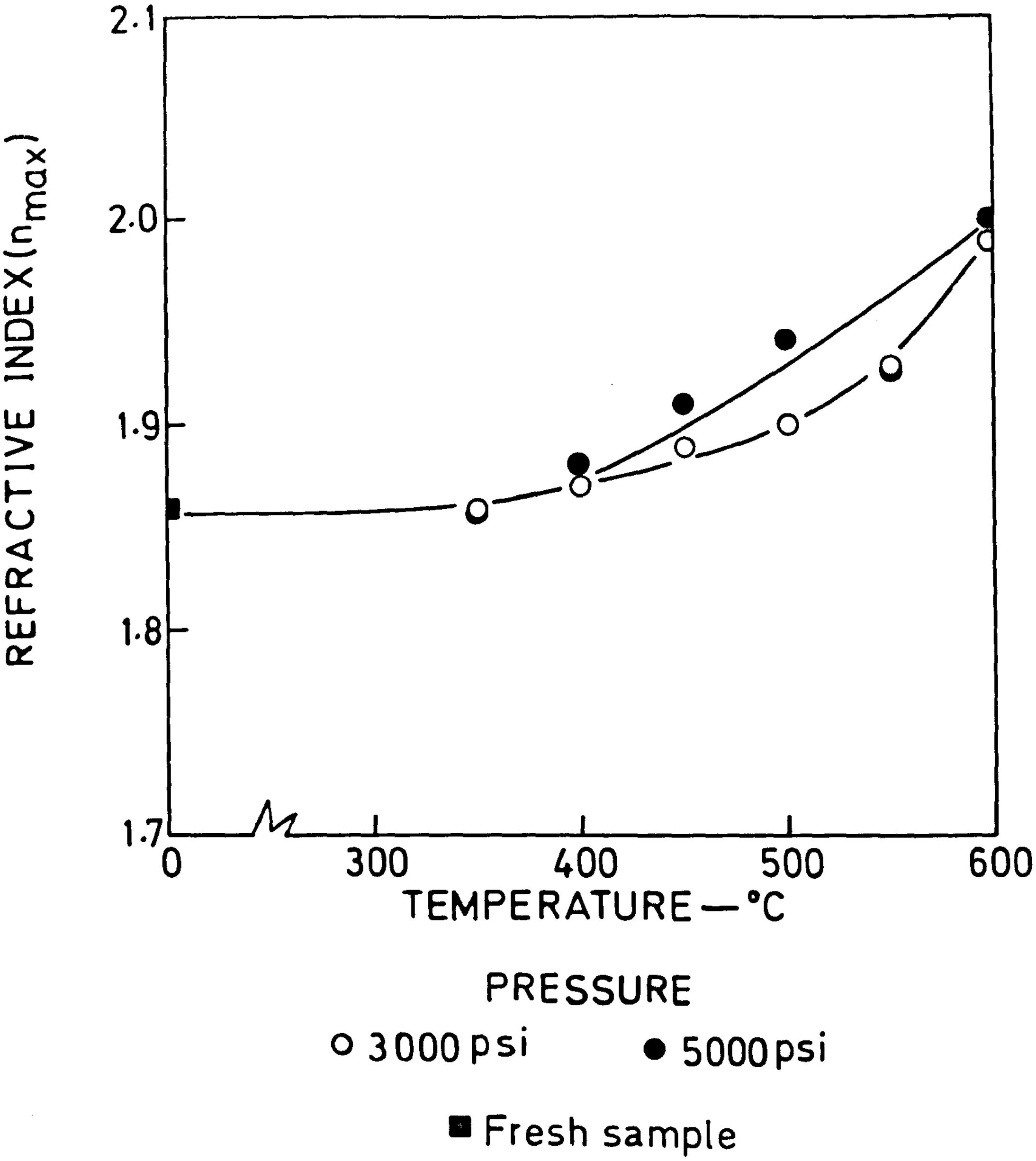
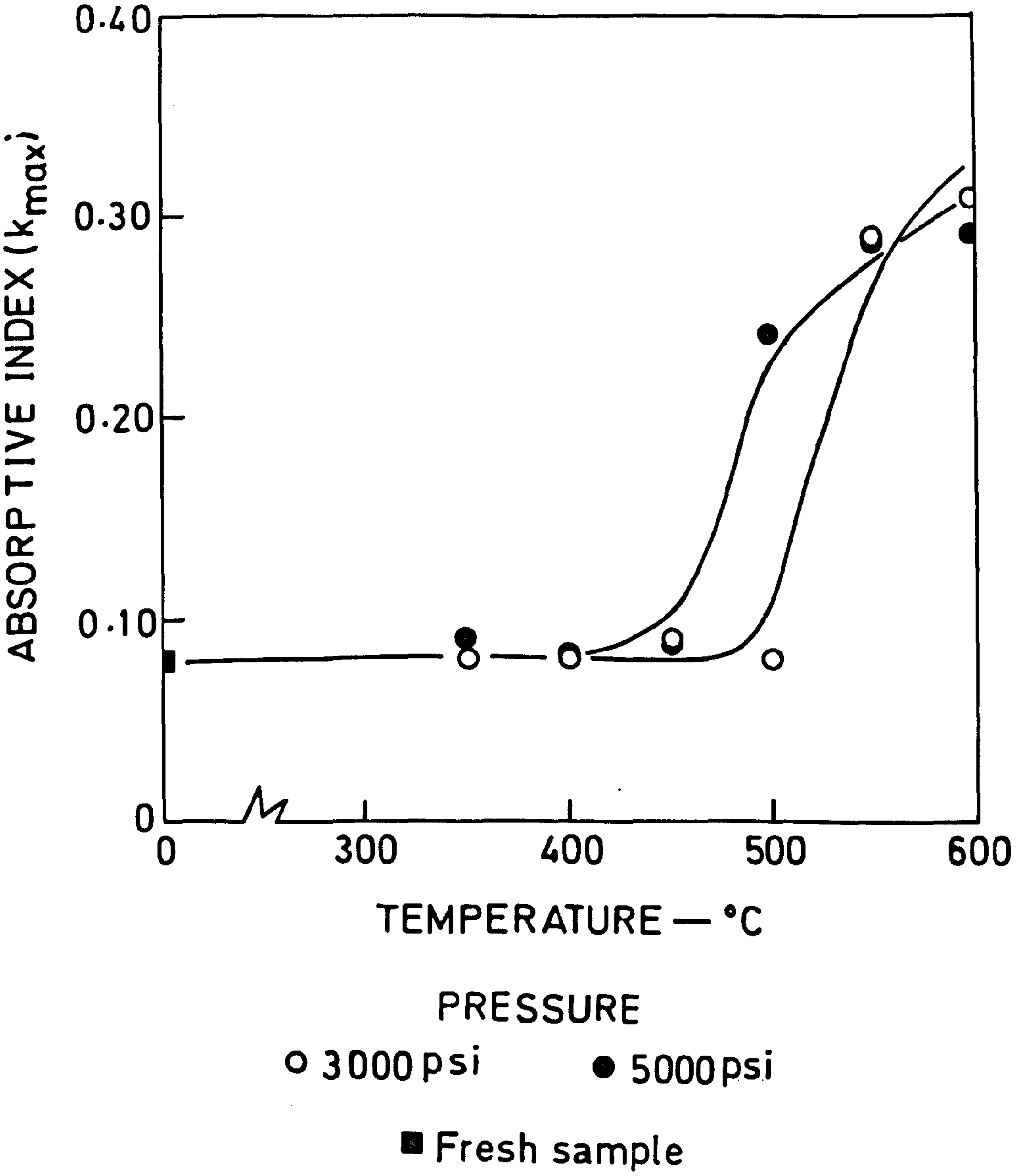

REFRACTIVE INDEX (n_{max})
2·1
2·0
1·9
1·8
1·7
0
300
400
500
600
TEMPERATURE — °C
PRESSURE
○ 3000 psi
● 5000 psi
■ Fresh sample

Fig 119 Variation with temperature of absorptive index of coking coal vitrinite (carbon = 87.9% daf), carbonised at different low pressures.

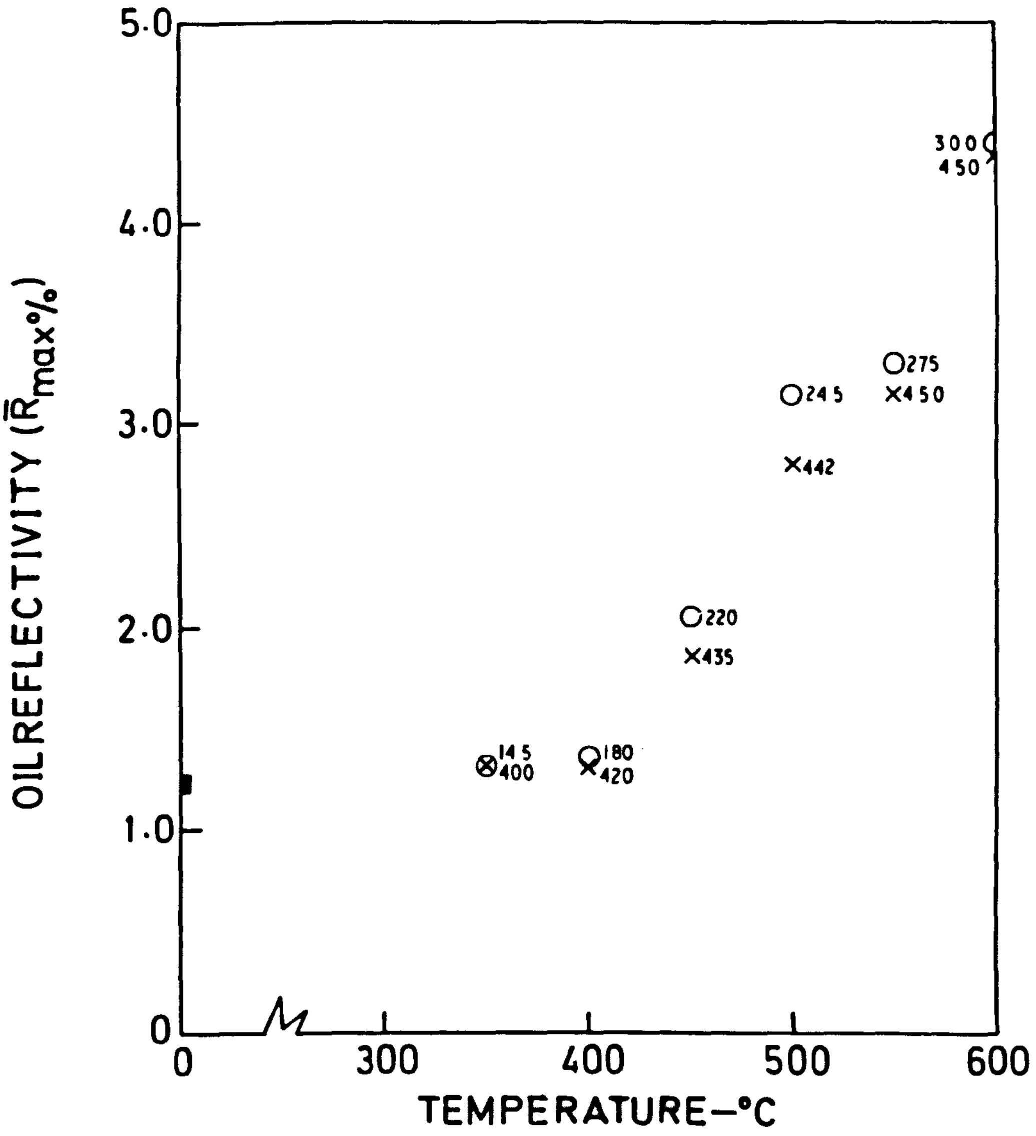

ABSORPTIVE INDEX (k_{max})
0.40
0.30
0.20
0.10
0
0
300
400
500
600
TEMPERATURE — °C
PRESSURE
○ 3000 psi
● 5000 psi
■ Fresh sample

separate. The curves intersect with one another in a transitional region (450° to 550°C). Below this region reflectivity is higher at one temperature the greater is the pressure; above 550°C the reverse relationship holds, reflectivity is higher the lower is the pressure for any temperature.

(ii) Bireflectance (Figs 117, 122 and 126)

Bireflectances in this set of experiments are calculated on the basis of the total number of reflectivity readings (approximately 25 maximum and 25 minimum) to give a better picture of changes in bireflectance-temperature curve at each level of pressure. Practically the same pattern as is seen in the reflectivity-temperature curves is shown here by the bireflectance curves in the low-pressure range (3000 and 5000 psi), namely, the sharp increase of bireflectance is delayed to higher temperatures with falling pressure level (Fig 117). The bireflectance plots at intermediate and higher pressures again maintain the same relation to one another as do the reflectivity plots, but the differentiation between the two pressure levels becomes more distinct (Fig 122). In the generalised curves (Fig 126), bireflectance decreases initially to a minimum at about 350° to 400°C, then increases continuously with carbonisation temperature. The bireflectance curve at atmospheric pressure (open boat) follows a higher trend than the high pressure curves after about 450°C, but is lower than the results at 3000 psi after 550°C and 5000 psi after 500°C.

Fig 120 Variation with temperature of oil reflectivity of coking coal vitrinite (carbon = 87.9% daf), carbonised under variable pressures.



NUMBERS DENOTE PRESSURE 10^2 psi

■ — Fresh sample

○ — Experiments at intermediate pressures

× — Experiments at high pressures

Fig 121 Variation with temperature of air reflectivity of coking coal vitrinite (carbon = 87.9% daf), carbonised under variable pressures.

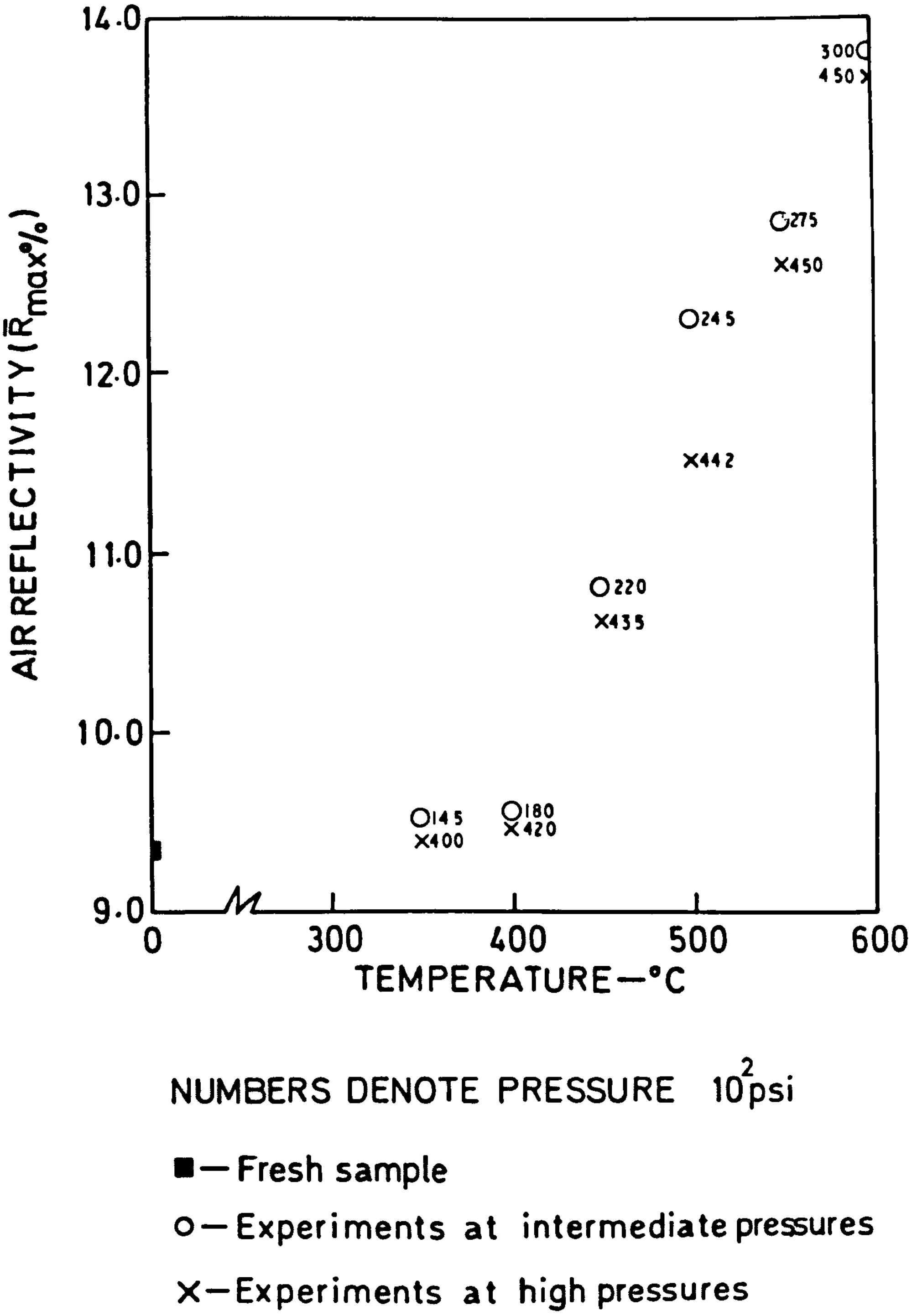

AIR REFLECTIVITY ($\bar{R}_{max}$%)
14.0
13.0
12.0
11.0
10.0
9.0
0
300
400
500
600
TEMPERATURE—°C
300
450
275
450
245
442
220
435
145
400
180
420
NUMBERS DENOTE PRESSURE 10^2 psi
■—Fresh sample
○—Experiments at intermediate pressures
×—Experiments at high pressures

Fig 122 Variation with temperature of oil bireflectance of coking coal vitrinite (carbon = 87.9% daf), carbonised under variable pressures.

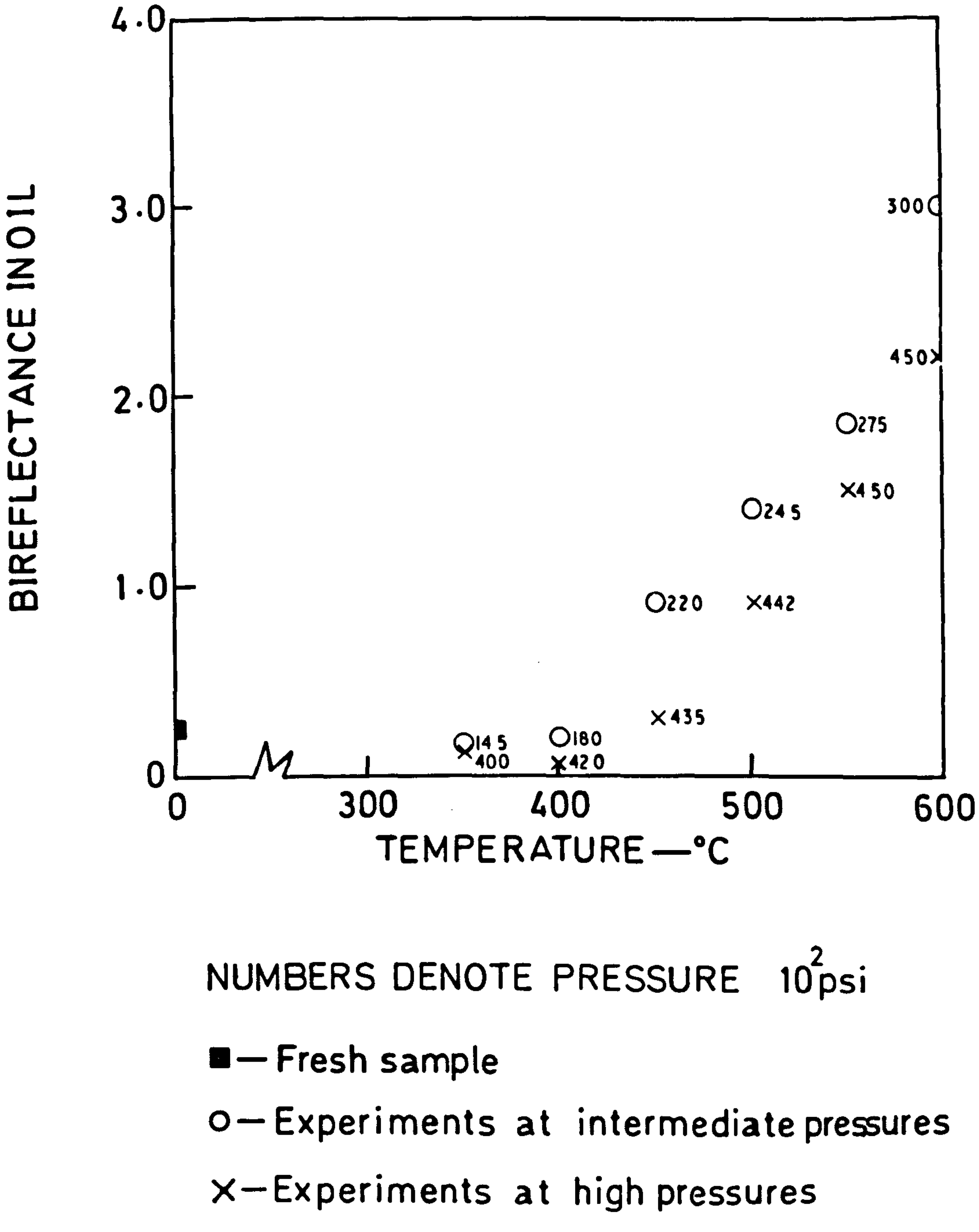

BIREFLECTANCE IN OIL
4.0
3.0
2.0
1.0
0
0
300
400
500
600
TEMPERATURE —°C
300
450
275
450
245
220
442
435
145
400
180
420
NUMBERS DENOTE PRESSURE 10^2 psi
■ — Fresh sample
○ — Experiments at intermediate pressures
× — Experiments at high pressures

Fig 123 Variation with temperature of refractive index of coking coal vitrinite (carbon = 87.9% daf), carbonised under variable pressures.

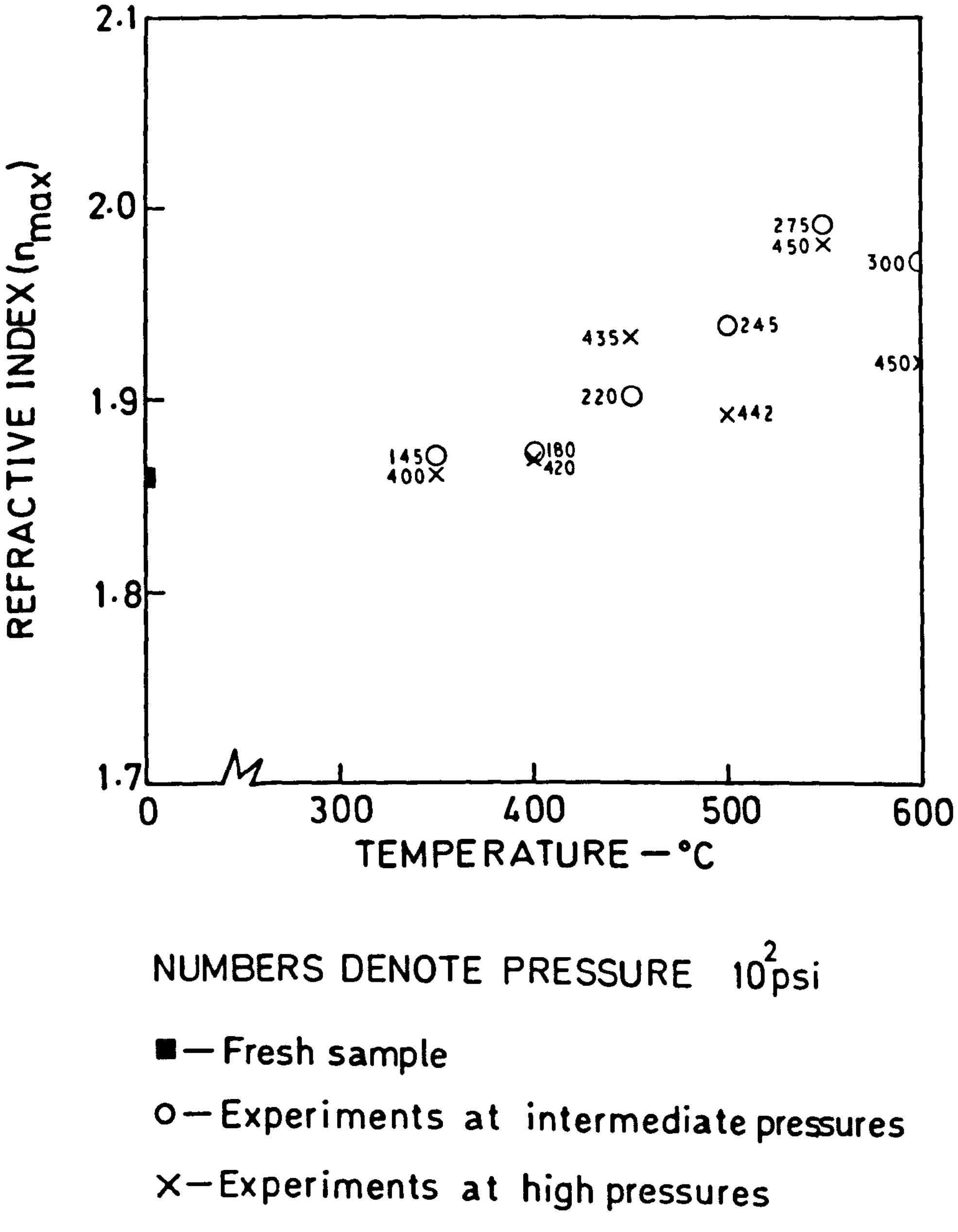
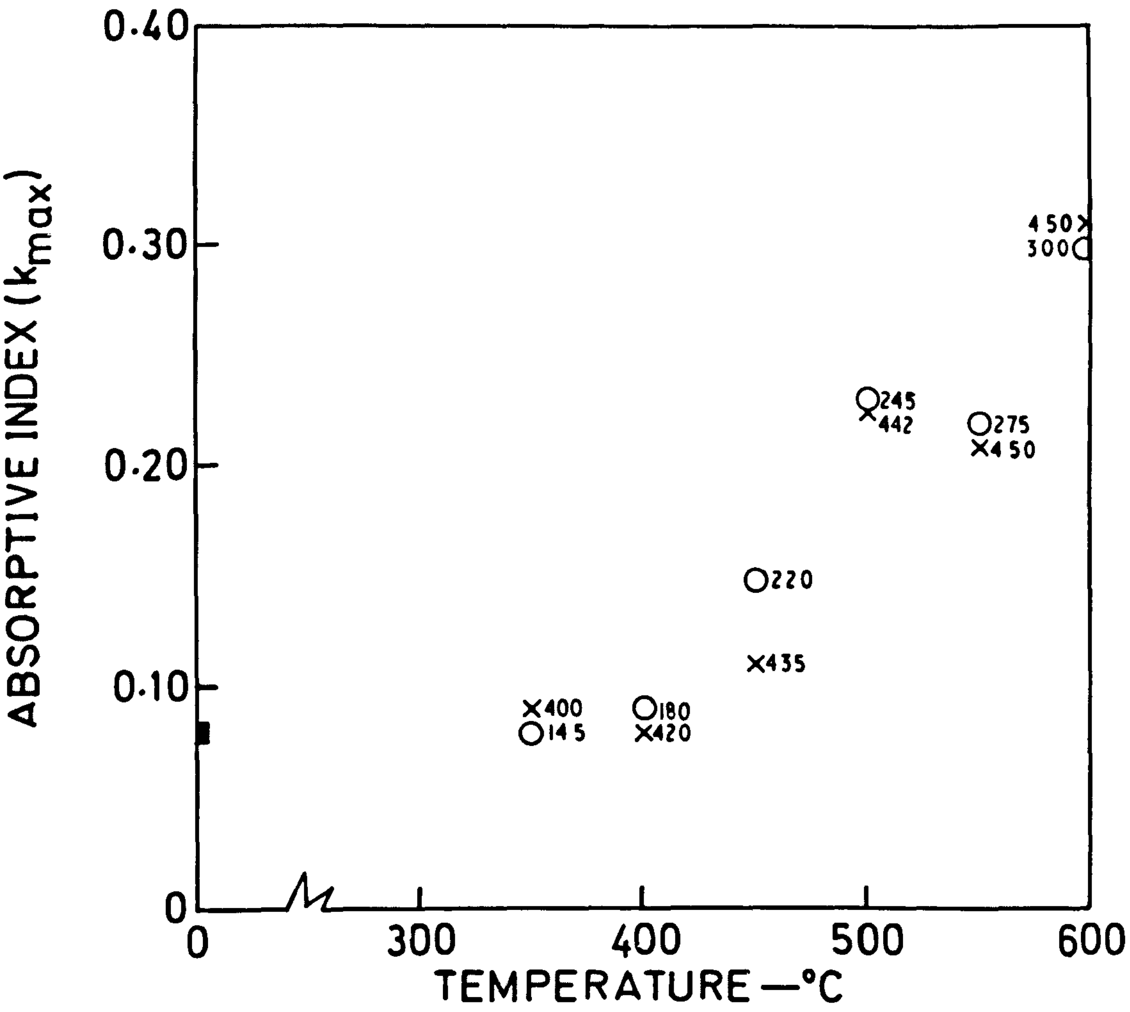

REFRACTIVE INDEX (n_{max})
2·1
2·0
1·9
1·8
1·7
0
300
400
500
600
TEMPERATURE — °C
145
400
180
420
435
220
245
442
275
450
300
450
NUMBERS DENOTE PRESSURE 10^2 psi
■ — Fresh sample
o — Experiments at intermediate pressures
× — Experiments at high pressures

Fig 124 Variation with temperature of absorptive index of coking coal vitrinite (carbon = 87.9% daf), carbonised under variable pressures.



NUMBERS DENOTE PRESSURE 10^2 psi

■ — Fresh sample

○ — Experiments at intermediate pressures

× — Experiments at high pressures

(iii) Refractive Index (Figs 118, 123 and 127)

The refractive index-temperature curves at the low pressure levels increase continuously after 400°C up to 600°C and is the higher the greater is the pressure level (Fig 118). The refractive index plots of the carbonised residues increase continuously up to 550°C for the intermediate and high pressures (ca 45000 psi) and then decrease with further carbonisation to 600°C, the decrease in the level of the refractive index being greater the higher is the level of pressure (Fig 123), but the generalised curves probably give a fair representation of refractive index rising with increasing temperature. The refractive index for carbonisations under atmospheric pressure is higher than those carbonised under pressure (Fig 127).

(iv) Absorptive Index (Figs 119, 124 and 128)

The absorptive index-temperature curves of the residues carbonised at different pressures show almost similar parallel changes to those of reflectivity-temperature curves.

Fig 125 Variation of generalised curves of oil reflectivity-temperature of coking coal vitrinite (carbon = 87.9% daf), at different pressures.

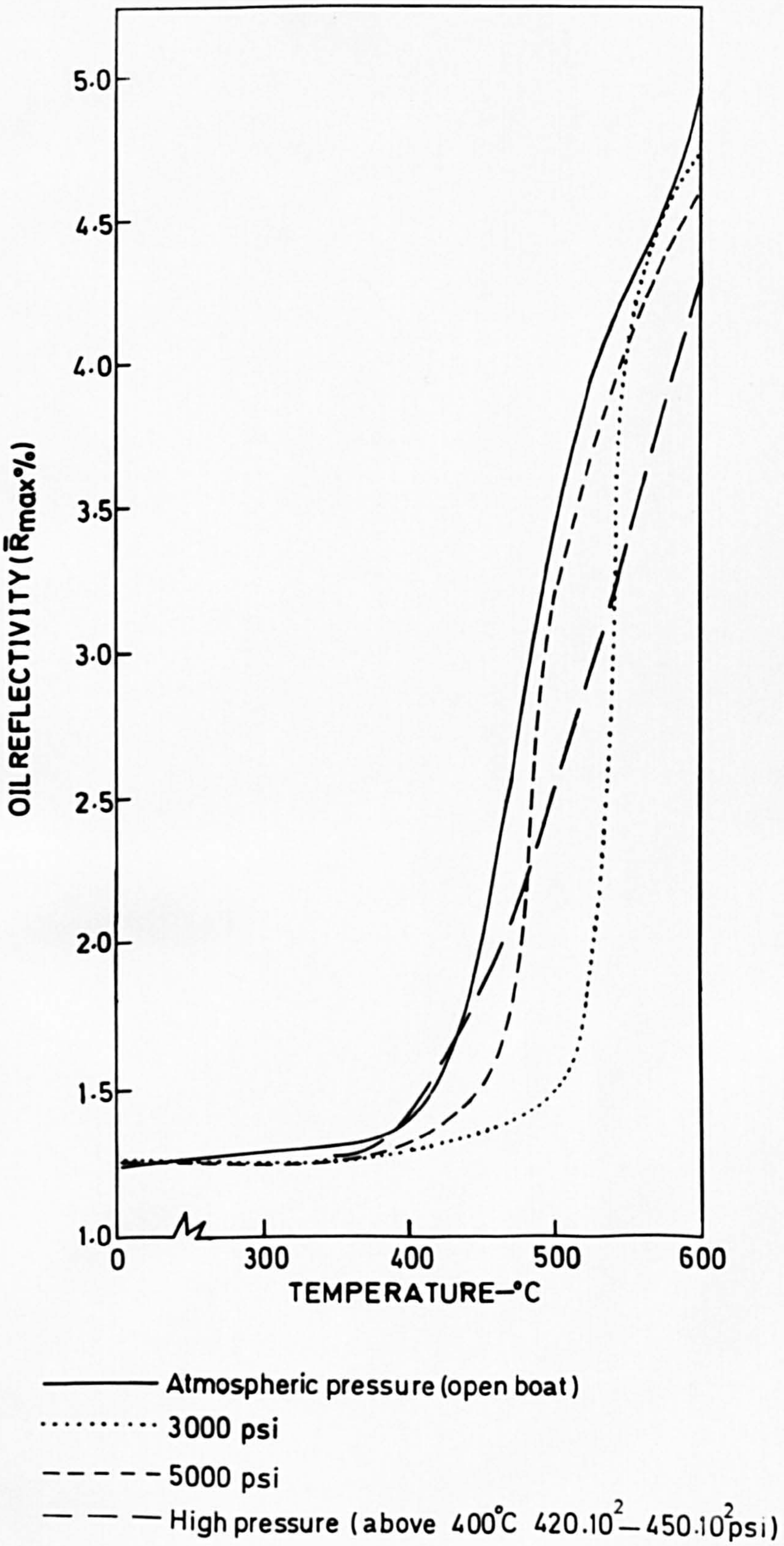

OIL REFLECTIVITY ($\bar{R}_{max}$%)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
300
400
500
600
TEMPERATURE—°C
Atmospheric pressure (open boat)
3000 psi
5000 psi
High pressure (above 400°C 420.10^2—450.10^2 psi)

Fig 126 Variation of generalised curves of oil bireflectance with temperature of coking coal vitrinite (carbon = 87.9% daf), at different pressures.

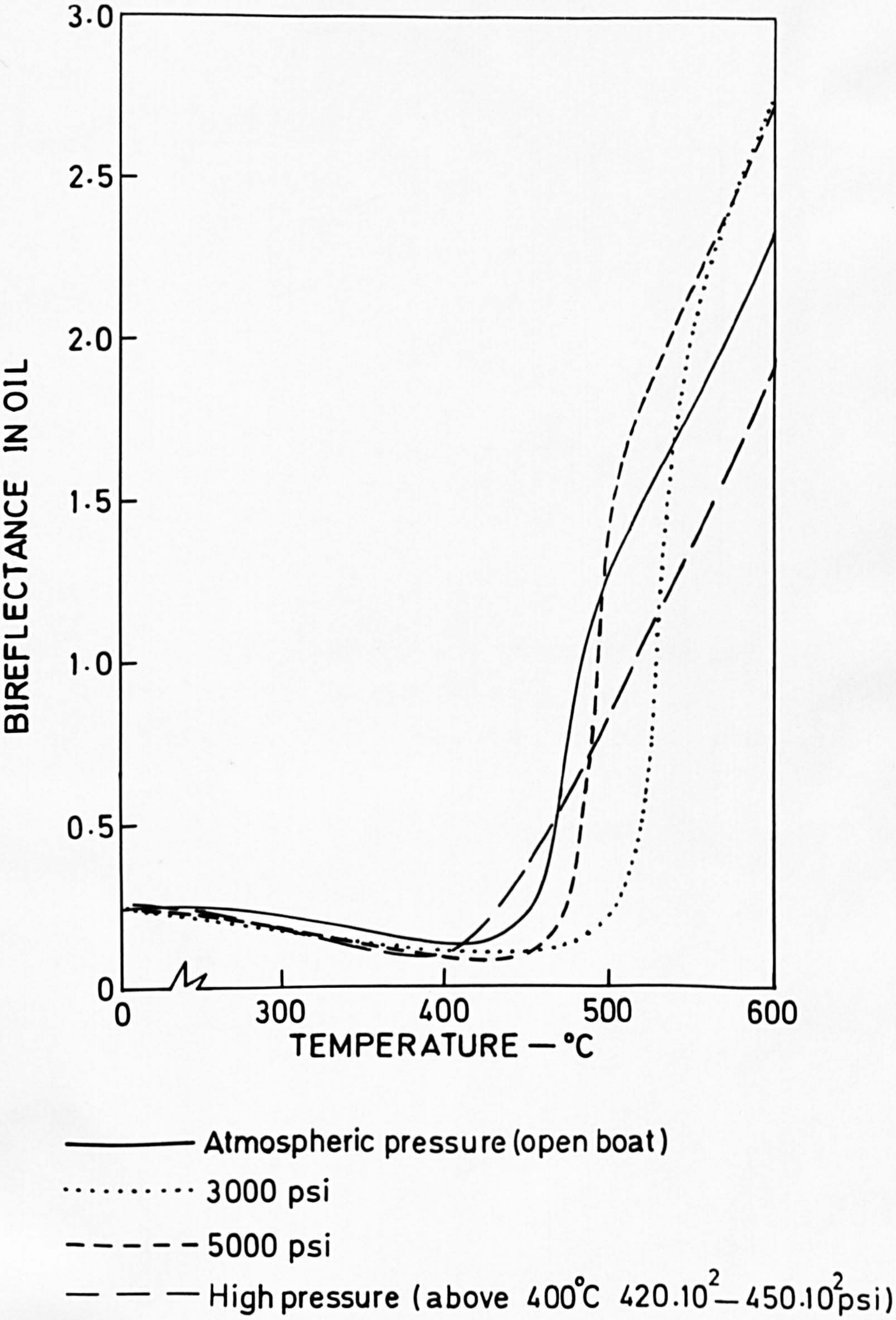

BIREFLECTANCE IN OIL
3.0
2.5
2.0
1.5
1.0
0.5
0
0
300
400
500
600
TEMPERATURE — °C
Atmospheric pressure (open boat)
3000 psi
5000 psi
High pressure (above 400°C 420.10² — 450.10² psi)

Fig 127 Variation of generalised curves of refractive index with temperature of coking coal vitrinite (carbon = 87.9% daf), at different pressures.

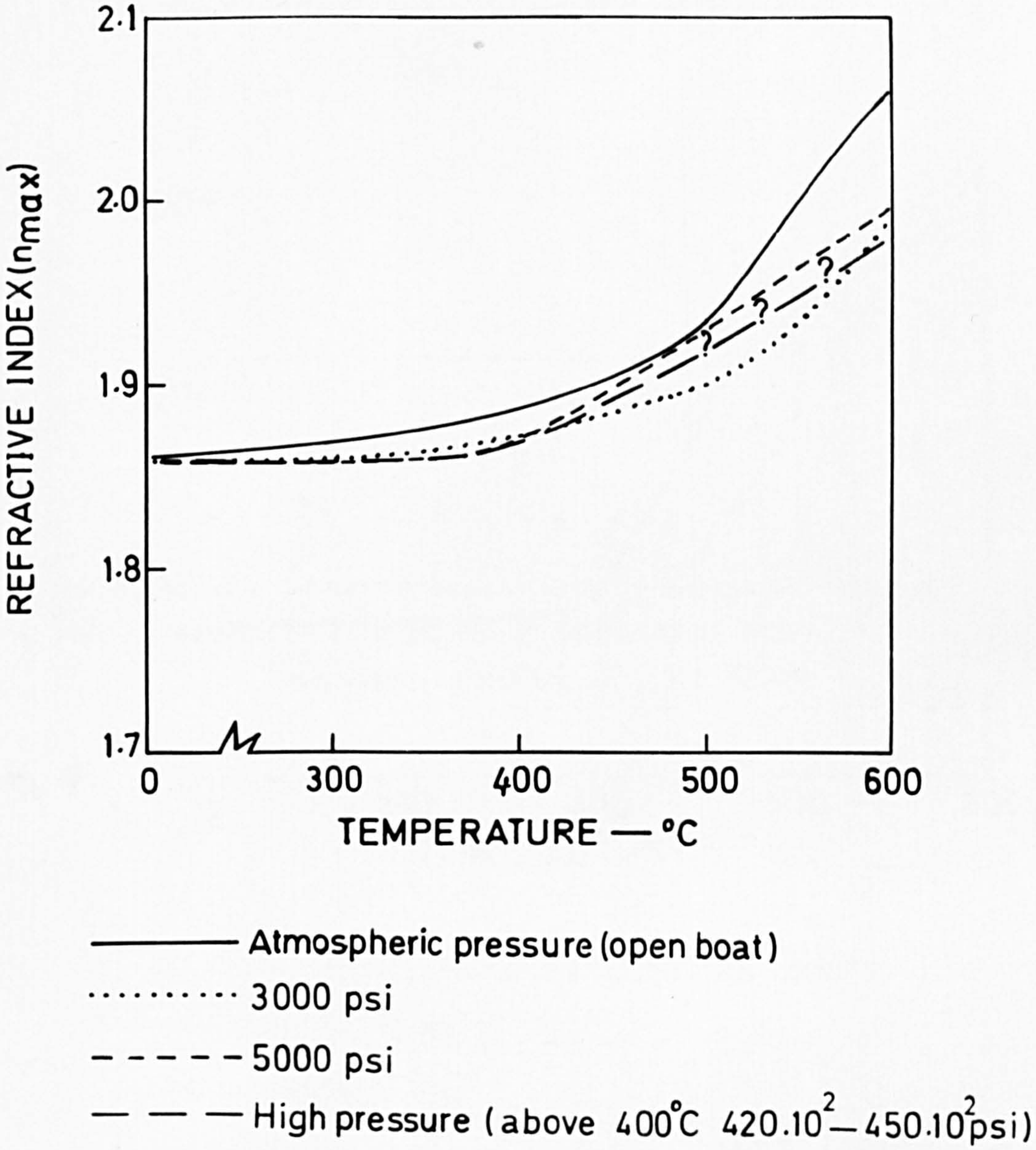
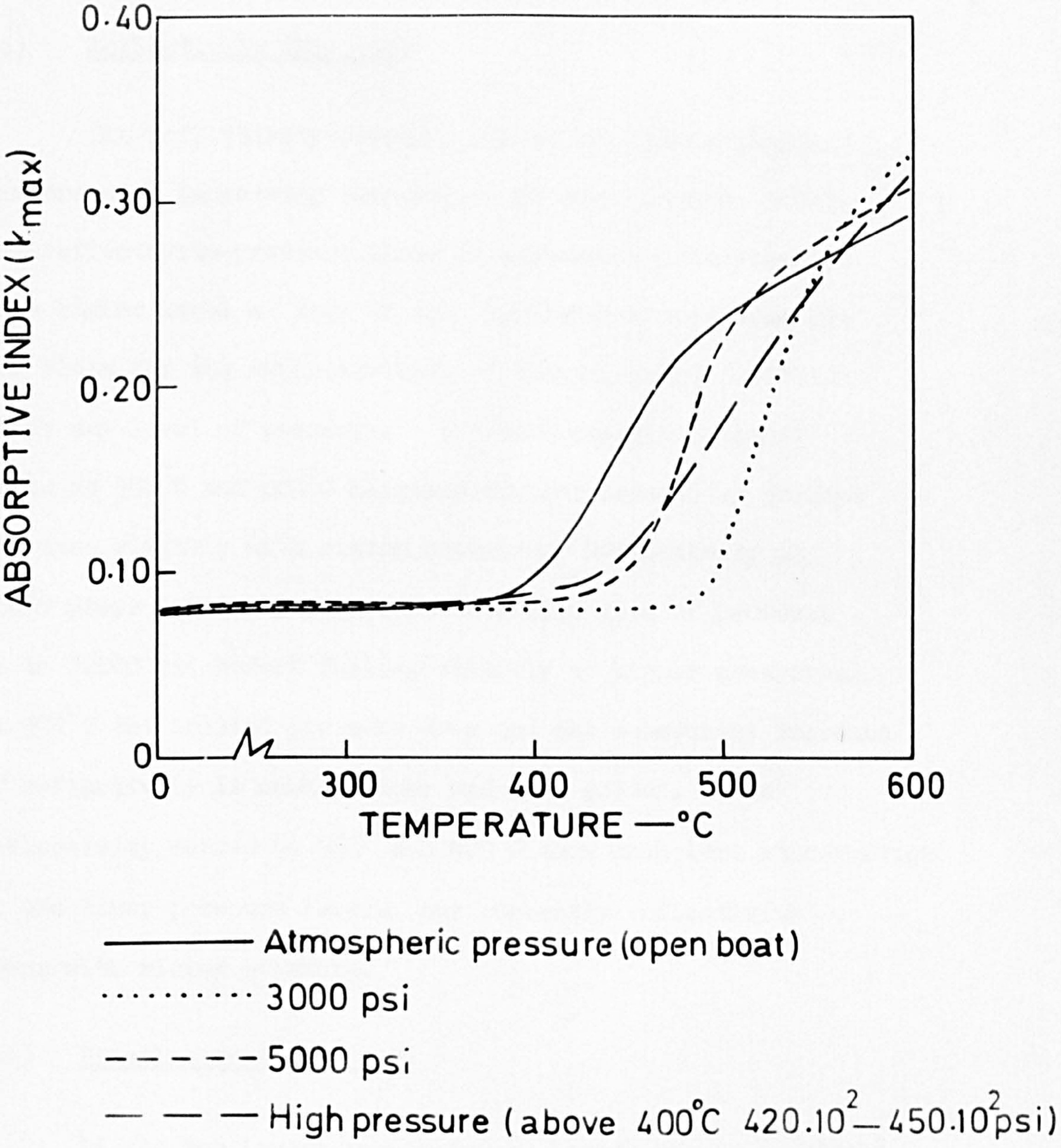

2.1
2.0
1.9
1.8
1.7
REFRACTIVE INDEX (n_{max})
0
300
400
500
600
TEMPERATURE — °C
Atmospheric pressure (open boat)
3000 psi
5000 psi
High pressure (above 400°C 420.10^2 – 450.10^2 psi)

Fig 128 Variation of generalised curves of absorptive index with temperature of coking coal vitrinite (carbon = 87.9% daf), at different pressures.


0.40
0.30
0.20
0.10
0
ABSORPTIVE INDEX (k_{max})
0
300
400
500
600
TEMPERATURE —°C
Atmospheric pressure (open boat)
3000 psi
5000 psi
High pressure (above 400°C 420.10^2 – 450.10^2 psi)

(c) Optical Properties - pressure curves

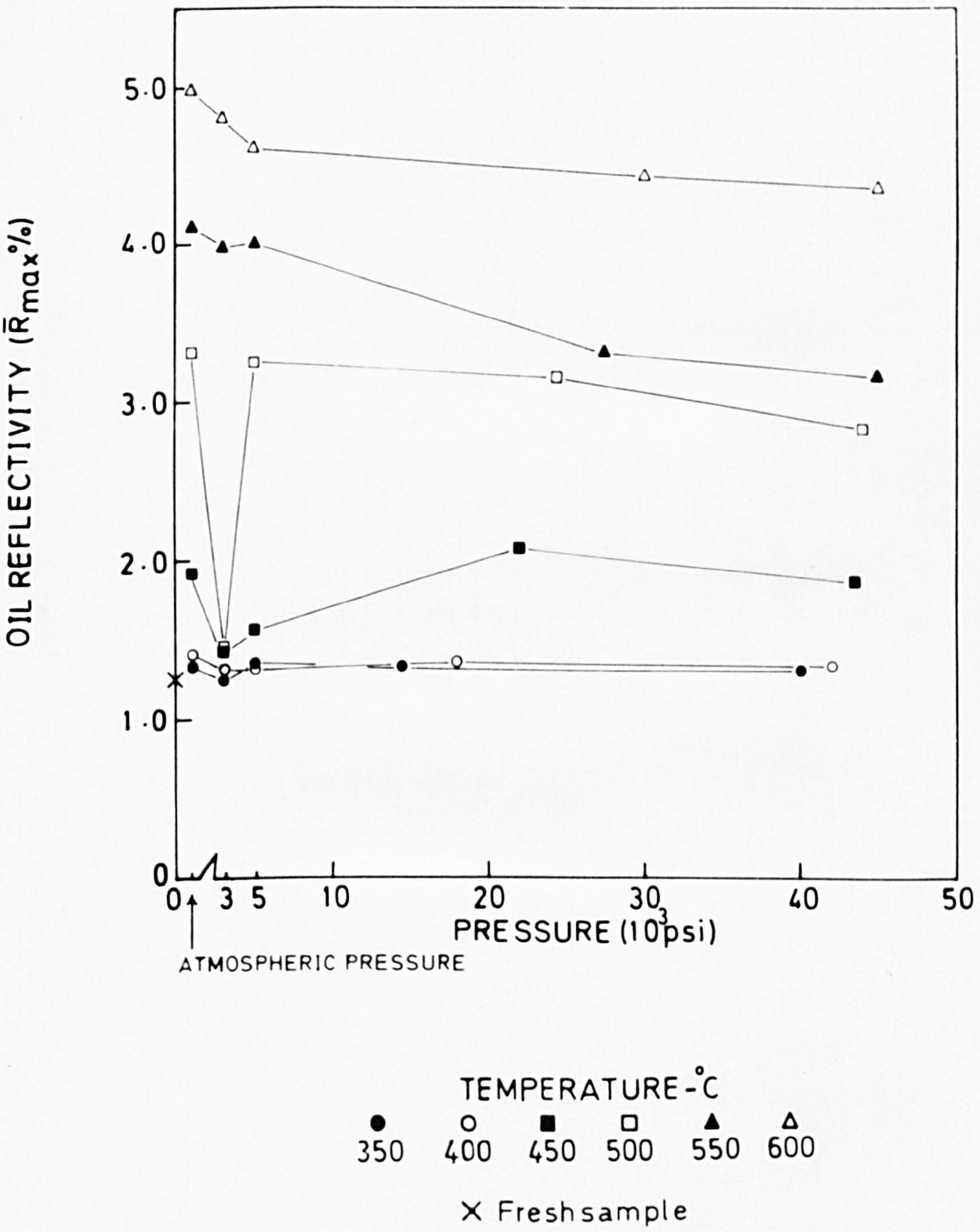
(i) Reflectivity (Fig 129)

The reflectivity-pressure curves maintain a sequential pattern with increasing temperature at each pressure level. The reflectivity-pressure plots at atmospheric pressure are at a higher level at each of the temperatures used than are the plots for the reflectivities of corresponding residues under any level of pressure. The reflectivity-pressure plots at 350°C and 400°C maintain similar levels, or perhaps decrease slightly with rising pressure. Reflectivity at 450°C drops initially then increases with rise of pressure up to 22000 psi before falling slightly to higher pressures. At 500°C the initial pressure drop and the subsequent increase of reflectivity is much greater and more sudden. The reflectivity curves at 550° and 600°C show much less interruption at the lower pressure levels, but generally reflectivity drops with rising pressure.

(ii) Bireflectance (Fig 130)

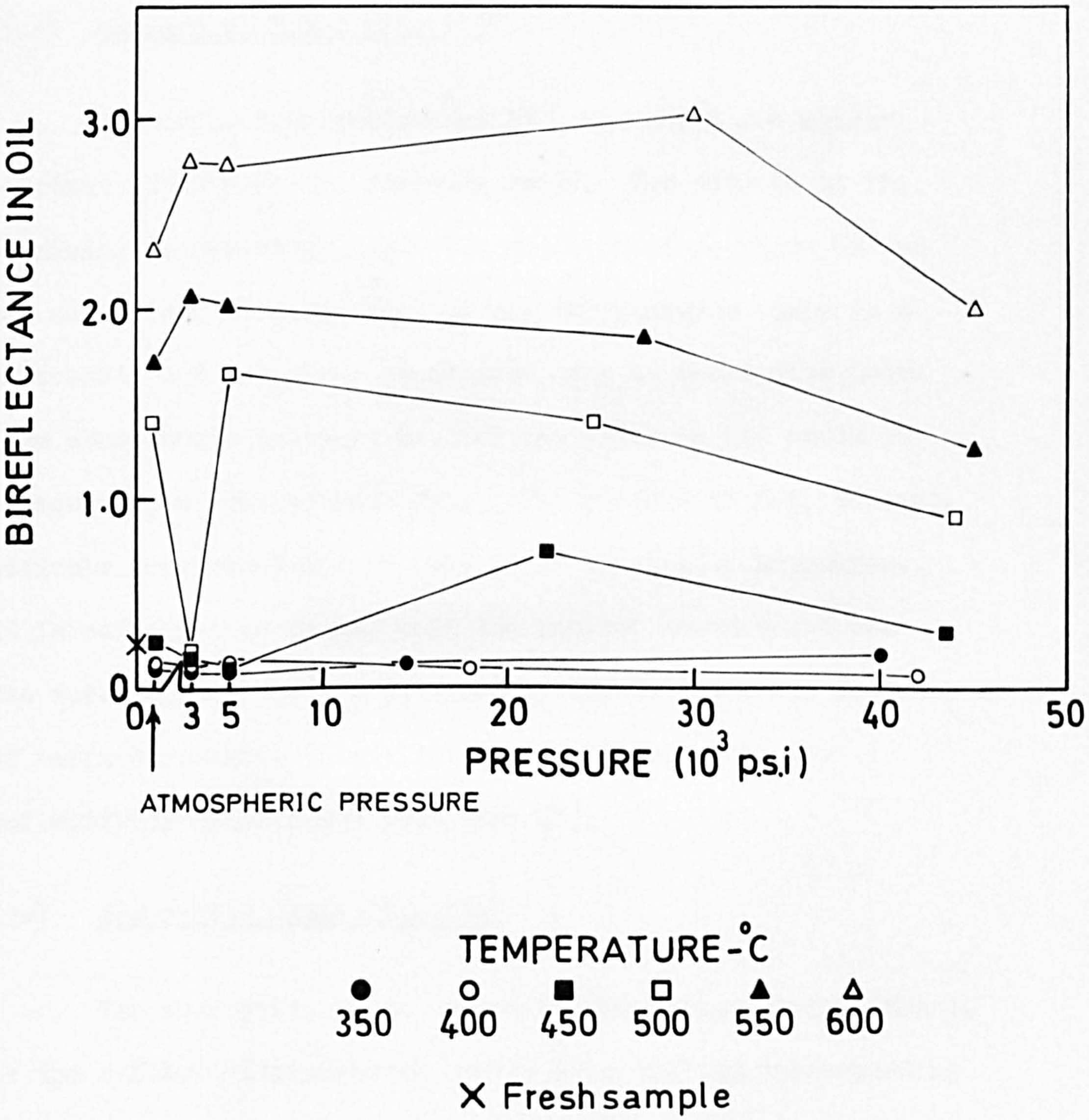
At the two lowest temperatures, bireflectance is almost constant over the pressure range. At 450° and 500°C there is a drop in bireflectance from its level at atmospheric pressure, followed by a rise and then a subsequent fall to the highest pressure level employed - the rise of bireflectance is sharper at the higher temperature. The two highest temperatures

Fig 129 Variation with pressure of oil reflectivity of coking coal vitrinite (carbon = 87,9% daf), carbonised at different temperatures.



OIL REFLECTIVITY ($\bar{R}_{max}$%)
5.0
4.0
3.0
2.0
1.0
0
0
3
5
10
20
30
40
50
PRESSURE (10^3psi)
ATMOSPHERIC PRESSURE
TEMPERATURE - °C
● 350
○ 400
■ 450
□ 500
▲ 550
△ 600
× Freshsample

Fig 130 Variation with pressure of oil bireflectance of coking coal vitrinite (carbon = 87.9% daf), carbonised at different temperatures.


BIREFLECTANCE IN OIL
3.0
2.0
1.0
0
0
3
5
10
20
30
40
50
PRESSURE (10³ p.s.i)
ATMOSPHERIC PRESSURE
TEMPERATURE-°C
● 350
○ 400
■ 450
□ 500
▲ 550
△ 600
× Freshsample

show an initial rise in bireflectance to 3000 psi, but eventually the reflectivity falls to below or around the value at atmospheric pressure, the fall possibly being more pronounced at higher pressures.

(iii) Refractive Index (Fig 131)

The refractive indices at 350° and 400°C are almost constant throughout the pressure range. The pattern at the remaining temperatures over the whole pressure range is not too clear, but it seems that at all temperatures there is a noticeable and sometimes pronounced drop in refractive index from atmospheric pressure to 3000 psi which in all cases is followed by a rise to 5000 psi. The pattern is not, however, entirely consistent and is less so at the higher pressures. It is not possible to say what the general trend would be. The intermediate pattern is probably due to the lower accuracy of refractive-index determination than is possible for reflectivity measurement (see Part II).

(iv) Absorptive Index (Fig 132)

The absorptive index curves follow rather similar trends to the reflectivity-pressure curves (Fig 129) at corresponding temperature levels, but the pattern is less consistent, again, presumably due to the lower accuracy of determination of absorptive index.

Fig 131 Variation with pressure of refractive index of coking coal vitrinite (carbon = 87.9% daf), carbonised at different temperatures.

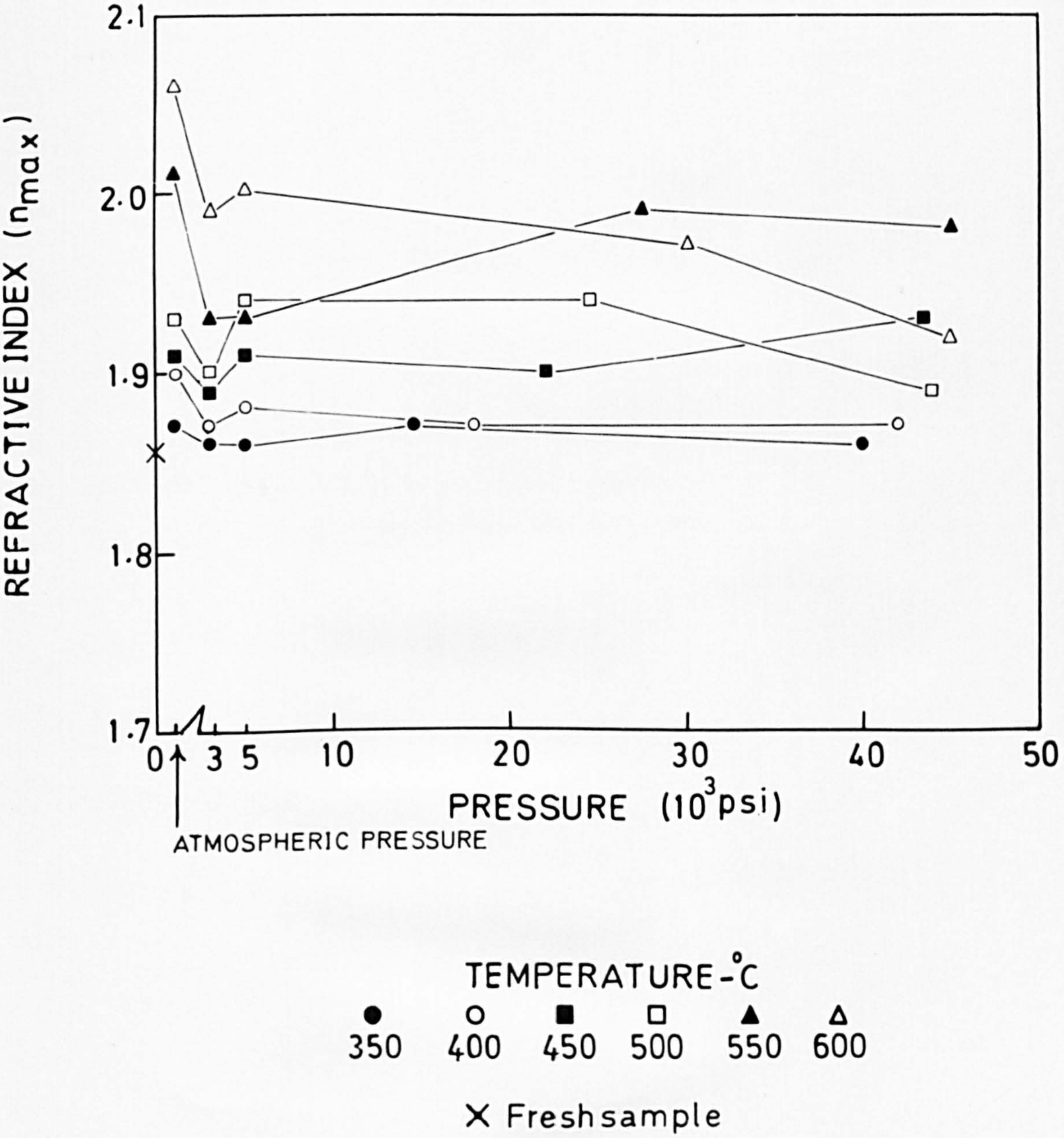
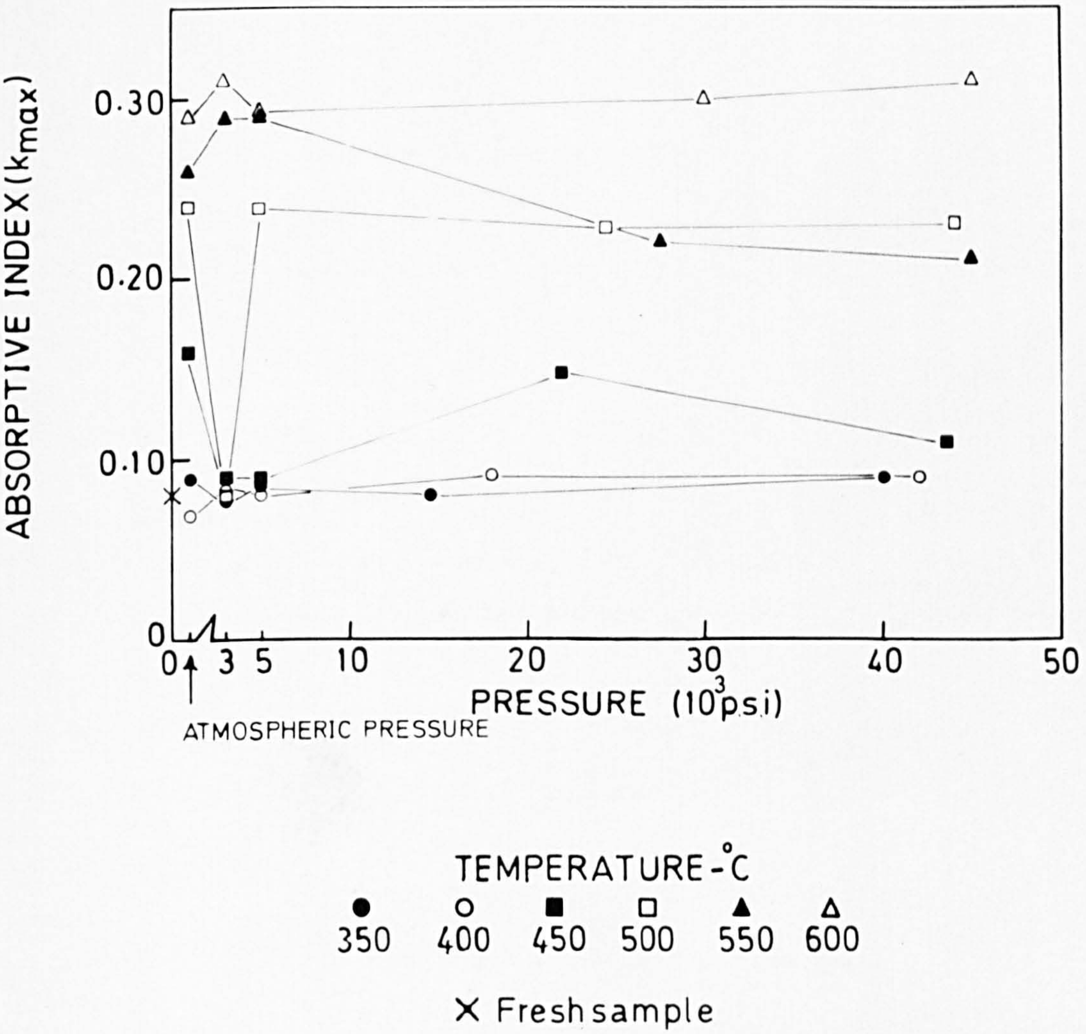

REFRACTIVE INDEX (n_{max})
2.1
2.0
1.9
1.8
1.7
0
3
5
10
20
30
40
50
PRESSURE (10^3 psi)
ATMOSPHERIC PRESSURE
TEMPERATURE-°C
● 350
○ 400
■ 450
□ 500
▲ 550
△ 600
× Freshsample

Fig 132 Variation with pressure of absorptive index of coking coal vitrinite (carbon = 87.9% daf), carbonised at different temperatures.


ABSORPTIVE INDEX (k_{max})
0.30
0.20
0.10
0
0
3
5
10
20
30
40
50
PRESSURE (10^3 p.s.i)
ATMOSPHERIC PRESSURE
TEMPERATURE-°C
● 350
○ 400
■ 450
□ 500
▲ 550
△ 600
× Fresh sample

D. Discussion

1. Morphology

The above work clearly indicates that the final pressure has an important effect on the morphology of the resulting carbonised residues. It is now established that a number of factors, e.g. heating rate, influence the morphological behaviour of carbonised residues, e.g. anisotropy, the character of the devolatilisation vacuoles, mosaic size, etc. During open-boat carbonisation the anisotropic vitrinites become plastic and almost isotropic with approach to the decomposition temperature, i.e. about 400°C, due to the destruction of the original ordering of molecular structure (see Goodarzi and Murchison 1972). Further increase of temperature to about 450°C results in some re-ordering of the molecular structure and the development of anisotropy, which continues to improve with developing mosaic structure up to 600°C. In the present study, with runs at different pressure levels, but within the same temperature range (i.e. 350° to 600°C), the anisotropy, devolatilisation vacuoles, mosaic structures develop, but the temperature of their development is greatly dependent on the pressure level. There are certain consistent patterns between residues of runs carried out in the bomb, but these trends do not necessarily extend to the open-boat carbonisations.

A comparison is now made between the runs at different pressures in the bomb and then with the open-boat residues.

The morphological studies indicate that the final pressure apparently has an important effect on the morphology of the resulting carbonised residues.

(a) Perhaps surprisingly, the lower is the pressure, the more prolonged is the devolatilisation phase and the longer it takes for the mosaic structure to develop - the open-boat carbonisation does not fit with this pattern.

(b) The mosaic units are the larger the lower is the pressure level, but in general all the samples carbonised under pressure develop larger mosaic units than samples carbonised at atmospheric pressure.

(c) The orientation of mosaic structures becomes more regular with decrease of pressure level, and is even better for residues carbonised at atmospheric pressure, so here is one constant trend that extends to the open-boat carbonisations.

(d) The devolatilisation vacuoles become more numerous, but their size decreases and they also develop an irregular shape with rise of pressure.

(e) The development of perfectly rounded devolatilisation vacuoles is characteristic of the residues at highest pressure. The residues carbonised at atmospheric pressure do not develop this type of vesiculation. Melvin (1967) and Aganoglu (1972), examining naturally heat-affected coal, demonstrate the formation of such a vacuole type at some distance from the heat source.

The above pattern indicates one important point, namely increase in fluidity with decrease of pressure in the bomb, because it is known that the decomposition point is raised to a higher temperature by rise of pressure (see Hamman 1957 and Berkowitz 1967). Viscosity increases with rise of pressure, and since the maximum viscosity is followed by the resolidification of the plastic vitrinite (see for example Brown 1956), it is not surprising that the devolatilisation phase is shorter with higher pressures. This feature is clearly apparent in the temperature of development of the mosaic structure which decreases from 550° to 450°C with rise of pressure. Development of a mesophase at 450°C in the runs at intermediate pressures indicates an intermediate stage between plastic and resolidification phases. Thus, because of these differences in morphological characters of residues carbonised under pressure, then the pressure level, when referring to the morphology of such samples, should always be quoted.

Further, it appears that there is a similarity between carbonised residues with increase of pressure to those carbonised at atmospheric pressure with decrease of heating rate, namely a decrease in the size of the mosaic units and changes in the mosaic texture with falling heating rate. Since the reduction in mosaic size is related to decrease in fluidity with decrease of heating rate, then probably the same argument can be applied to carbonised vitrinites under pressure when the pressure level increases progressively.

The development of larger mosaic units under pressure than in the vitrinite carbonised at atmospheric pressure is probably due to a greater level of fluidity of the vitrinite under pressure, because of the influence of the metaplast which is present for a greater length of time under pressure and so allows the growth of mosaic units to sizes well beyond those formed at atmospheric pressure. The orientation of the mosaic becomes greater the higher is the pressure up to the intermediate pressure level but at high pressure levels, only occasional mosaic units develop some common orientation. Finally, the development of perfectly rounded vacuoles in residues from 'pressure' carbonisations are compared with vitrinite carbonised at atmospheric pressure, particularly during the plastic phase (about 400°C). Probably the influence of pressure maintains the shape of the vacuoles, which is probably also the reason for the perfectly rounded vacuoles found in naturally heated coals (see the results of Melvin 1968 and Aganoglu 1972).

2. Optical Properties

(a) Introduction

In discussing the changes observed in the optical properties of the coking coal vitrinite carbonised under pressure, two factors must be borne in mind. First, as stated, in the earlier section on the morphology of these samples, open-boat carbonisation takes place in a radically different environment to that in the pressure 'bomb'. In open-boat carbonisation volatile products are swept from the system and take no further part in the reactions. In the sealed capsule of the bomb, the volatile products given off, once active decomposition begins, are an intimate part of the system and their presence must influence the properties of the final product.

A second factor to be remembered is the variation which occurred in both temperature and pressure of the experiments at 'intermediate pressure', i.e. in the pressure range from 14500 to 30000 psi approximately. This discussion, therefore, begins with a consideration of the variations shown by the reflectivities of the three runs at constant pressure, i.e. 3000, 5000 and approximately 45000 psi; then comparisons are made with the optical variations shown by the residues from open-boat carbonisations before any comparison is attempted with runs at intermediate pressures. Reflectivity, bireflectance, refractive index and absorptive index plots against temperature for the different pressure levels are first considered before any comment is made on the relevance of the reflectivity-pressure plots at different temperature levels.

(b) Optical Properties- temperature curves

(i) Reflectivity (Figs 116, 120, 121 and 125)

It appears that the decomposition phase is delayed to considerably higher temperature (above 500°C) at the lowest pressure level (3000 psi) employed (Fig 116). The results of Goodarzi (1971) and Goodarzi and Murchison (1972) for vitrinites carbonised under atmospheric pressure show that a sharp increase of reflectivity (Fig 13) commences only when the vitrinite becomes plastic and approaches the active decomposition phase. The delay in active decomposition must be due to the applied pressure shifting the decomposition point of the vitrinite to a higher temperature (see Hamann 1957) and inhibiting the development of aromatic structure. The continuous increase of reflectivity after the initial sharp jump is as usual due to rapid coalescence and growth of aromatic structures.

The sharp increase of reflectivity in the second set of low-pressure experiments (5000 psi) commences at about 450°C, indicating that 'active decomposition' apparently begins at a lower temperature at this higher level of pressure. This feature must be due to a greater viscosity of the plastic vitrinite caused by the higher pressure, which must also bring forward the commencement of the resolidification phase (possibly to 500°C compared with 550°C).

Turning now to the run with the highest pressures used, pressures which were almost constant, the decomposition begins at an even lower temperature, again presumably due to further depression of the temperatures of decomposition and resolidification. From the slope of the curve, apparently the concentration of the aromatic structures and their growth is less rapid at this pressure level, because of suppression of the plastic phase (see for example discussion on Rate of Heating in Part III).

The next point to examine is the relationship between these three curves and the curve for open-boat (atmospheric) carbonisation, particularly in their later stages. Comparing the three reflectivity-temperature curves (Fig 125) at the different pressure levels, it appears that with rising pressure the duration of plasticity of the carbonised residues is increasingly shortened, resulting in a lower reflectivity level at the start of plasticity. These data can be compared with the effect of heating rate and it appears that there are some similarities between the two sets of results, i.e. there is a decrease in fluidity with reduction of the heating rate and/or increase of pressure. But, if this explanation is correct, why should the reflectivity-temperature curves coincide at the start with the curve for highest pressure; also, what about the cross-cutting relationship of the reflectivity-temperature curves for the 'bomb' materials?

If the upper parts of the four curves are examined, there is a relationship between them which might reasonably be expected, viz. that as pressure increases, the reflectivity at any temperature (above approximately 550°C) is lower. This relationship would be predicted since pressure would be expected to inhibit chemical reaction and properties dependent on those ractions. The relationship is not apparent at lower temperatures and it appears that the expected relationship is only generated once resolidification has occurred in all cases.

Reference must now be made again to the morphological structure described in Vol III (see Appendix V). Based on the mosaic sizes in the photomicrographs, the largest mosaics in the runs at pressures higher than atmospheric is found in the samples at 3000 psi and apparently resolidification does not occur until a temperature above 500°C. In the experiments at 5000 psi, the mosaic is smaller, but resolidification took place after 400°C at high pressure experiments and the mosaic is very small indeed. These morphological features alone indicate that the temperature of the start of the plastic phase is gradually lowered and also that the phase itself is increasingly shortened (see also the bireflectance curves in this section and again the section on Rate of Heating).

The effects producing these features also influence the slopes of the reflectivity curves which can be explained as follows: At a pressure of 3000 psi the plastic stage begins around 400°C and seemingly the metaplast is dispersed within the solid phase and can react over a time period extending over a temperature range of more than 100°C. Eventually the rapid rise of reflectivity between 500° and 550°C is caused by the metaplast splitting into solid and gas due to rise of temperature. Increase of pressure to 5000 psi lowers the temperature at which the metaplast splits up and the reflectivity rises sooner and this pattern is repeated at 45000 psi. In the open-boat (atmospheric) carbonisation, the environment is different, as explained above; volatiles are not confined and after the metaplast has reacted it decomposes and the gases are swept out of the system. It seems that the different temperatures of decomposition of the metaplast, therefore, govern the slopes and intersection points of the curves.

It is now possible to examine the position in this sequence of runs at intermediate pressures in which both temperatures and pressures vary. In general, despite the variability, the curve shows a similar form to the others. The reflectivity jump occurs at 400°C (18000 psi) and must indicate the temperature of the onset of plasticity. Relatively little can be said about precise relationships, but it does appear that at each reflectivity-temperature plot (Fig 120), the relationship which might be expected, i.e. a lower reflectivity with higher pressures is maintained, but there is no cross-cutting relationship between the two sets of plots in this case. Comparison of the mosaic sizes also shows a sensible relationship - at the lower pressure, there is a larger mosaic at any given temperature level. It seems also that a reflectivity-temperature curve based on intermediate pressures would fit approximately into the correct position on Fig 125.

The present reflectivity results after the resolidification point agree with those of Huck and Patteisky (1964) and Melvin (1974) who state that the reflectivity of a bituminous-rank vitrinite carbonised under atmospheric pressure is higher than that of the same vitrinite carbonised under pressure at the same temperature level. The data also agree with a statement by Berkowitz (1968), who states that the influence of pressure is negligible up to 400°C. This feature is apparent in the very slight changes in the reflectivity-temperature curves of the vitrinites in this temperature range (Fig 125).

The sharp increase of reflectivity-temperature curves between 400° and 600°C indicates molecular structural changes, e.g. increase in the concentration of aromatic lmaterial and/or increase in aromatic-layer diameter. Berkowitz (1968) also indicates that the effect of pressure is more pronounced in Phase II of the carbonisation process (between 400° and 650°C), when pressure influences the evolution of volatile matter and retards the carbonisation process. The delay is indicated by the higher level of the reflectivity curve for the vitrinite carbonised at atmospheric pressure between 400° and 600°C than the residues of carbonisations under pressure.

The present results are difficult to compare directly with the findings of Chandra (1965) but appear to be contrary to them. The length of the soak period in the present study was about one hour. It is known that lengthening the 'soak period' results in an increase of reflectivity of carbonised residues (see Mackowsky 1961;

de Vries *et al.* 1968; Ghosh 1968). The results of Part IV show that the reflectivity of carbonised bituminous vitrinites increases with length of soak period at temperatures as low as 350°C, so the present results cannot be compared directly with the findings of Chandra due to different lengths of 'soak periods'.

The results of Hryckowian *et al.* (1963) show an increase in level of reflectivity of anthracitic vitrinites at the same temerature level as pressure rises above atmospheric (Fig 113). Although the authors state the effect of pressure is negligible, this does not seem true from Fig 113, there being nearly 17% difference in oil reflectivity of the products between carbonisation under 2000 psi as compared with atmospheric. The higher reflectivity level with pressure in the anthracites is probably due to the carbonisation taking place totally in the solid phase.

Lastly, the results of the present study disagree with the findings of Bostick (1974) who maintains that the reflectivity of vitrinites carbonised under pressure is similar to that of vitrinite carbonised without pressure. Bostick, however, carbonised under pressure in the presence of water vapour, and it is, therefore, possible that the presence of water vapour affected the results of the experiments, perhaps resulting in a partial oxidation of the material in the bomb, so resulting in an increase in the level of reflectivity that compensated for the reduction in reflectivity resulting from pressure increase.

(ii) Bireflectance (Figs 117, 122 and 126)

Comparing the bireflectance-temperature curves (Fig 117) at approximately constant pressure levels in the bomb, it appears that the plasticity of the vitrinite and the temperature range over which the vitrinite remains almost isotropic increases with decrease of pressure in the bomb. This longer plastic stage then probably results in a better ordering of the molecular structure, which is indicated by the very sharp rise in the bireflectance with temperature for the carbonised vitrinite at the lower pressure levels. The size of the mosaic units also becomes larger the lower is the level of pressure in the bomb (see section on Morphology), which further indicates the relation that exists between mosaic size, plasticity and the level of bireflectance. Referring to Part III (Rate of Heating), it was shown there that the mosaic size becomes larger and the bireflectance becomes higher the faster is the heating rate and the greater the fluidity. It appears that the same relationship applies here, but pressure replaces heating rate. An examination of optical properties at an early stage of this programme for this vitrinite carbonised under pressure at different heating rates, which were rather close, did not show great contrast.

In a comparison of the four bireflectance curves (Fig 126) it is clear that the initial decrease of bireflectance of the carbonised vitrinites with increase of carbonisation temperature at pressures ranging from atmospheric to high pressure level is due to the onset of plasticity and breakdown of initial ordering of molecular structure of the vitrinite (see Taylor 1960; Davis 1965 and Goodarzi and Murchison 1972). The increase of bireflectance of the carbonised residues at different pressure levels should be due to the progressively better ordering of the molecular structure brought about by the increasing carbonisation temperature (see de Vries et al 1968; Marshall and Murchison 1971 and Goodarzi and Murchison 1972). However, it is now generally known that vitrinites carbonised under pressure develop a higher level of anisotropy and/or bireflectance than at atmospheric pressure (see Huck and Patteisky 1964; Chandra 1965 and Melvin 1974).

The change in the slopes of the bireflectance-temperature curves indicates the ending of the plastic stage and further development of anisotropy proceeds in the solid phase. If the section on Morphology is consulted, the first appearance of the mosaic coincides with the change in slope of the curves. It also appears that carbonisation under low pressures (but above atmospheric) eventually yields residues with a higher degree of ordering (as estimated by bireflectance) than either open-boat carbonisation or carbonisation under high pressure. This conclusion agrees with the results of Hryckowian et al. (1963) for the bireflectance of residues of anthracitic vitrinite carbonised below 600°C at pressure levels of 15000 and 25000 psi. The bireflectance is lower than for vitrinite carbonised at the same temperature level but at pressures of 5000 and 10000 psi. A direct comparison between the anthracitic vitrinite and the bituminous vitrinite carbonised under pressure should not be made, due to the softening of bituminous vitrinite during carbonisation under pressure, which partially obliterates the effect of pressure. If, however, the pressure which causes a decrease in the bireflectance of anthracitic vitrinite is between 15000 and 20000 psi, then it can be expected that a higher level of pressure, e.g. 45000 psi will be required to inhibit the ordering of molecular structure and hence reduce the level of bireflectance in carbonised bituminous vitrinite. Fig 126 also indicates that increase of pressure suppresses and shortens the period of thermal decomposition of the vitrinite carbonised under pressure and raises the viscosity of the plastic mass. The higher the level of pressure the shorter the length of the plastic stage. Thus the vitrinite undergoes similar conditions of carbonisation in some respects as it would if it were carbonised at a progressively slower rate of heating with progressive increase of pressure level. The results of Brown and Taylor (1961); Cook _et al._ (1972) and the results presented in Part IIIof this thesis indicate that the faster the rate of heating the better is the resultant ordering of the molecular structure. Hence, the higher bireflectance, due to enhanced fluidity, possibly explains the lower trend of the bireflectance curve of the carbonised residues in the high pressure run (45000 psi) than in the residues carbonised at atmospheric pressure.

Having shown that the four bireflectance curves follow an explainable trend, brought about by their varying levels of fluidity and reordering of their molecular structures, the bireflectance pattern of the experiments at variable intermediate pressures can be examined (Fig 122). The plastic phase is again considerably shortened, because the bireflectance of the carbonised vitrinite remains at a lower level than that for carbonised fresh vitrinite up to 400°C. The first bireflectance jump, between 400° and 450°C, marks the end of the plastic phase which is also made evident by partial development of mosaic structures (see 'Morphology' and Appendix V, Volume III).

In comparison with the other bireflectance curves, which follow an expected pattern and/or better reordering of the molecular structure, with rising of pressure from atmospheric to the low pressure range (3000 to 5000 psi), a lower bireflectance curve for a higher pressure level than atmospheric would be due to prevention of the ordering of the molecular structure. The bireflectance data at intermediate pressures do not follow the consistent pattern of the other bireflectance curves and this anamolous behaviour at the intermediate pressure level must probably be explained by the continually varying pressures with temperature rise.

(iii) Refractive Index (Figs 118, 123 and 127)

The behaviour of the refractive index-temperature curves of vitrinite carbonised under atmospheric pressure were discussed in an earlier section (see Part I). It is now well established that the trends of these curves for carbonised vitrinites reflect specific molecular structural changes, e.g. modification of the crystallite height (see Goodarzi 1971 and Goodarzi and Murchison 1972).

There are inconsistencies in the refractive index data, possibly due to the small number of points employed and also to the fact that a relatively restricted temperature range was used - a more satisfactory pattern might probably have been apparent if a range of temperature up to 900°C or higher had been used. As it is, the vitrinite carbonised under atmospheric pressure shows the most rapid change in 'L_c' which represents a number of phenomena, and it appears that the vitrinite carbonised under the lowest pressure shows the least rapid change in refractive indices. It is, however, difficult to separate the curves for the three pressure levels from one another, although it does seem that the refractive index in general for a particular temperature is the higher the greater is the pressure.

(iv) Absorptive Index (Figs 119, 124 and 128)

Little can be said about the trend of the absorptive index of the carbonised residues at the different levels of pressure. The continuous increase of absorptive index against temperature at all pressure levels after 400°C up to 600°C is as previously attributed to lateral growth of the aromatic lamellae (see Hirsch 1954).

(c) Optical Properties - pressure curves

(i) Reflectivity (Fig 128)

The slight increase of reflectivity at 350° and 400°C indicates that increase in aromaticity and growth of aromatic structure is very small over the pressure range. Indeed, the results of Goodarzi (1971) and Goodarzi and Murchison (1972) indicate that the rate of reflectivity change before active decomposition is negligible (see also Davies 1965; de Vries 1968 and Ghosh 1968). The increase of reflectivity at 450°C for the open-boat carbonisation indicates rise in aromaticity and increased lateral growth of the crystallites, but the much reduced reflectivity level with rise of pressure to 3000 psi shows that active decomposition of the vitrinite is delayed, presumably because of the effect of pressure. The subsequent rise in reflectivity with pressure to a similar level as that for the open-boat carbonisation at intermediate and high pressures indicates that the factor delaying the active decomposition is removed. The very sharp drop of reflectivity for 3000 psi at 500°C compared with both the reflectivities for the residues in open-boat carbonisation and carbonisation at 5000 psi also indicates that the active decomposition of the carbonised vitrinite is well through at atmospheric pressure and at 5000 psi, but that it has not begun at 3000 psi. This apparently strange result was, at first, attributed to some inconsistency in experimental procedure. However, subsequent carbonisations under the same pressures and temperature conditions showed that no experimental error was involved and that the much lower level of reflectivity had purely and simply to be attributed to the particular pressure level inhibiting the active decomposition and then maintaining fluidity up to an unexpectedly high temperature (500°C). Leaving aside the residues at 3000 psi for the curve at 500°C, the general trends of reflectivity-pressure curves at higher pressures and at temperatures ranging between 500°C and 600°C indicate a lower level of growth and concentration of aromatic structures with rising pressures, although quite clearly temperature has a much more pronounced influence on the growth and concentration than does pressure.

(ii) Bireflectance (Fig 129)

The lower levels of bireflectance at 350° and 400°C than for the fresh vitrinite throughout the pressure range indicate destruction of the initial ordering of the molecular structure within the crystallites due to softening (see for example Taylor 1961 and Goodarzi and Murchison 1973). The initial decrease of bireflectance from its level at atmospheric pressure to lower levels at 3000 and 5000 psi at 450°C and 3000 psi at 500°C indicates that although reordering of the molecular structure is well advanced for residues at atmospheric pressure, the residues at low pressures are still in the pre-decomposition phase. Rise of temperature from 450° to 500°C results in only a shift of the pressure at which the residue remains in pre-active decomposition to a lower level. Increased bireflectance with rise of pressure indicates better ordering of the molecular structure brought about by pressure. The subsequent fall of bireflectance at high pressures is probably due to the effect of pressure inhibiting greater reordering of molecular structure within the crystallites.

The initial rise of bireflectance with increase of pressure at 550° and 600°C indicates that increase of pressure results in the better ordering of molecular structure in the solid, which is more pronounced the higher is the temperature (apparent by the initial sharp increase of bireflectance). The subsequent fall of bireflectance after intermediate pressure levels (around 27000 psi) is probably due to the inhibiting effect of high pressures on the ordering of the molecular structure (see discussion on bireflectance - temperature curves). Presumably if the temperature were further increased, however, ordering would be further improved.

(iii) Refractive Index (Fig 130)

The initial drop of refractive index from levels at atmospheric pressures to those at 3000 psi throughout the temperature range indicates the inhibiting effect of pressure on the growth of crystallite height, and is more apparent as temperature rises. At 350°C and 400°C the difference in crystallite height is negligible as might be expected. However, results of Diamond (1960) show that crystallite heights of coking coal start to increase after being carbonised above 400°C and further, the results of Goodarzi (1971) and Goodarzi and Murchison (1972) show an increase in the refractive index of coking coal vitrinite after 400°C. After a slight rise of pressure, the increase of refractive index between 3000 and 5000 psi probably indicates slight growth of crystallite height, but a clear interpretation of the behaviour of the refractive index curves and/or the growth of crystallite heights is rather difficult at pressures higher than 5000 psi.

(iv) Absorptive Index (Fig 131)

The behaviour of the absorptive index-pressure curve indicates changes in crystallite diameter, (L_a), of the aromatic structures and similar but less distinctive patterns as for the reflectivity-pressure curves are evident here. The less consistent patterns in these data are due to lower accuracy in the determination of the absorptive index.

E. CONCLUSION.

The following conclusions can be drawn from the results presented in this part of the project:

(a) Morphological

(i) The mosaic units are the larger the lower the level of pressure in the bomb. In the bomb the resolidification point (appearance of mosaic) decreases with rising pressure.

(ii) The morphological changes which result in formation of mosaic structure can be observed more clearly at lower pressures.

(iii)The morphological features of vitrinite carbonised under pressure resembles those of naturally thermally metamorphosed coal.

(b) Optical

(i) Reflectivity is the higher the lower is the level of pressure in the bomb, particularly after carbonisation above the resolidification temperature.

(ii) Bireflectance, which indicates the ordering of molecular structure, increases with rise of temperature and pressure below the resolidification point, but above this point, higher levels of pressure inhibit the increase of bireflectance and the relationship is reversed.

(iii) The refractive index-temperature curves show that increasing pressure in general inhibits the growth of height of the aromatic lamellae.

PART VII OPTICAL PROPERTIES OF VITRINITES TREATED AT HIGH TEMPERATURE

A. General Introduction

The work described in this section considers the optical properties of vitrinite (carbon = 80.0 and 87.9% daf and 94.2%dmmf) heat-treated over temperatures ranging from 1000° to 2400°C. These experiments arise directly from earlier work by the Writer (Goodarzi 1971).

Changes in the molecular structure of carbons heat-treated above 1000°C have been the subject of many investigations, some of which have been concerned with the variation of density, electrical resistivity, diamagnetic susceptibility, X-ray diffraction and other physical properties. However, to the author's knowledge, there has been no systematic study of the optical properties of carbons at such high temperature.

B. Previous related work

1. Introduction

The reaction of carbon to heat treatment is primarily dependent on the original molecular structure of carbon. A review of the molecular changes occurring during the heat-treatment of 'soft' (graphitising) and 'hard' (non-graphitising) carbon is given by Mrozowski (1956, 1971). The heat-treatment of soft carbons up to 800°C results in devolatilisation of the non-carbon parts of the molecule and the development of an energy gap - an energy gap is developed due to mobile electrons having energy falling into bands, one empty and one electron occupied (see Coulson 1947). The 'Carbon molecule' consists of turbostratic crystallites of about 30Å diameter, which are built of condensed but disordered planes of benzene rings stacked parallel, but equidistant to one another. The crystallites are surrounded by disordered material, but they grow with increase of temperature at the expense of the disordered material. The energy gap diminishes rapidly with increase of crystallite diameter (L_a) up to 1300°C: crystallites grow by coalescence with smaller crystallites up to 2100°C, when the crystallite diameter is about 150Å. Further increase of temperature results in the development of a three-dimensional graphitic structure.

Due to strong intermolecular bonding 'hard' carbons resist the increase of temperature up to quite high levels and crystallites grow at a relatively slower rate than do those of 'soft' carbons.

The graphitisation of these hard carbons occurs at two distinctive stages: the first at 1800° - 2100°C, resulting in partial graphitisation and the second at about 2800°C when the remainder of the material starts to graphitise rapidly.

The high-temperature (above 1000°C) process may be divided into stages (see Honda 1959).

semi-graphitisation	..	ca. 1000°-1400°C,
graphitisation	..	ca. 1400°-2300°C, and
crystallisation	..	ca. 2300°C.

(a) Semi-graphitisation (ca. 1000°C - 1400°C)

This stage is accompanied by decomposition and rearrangement of the molecular structure, resulting in high yields of hydrogen (Honda 1956). The crystallite diameter (L_a) and height (L_c) increase throughout this stage (see Blayden et al. 1944; Franklin 1951; Warren 1956 and Loebner 1956). The results of Ouchi (1955) also indicate an increase in (L_c) with rise of temperature, but show that (L_a) decreases between 1200° and 1400°C to a minimum before increasing once again towards the end of this stage. The decrease in (L_a) is due to the destruction of the two-dimensional bonding of the condensed aromatic molecules and further increase of (L_a) is related to coalescence of mobile lamellae. The sharp decrease in density and electrical resistivity throughout this stage (see Pinnick 1956), the increase in diamagnetic susceptibility (see Honda 1959) and microhardness to a maximum at 1200°C (see Honda and Sanada 1957), and the subsequent decrease of microhardness with increase of temperature is also indicative of the destruction of the intermolecular bonding. Ouchi (1955) also used smaller temperature intervals (100°C) than did Blayden (1944); Franklin (1951); Warren (1956) and Loebner (1956), which may be a possible explanation for the failure to detect a minimum in (L_a) in these other investigations. The pronounced decrease of electrical resistivity (see for example Ouchi 1955; Pinnick 1956 and Loebner 1956) is due, according to Pinnick (1956), to the devolatilisation of peripheral groupings which are bonded to the aromatic structure by π electrons, resulting in pairing of the ξ and π electrons and the development of an energy gap (see for example Loebner 1956 and Mrozowski 1956 and 1971). The energy gap decreases continuously with increase of crystallite diameter (L_a) throughout this stage. The diamagnetic susceptibility remains constant or increases slightly (see Ouchi 1955; Honda 1956). According to Ouchi (1955) density increases with rise of temperature, although the results of Franklin (1951) suggest that the density of hard carbons decreases after 1000°C. Microhardness of carbon (coal: carbon = 65 to 93% daf) increases up to 1200°C and then decreases with rise of temperature, and this decrease is less marked for hard carbon. The sharp increase in microhardness up to 1200°C is related to the development of a three-dimensional structure consisting of molecules with primary bonding (see Honda 1956 and Sanada 1957).

(b) Graphitisation stage (ca. 1400° to 2300°C)

The dimensional growth of crystallites is the primary process in this stage. The heat-treated residue approaches approximately the structural level of elementary carbon at about 1500°C (see Blayden 1969). The crystallite diameter (L_a) and height (L_c) increase continuously throughout this stage (see for example Franklin 1951; Ouchi 1955; Warren 1956 and Loebner 1956). The first steps in the graphitisation of hard carbon take place in this stage, (see for example Franklin 1951; Loebner 1956 and Mrozowski 1956 and 1971), when a partial graphitisation occurs. The electrical resistivity remains almost constant (see Ouchi 1955; Pinnick 1956 and Loebner 1956), due to increase in layer diameter (L_a) and a consequent decrease in pairing of σ and π electrons, but towards the end of this stage, at about 2200°C, the resistivity of hard carbons falls (see for example Loebner 1956). This decrease is related to the commencement of the second stage of graphitisation in hard carbon. The energy gap becomes smaller and approaches that of graphite (Mrozowski 1971), and the diamagnetic susceptibility increases (see Ouchi 1955; Honda 1956 and Murchand 1973), due to the completion of two-dimensional ordering (Ouchi 1955). The density, according to Ouchi (1955), either remains constant in hard carbon, or increases slightly in soft carbon, although Franklin (1951) maintains that the densities of soft and hard carbon increase with rise of temperature in this stage. However, as previously noted, the temperature interval used by Franklin is very large. The microhardness of carbon decreases continuously with increase of temperature up to 2000°C (see Honda and Sanada 1957).

(c) Crystallisation Stage (above 2300°C)

This stage is characterised by the development of three-dimensional graphite ordering which takes place by slow transformation of turbostratic crystalline ordering (see Loebner 1956; Mrozowski 1971 and Marchand 1973) The (L_a) and (L_c) increase with rise of temperature (see Franklin 1951; Warren 1956 and Loebner 1956), but the increase of (L_c) appears to be greater (see Loebner 1956). Also, the electrical resistivity of soft carbon falls with increase of temperature throughout this stage (see Pinnick 1956). According to Marchand (1973) the diamagnetic susceptibility, which is indicative of two-dimensional aromatic systems, decreases throughout this stage due to the development of three-dimensional ordering.

2. Morphology

The morphology of carbon residues heated to above 1000°C have been studied by optical and electron-scanning microscopical methods by a number of workers.

(a) Optical Microscopy

Relatively little systematic study of the changes in morphology of vitrinites at high temperature has been carried out in comparison to the many morphological studies of carbonised vitrinites during the carbonisation process. The results of Alpern and Chauvin (1957) show that vitrinite (V.M. = 3% to 10%) on heating to about 1000°C develops a vesiculted, swollen and highly reflecting central zone with a broad, but much less vesiculated, low-reflecting marginal zone (see Plates 7 and 8, p. 212). Pre-distillation of particles in the presence of nitrogen and subsequent combustion at 1000°C reduces the amount of highly reflecting materials in the central zone. Abramski and Mackowsky (1961) state that the size of mosaic units in carbonised coking-coal vitrinite does not change with increase of temperature up to 1500° to 1700°C (see Plates 66 and 68, pp 394; 396), but examination of the photomicrographs produced by these authors reveals that the high-temperature residues develop more vacuoles than low-temperature coke. Further, Brooks and Taylor (1965) state that the mosaic structure of semi-coke does not alter, even at a temperature of 2500°C (see Plate 23 of the above paper), but that it shrinks perpendicular to the lamellae.

Marsh *et al.* (1971) maintain that the mosaic structure formed on the carbonisation of gilsonite pitch at about 410°C maintains its identity and does not change, even on heating to 2800°C (see Plates 3 and 6 pp 253; 254) but observation of Marsh's photographs suggests that the orientation of the mosaic structure becomes more regular by 2800°C. These morphological studies indicate that the residues of softening vitrinites at high-temperature maintain rather similar morphological features to those at carbonisation temperatures, whereas non-softening vitrinites develop a distinctive morphological character, which has not yet been observed in the low-temperature carbonised residues (see for example Abramski and Mackowsky 1961; Davis 1965; Marshall and Murchison 1971 and Goodarzi 1971).

(b) Electron Microscopy

'Botryodial' structures observed at 410°C by Marsh *et al.* (1971) apparently do not melt or fuse on graphitisation to 2800°C. However, the size of the 'botryodial' structural units (apparent from Plates 9 and 10, p 255) decreases on heating to 2800°C. The 'botryodial' structure was related by Marsh (1973) to the mosaic sizes observed by optical microscopy. Brooks and Taylor (1965) indicate that mesophase shrinks preferentially (perpendicular to lamellar), which means there is a change in the shape of the mosaic units, resulting in the development of micropores, due to shrinkage of the mosaic units, either uniformy (Marsh *et al.* 1971), or preferentially (Brooks and Taylor 1965). The results presented in Part III and IV of this Thesis show changes in the morphology of low-temperature carbonised residues of macerals, i.e. increase or decrease in mosaic size which is accompanied by a rise or fall of reflectivity and bireflectance. If the same principles can be applied to vitrinites heat-treated at high temperature, then a decrease in reflectivity of high-temperature, heat-treated residues of coking vitrinites might be expected.

3. Optical Properties

To the author's knowledge there is no systematic work available on the optical properties of high-temperature vitrinites, i.e. carbons in the temperature range between 1000° and 3000°C. However, Abramski and Mackowsky (1961) believe that the intensity of anisotropy of high-temperature, coking coal vitrinites at about 1500° to 1700°C is higher than that of the low-temperature residue. The results of Gillot et al. (1968) (in photomicrographs) indicates that the reflectivity of petroleum coke carbonised under vacuum at temperatures ranging from 1300° to 1500°C with a 'soak period' of 80 to 750 hours decreases with rise of temperature. The recent work of Khavari (1975), indicates that the reflectivity, refractive and absorptive indices of carbonaceous materials, such as gilsonite, grahamite and impsonite (carbon 84.0 to 88.0% daf) increase slowly between 1000° and 1400°C and then decrease on heat-treatmentkto 2500°C, whereas the same optical properties of shungite (carbon = 96.0% daf) increase slowly between 1000° and 2500°C. Khavari (1975) relates the decrease of the optical properties of the carbonaceous materials examined by her to tension brought about by the high temperature. However, gilsonite, grahamite and impsonite develop mosaic structures during carbonisation process, whereas the residue of shungite do not develop such structures.

4. Summary

In summary, the effect of semi-graphitisation through to crystallisation (1000° to 2400 °C) on carbons of different origin appears to be more severe than carbonisation at lower temperatures. The molecular structure of carbons suffers breakdown in the reordering of the molecular structure during the carbonisation process. The secondary reordering of molecular structure, which commences at the semi-graphitisation stage (1000° to 1400 °C), appears to be more severe in soft carbons than in hard carbons, because of the loose cross-linking and better reordered structure developed by soft carbons during the carbonisation process. The transformation from the two-dimensional turbostratic structure to a three-dimensional graphitic structure is continuous and takes place at a much lower temperature, whereas in hard carbons the transformation is slow and requires a much higher level of thermal energy because of the strong cross-linking and randomly-ordered carbonised residues. The transformation of turbostratic crystallites to graphitic ordering takes place in two or three stages and commonly commences at about the end of graphitisation stage (1400° to 2300°C).

The above observations are made mainly on the basis of changes in molecular structure revealed by X-ray diffraction studies, but this can commonly be observed at least partially in morphological studies and in the behaviour of some physical parameters, e.g. electrical resistivity, density, hardness, etc.

There is a decrease in the size of the mosaic units developed by low-temperature carbonisation of soft carbons, e.g. coking coal vitrinite during high-temperature heat-treatment. It appears that changes in physical parameters can be related to one another. Since optical properties are also physical properties which reflect changes of molecular structure of carbons occurring during the carbonisation process, then it might be expected that the optical properties of high-temperature, heat-treated carbons will also show changes of molecular structure taking place during heat-treatment.

C. Results, Description

1. Introduction

The morphological and optical changes of the high-temperature, heat treated residues of the three vitrinites (carbon = 80.0 and 87.9% daf and 94.2% dmmf) are described at temperature levels selected to cover the ranges reported by Honda (1959) (see p. 305)

(i) 1000 to 1400°C .. semi-graphitisation
(ii) 1400 to 2300°C .. graphitisation
(iii) and above 2300°C .. crystallisation

2. Morphology

In the present research programme both optical and electron microscopy were used to reveal morphological changes. The electron microscope cannot show structural differences such as isotropic and anisotropic components, but it can demonstrate the surface topography at high magnification, whereas, although the optical microscope has much lower final resolution than the 'Stereoscan', it can exhibit optical structural differences of various constituents.

(a) Optical microscopy (Plates 103 to 115)

The high-temperature, heat-treated residues of low-rank bituminous vitrinite (carbon = 80.0% daf) and anthracitic vitrinite (carbon = 94.2% dmmf) show similar morphological changes, i.e.

development of highly-reflecting isotropic material with high relief on heating in the semi-graphitisation stage (1000° to 1400°C). This material appears generally at about 1100°C (Plates 104a and 112b) and its amount increases with further rise of temperature up to 1250° to 1300°C, when the particles are covered by a 'shell' of the material (Plates 104c and 113). With further rise of temperature towards the end of this stage (1400°C), the amount of this material decreases and finally disappears at 1400°C. The anthracitic vitrinite develops perforated edges and vesiculation in the semi-graphitisation stage which disappears with rise of temperature toward the graphitisation stage; the intensity of anisotropy increases with rise of temperature.

The high-rank bituminous vitrinite (carbon = 87.9% daf), develops a fine-grained to flow-type mosaic texture, the state of polished surface deteriorates continuously and the granular mosaic shrinks with rise of temperature, resulting in a heterogeneous surface. The intensity of anisotropy decreases with rise of temperature.

(b) Electron-scanning microscopy

Topographical features on the natural and relief-polished surfaces of the high-temperature samples are shown in Plates 116 to 126. The magnifications are all below x4000.

The high-temperature residues of the low-rank bituminous vitrinite (carbon = 80.0% daf) and the anthracitic vitrinite (carbon = 94.2% dmmf) show non-coherent residues with rise of temperature. In the semi-graphitisation stage (1000° to 1400°C), there are two typical rareas, one with relief (Plates 116 and 125) the other smooth. The area with relief is the same as the high-reflecting isotropic material observed by optical microscopy. The anthracitic residues show perforated edges (Plate 125b) and vacuoles (Plates 112b, 113 and 114). These perforated edges and vacuoles disappear with rise of temperature (Plate 126).

The low-rank bituminous vitrinitic residues at about 1800°C, show characteristic 'botryodial' structure (Plate 117b). The high-rank, bituminous vitrinite (carbon = 87.9% daf) shows coherent residues and characteristic 'Botryodial' structure (Plate 121a).

3. Optical Properties

(a) Introduction

The optical properties of the residues of three vitrinites (carbon = 80.0%, 87.9% daf and 94.2% dmmf) heat-treated between 400° and 2400°C are plotted against temperature in Figs 133 to 138. Generalised curves of the optical properties against temperature of the same vitrinites are also shown in Figs 139 to 143. The optical properties of the residues of vitrinites carbonised between 400° and 950°C are also included on the graphs of the corresponding residues heat-treated between 1000° and 2400°C, to illustrate the total change of the optical properties against temperature of the residues in the range 400° to 2400°C. Since the changes in the optical properties of the residues of these vitrinites carbonised between 400° and 950°C have already been described and discussed in Part III, only the variation of the optical properties of the three residues heated between 1000° and 2400°C will be discussed here. The only variation in the heating conditions of the residues at high temperature lies in the 'soak period' which was one hour between 400° and 950°C and one minute between 1000° and 2400°C, all samples being pre-carbonised to 900°C before further heat-treatment.

(b) Reflectivity (a and b Figs 133 to 135 and Figs 139; 140)

The reflectivity-temperature curves in air and oil are as usual described together because of the similarity in their behaviour with rise of temperature.

The reflectivities curve of the residues of the low-rank vitrinite (a and b Fig 133) remain relatively constant from 1000°C up to approximately 1500°C, after which they decrease slowly but continuously with rise of temperature up to 2400°C. The reflectivity-temperature curve of the residues of the coking-coal vitrinite (a and b Figs 134) increases slightly between 1000° and 1100°C and then falls rapidly and continuously with further rise of temperature to 2400°C. Finally, the curve of the heat-treated anthracitic vitrinite (a and b Figs 135) increases between 1000° and 1300°C, then falls slightly with rise of temperature to about 1800°C, after which the reflectivity increases slowly but continuously with further heat-treatment up to 2400°C.

Fig 133 Variation with temperature of air and oil reflectivity, refractive index and absorptive index in a low-rank bituminous vitrinite (carbon = 80.0% daf), heated up to 2400°C.

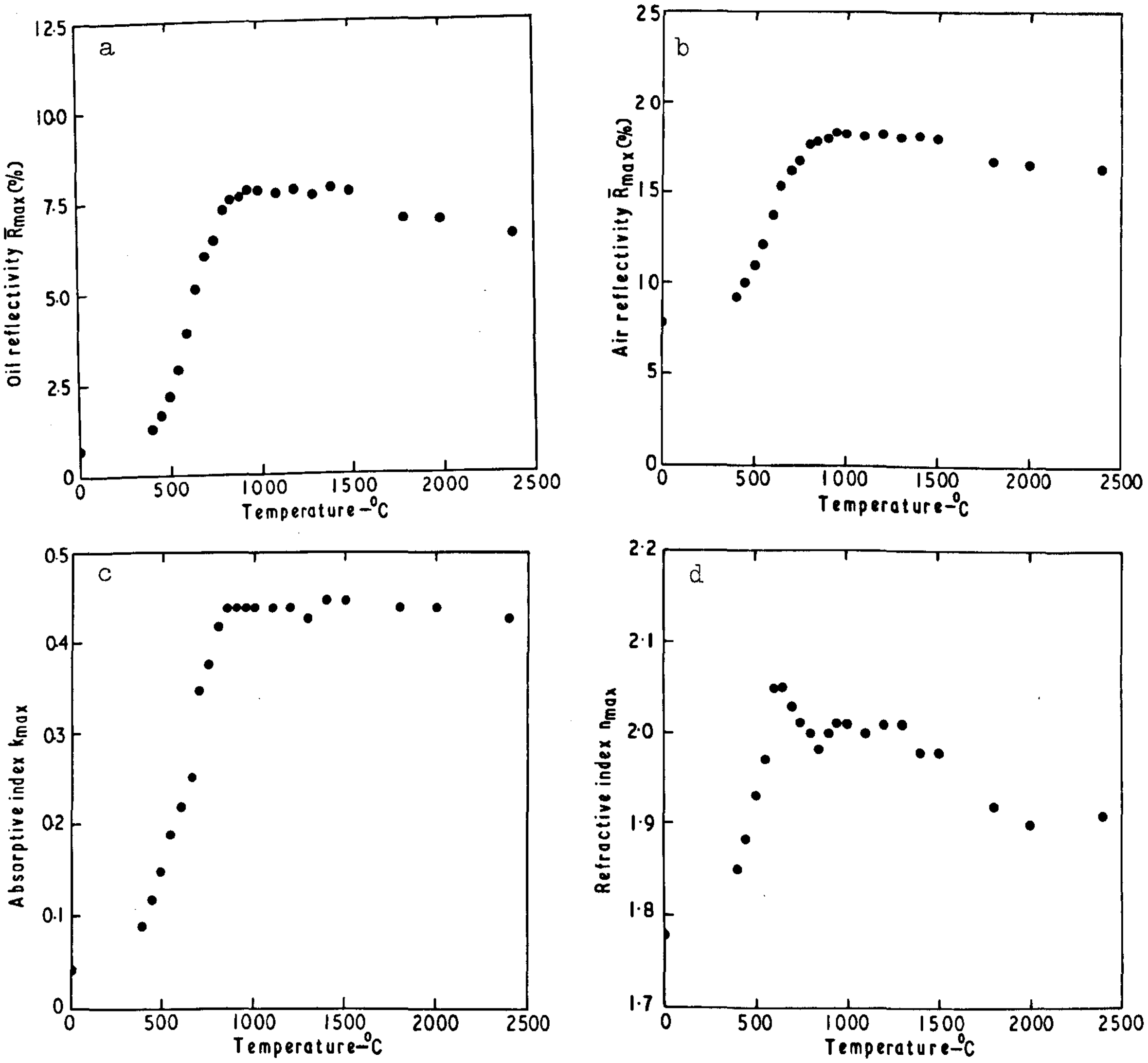

a
Oil reflectivity $\bar{R}_{max}$ (%)
12·5
10·0
7·5
5·0
2·5
0
0
500
1000
1500
2000
2500
Temperature – °C
b
Air reflectivity $\bar{R}_{max}$ (%)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Temperature – °C
c
Absorptive index k_{max}
0·5
0·4
0·3
0·2
0·1
0
0
500
1000
1500
2000
2500
Temperature – °C
d
Refractive index n_{max}
2·2
2·1
2·0
1·9
1·8
1·7
0
500
1000
1500
2000
2500
Temperature – °C

Fig 134 Variation with temperature of air and oil reflectivity, refractive index and absorptive index in a high-rank, bituminous vitrinite (carbon = 87.9% daf), heated up to 2400°C.

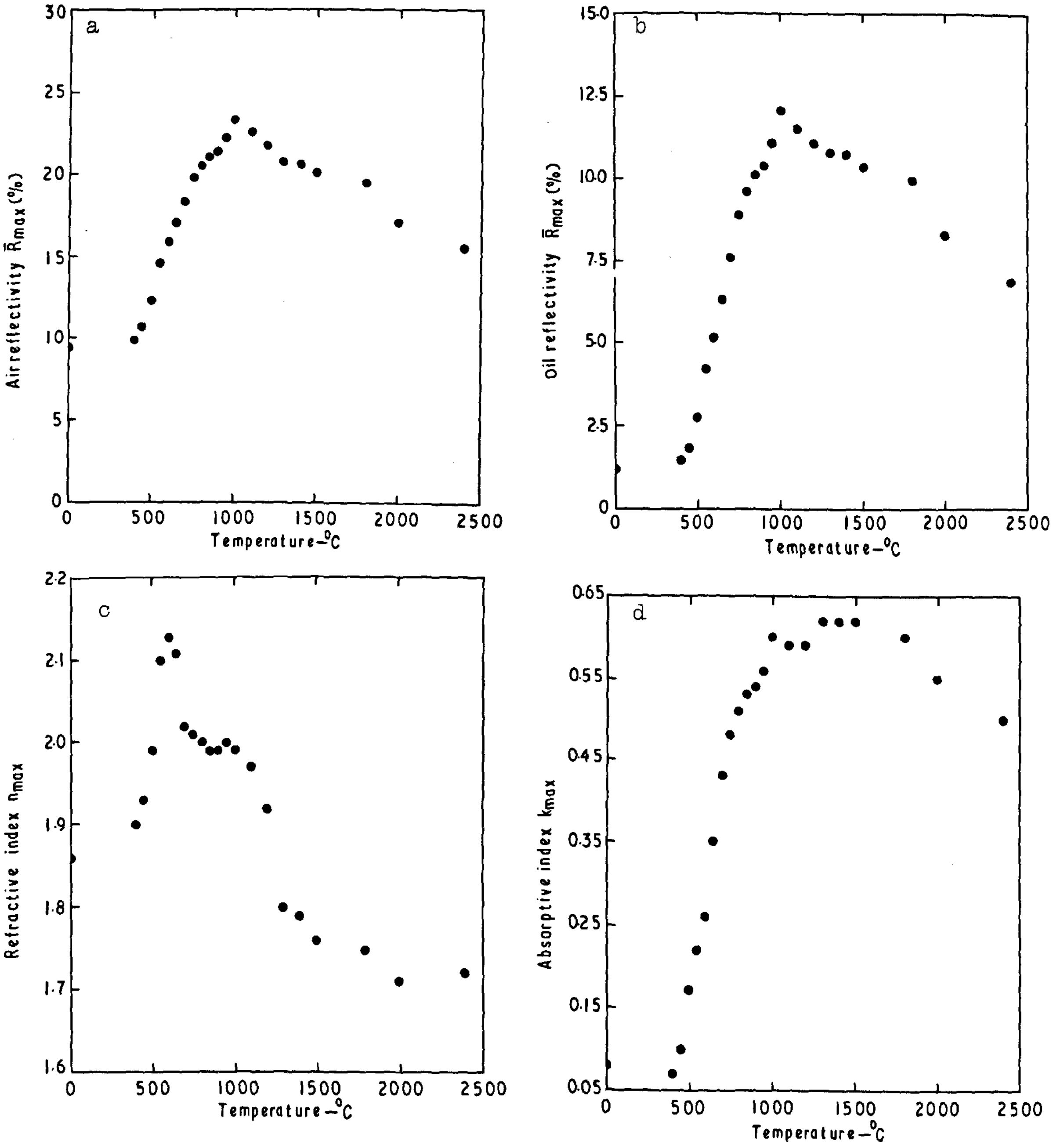
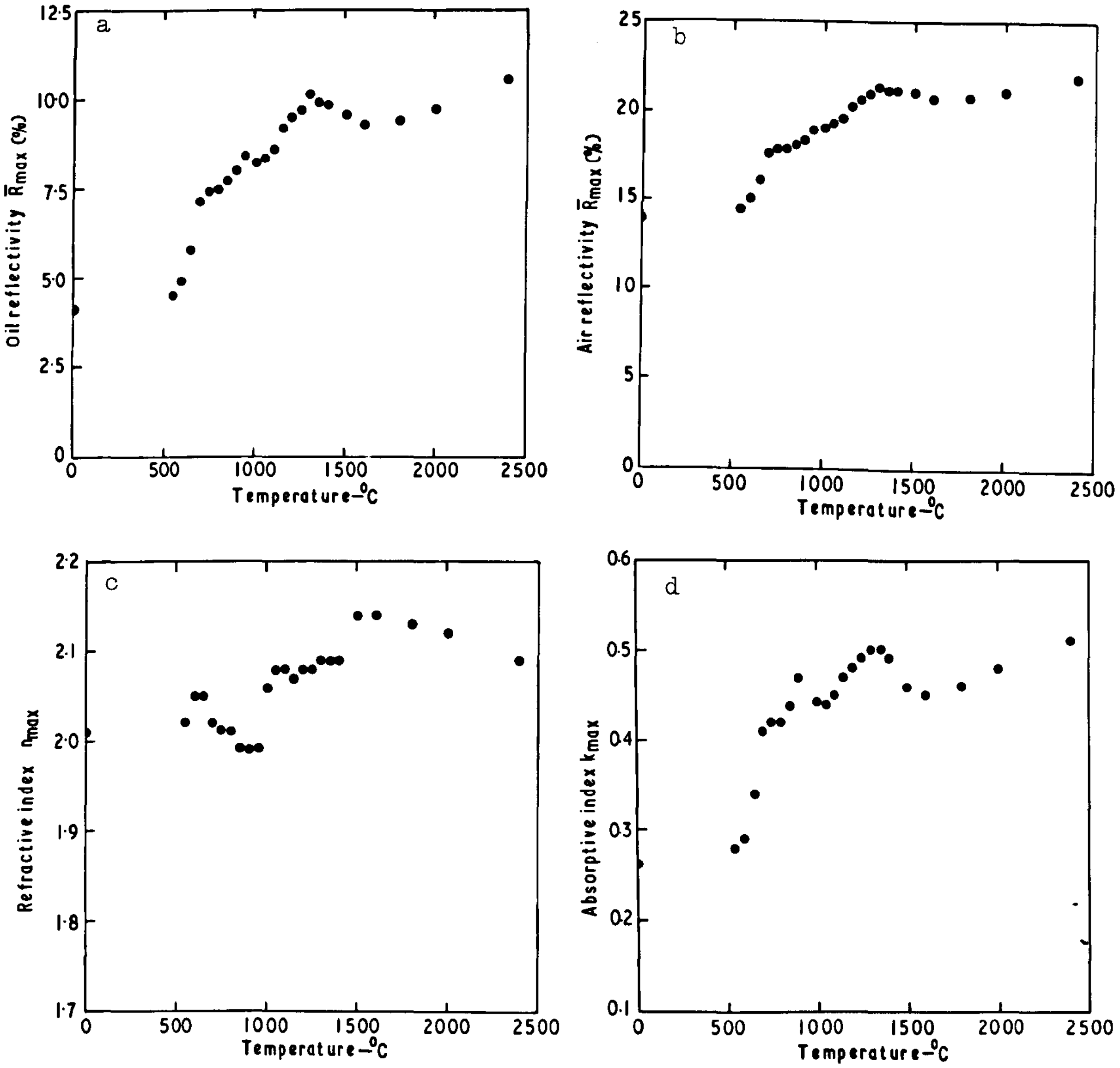

a
Air reflectivity $\bar{R}_{max}$ (%)
0
5
10
15
20
25
30
0
500
1000
1500
2000
2500
Temperature–°C
b
Oil reflectivity $\bar{R}_{max}$ (%)
0
2.5
5.0
7.5
10.0
12.5
15.0
0
500
1000
1500
2000
2500
Temperature–°C
c
Refractive index n_{max}
1.6
1.7
1.8
1.9
2.0
2.1
2.2
0
500
1000
1500
2000
2500
Temperature–°C
d
Absorptive index k_{max}
0.05
0.15
0.25
0.35
0.45
0.55
0.65
0
500
1000
1500
2000
2500
Temperature–°C

Fig 135 Variation with temperature of air and oil reflectivity, refractive index and absorptive index in an anthracitic vitrinite (carbon = 94.2% dmmf), heated up to 2400°C.


a
Oil reflectivity $\bar{R}_{max}$ (%)
0
2·5
5·0
7·5
10·0
12·5
0
500
1000
1500
2000
2500
Temperature–°C
b
Air reflectivity $\bar{R}_{max}$ (%)
0
5
10
15
20
25
0
500
1000
1500
2000
2500
Temperature–°C
c
Refractive index n_{max}
1·7
1·8
1·9
2·0
2·1
2·2
0
500
1000
1500
2000
2500
Temperature–°C
d
Absorptive index k_{max}
0·1
0·2
0·3
0·4
0·5
0·6
0
500
1000
1500
2000
2500
Temperature–°C

(c) Bireflectance (Figs 136 to 138 and 141)

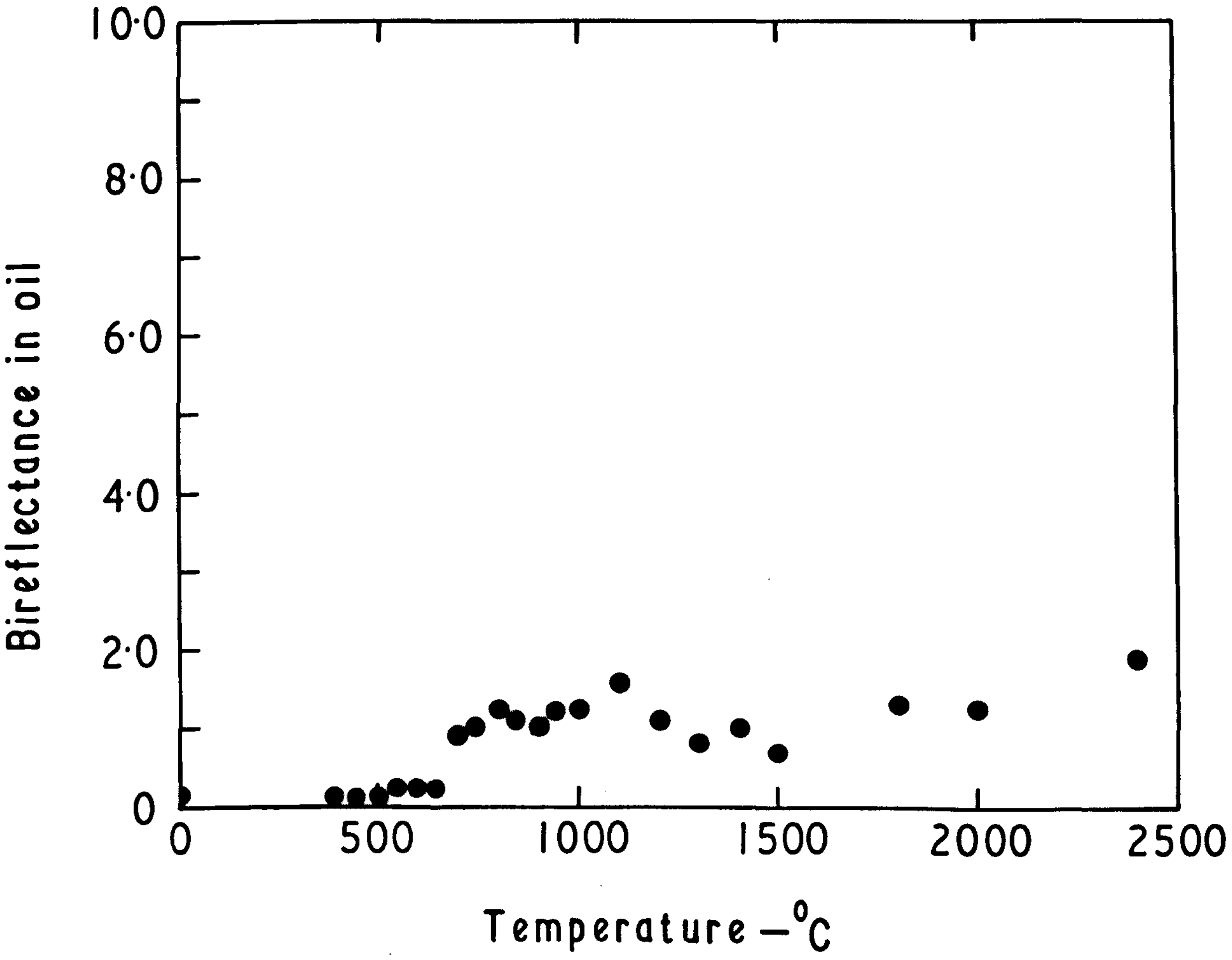
The bireflectance curve for the low-rank vitrinitic residues decreases slightly between 1000° and 1500°C, and thereafter the bireflectance increases irregularly but slowly with further increase of temperature up to 2400°C.

The bireflectance of the residues of the coking coal vitrinite decreases rapidly but irregularly with rise of temperature from 1000°C up to 1500°C, after which the bireflectance curve (so far as can be determined) probably maintains approximately the same level up to 2400°C. The bireflectance curve of the heat-treated anthracitic vitrinite increases continuously with rise of temperature between 1000° and 2400°C.

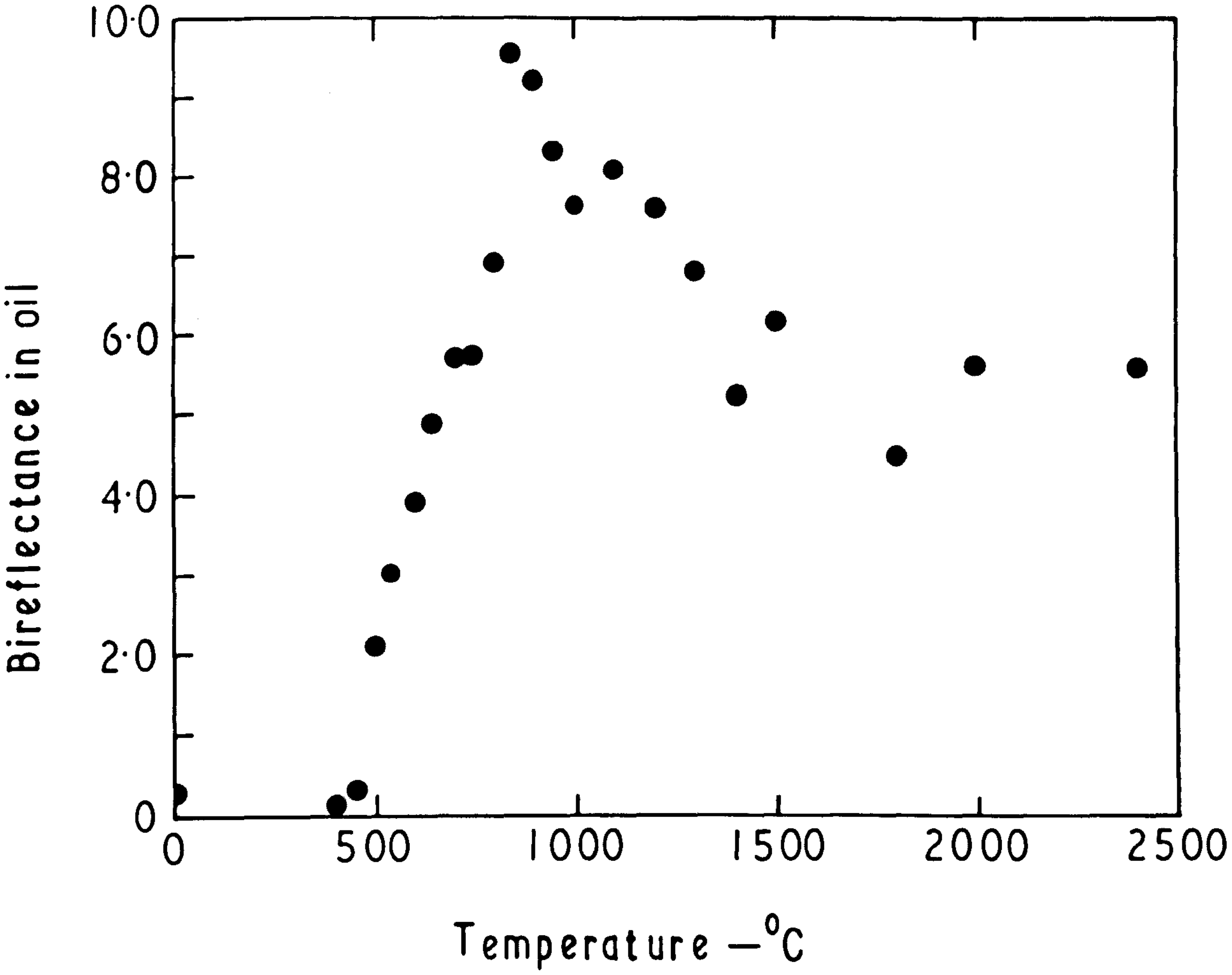
(d) Refractive Index (Figs 133d, 134c, 135c, 142)

The refractive-index curve of the residues of the low-rank vitrinitic residues maintains the same level between 1000° and 1300°C. Further increase in temperature results in a fall of refractive index up to 1800°C, after which it maintains approximately the same level up to 2400°C.

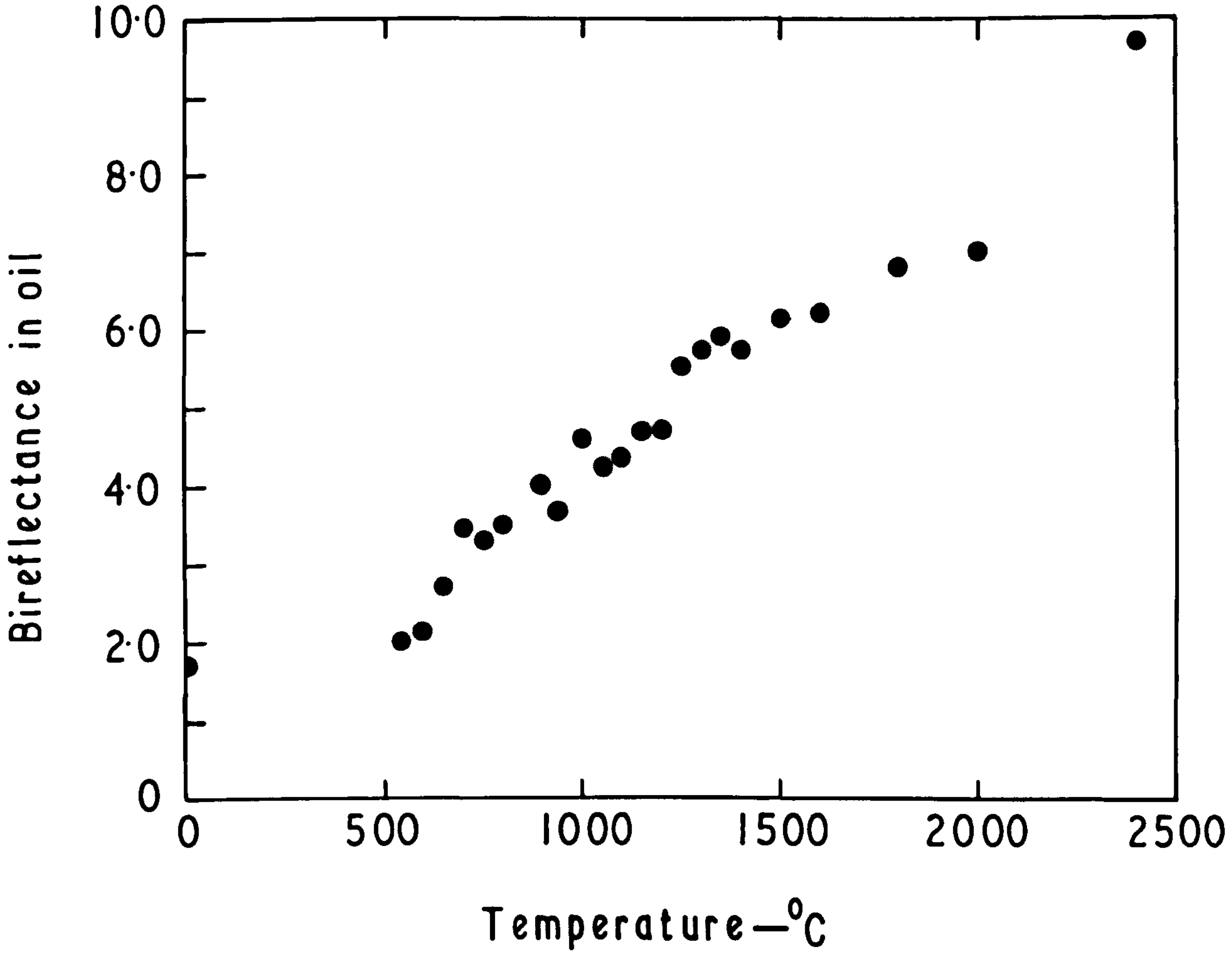
The refractive index of residues of heat-treated, coking coal vitrinite decreases very sharply with rise of temperature between 1000° and 2400°C. Finally the refractive index curves of the residues of the anthracitic vitrinite rise up to 1500°C and then maintain the same level up to 1600°C, after which the refractive index curve decreases slowly but continuously with further rise of temperature up to 2400°C.



0—1000°C One Hour Soak Period
1000—2500°C One Minute Soak Period



0—1000°C One Hour Soak Period
1000—2500°C One Minute Soak Period



0—1000°C One Hour Soak Period
1000—2500°C One Minute Soak Period

(c) Absorptive index (Figs 133c, 134d, 135d, 143)

The absorptive index curves of all three heat-treated vitrinitic residues show parallel changes to those of the corresponding reflectivity.

Fig 139 Generalised curves for variation with temperature of oil reflectivity of three vitrinites, heated up to 2400°C.

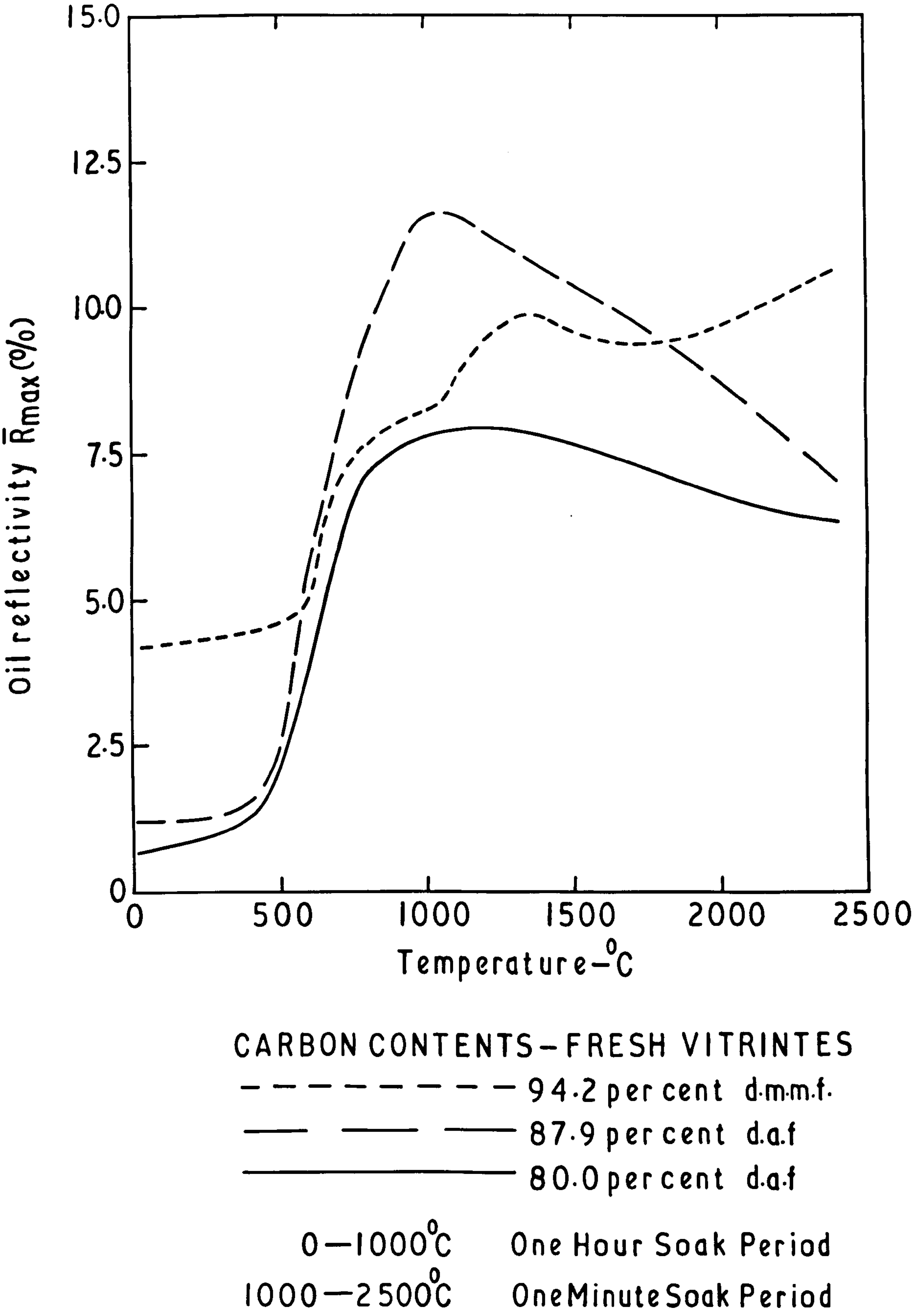

15.0
12.5
10.0
7.5
5.0
2.5
0
Oil reflectivity $\bar{R}_{max}$ (%)
0
500
1000
1500
2000
2500
Temperature–°C
CARBON CONTENTS – FRESH VITRINTES
94.2 per cent d.m.m.f.
87.9 per cent d.a.f
80.0 per cent d.a.f
0—1000°C One Hour Soak Period
1000—2500°C One Minute Soak Period

Fig 140 Generalised curves for variation with temperature of air reflectivity of three vitrinites, heated up to 2400°C.

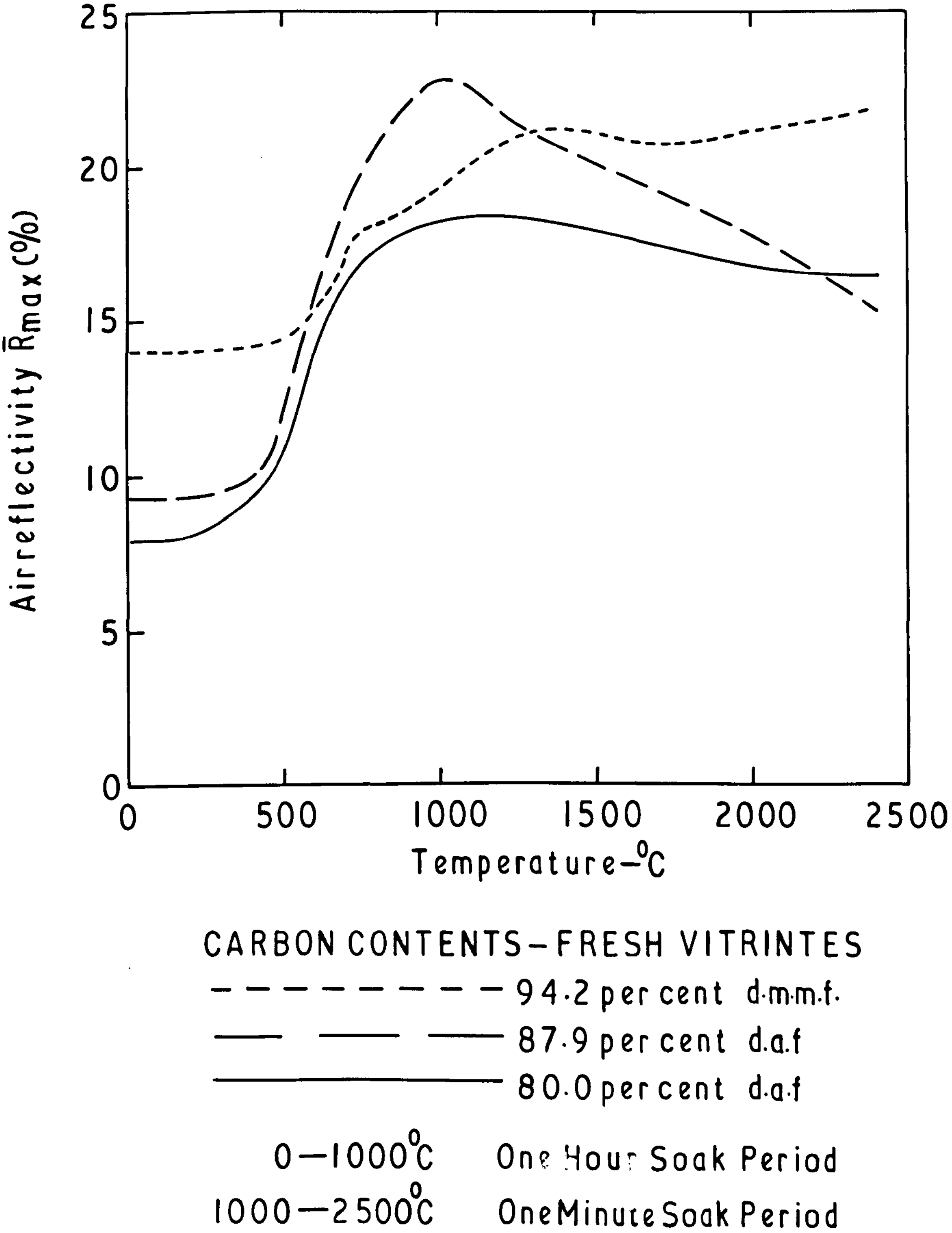

25
20
15
10
5
0
0
500
1000
1500
2000
2500
Airreflectivity $\bar{R}_{max}$ (%)
Temperature–°C
CARBON CONTENTS – FRESH VITRINTES
94·2 per cent d·m·m·f·
87·9 per cent d.a.f
80·0 per cent d.a.f
0—1000°C One Hour Soak Period
1000—2500°C One Minute Soak Period

Fig 141 Generalised curves for variation with temperature of oil bireflectance of three vitrinites, heated up to 2400°C.

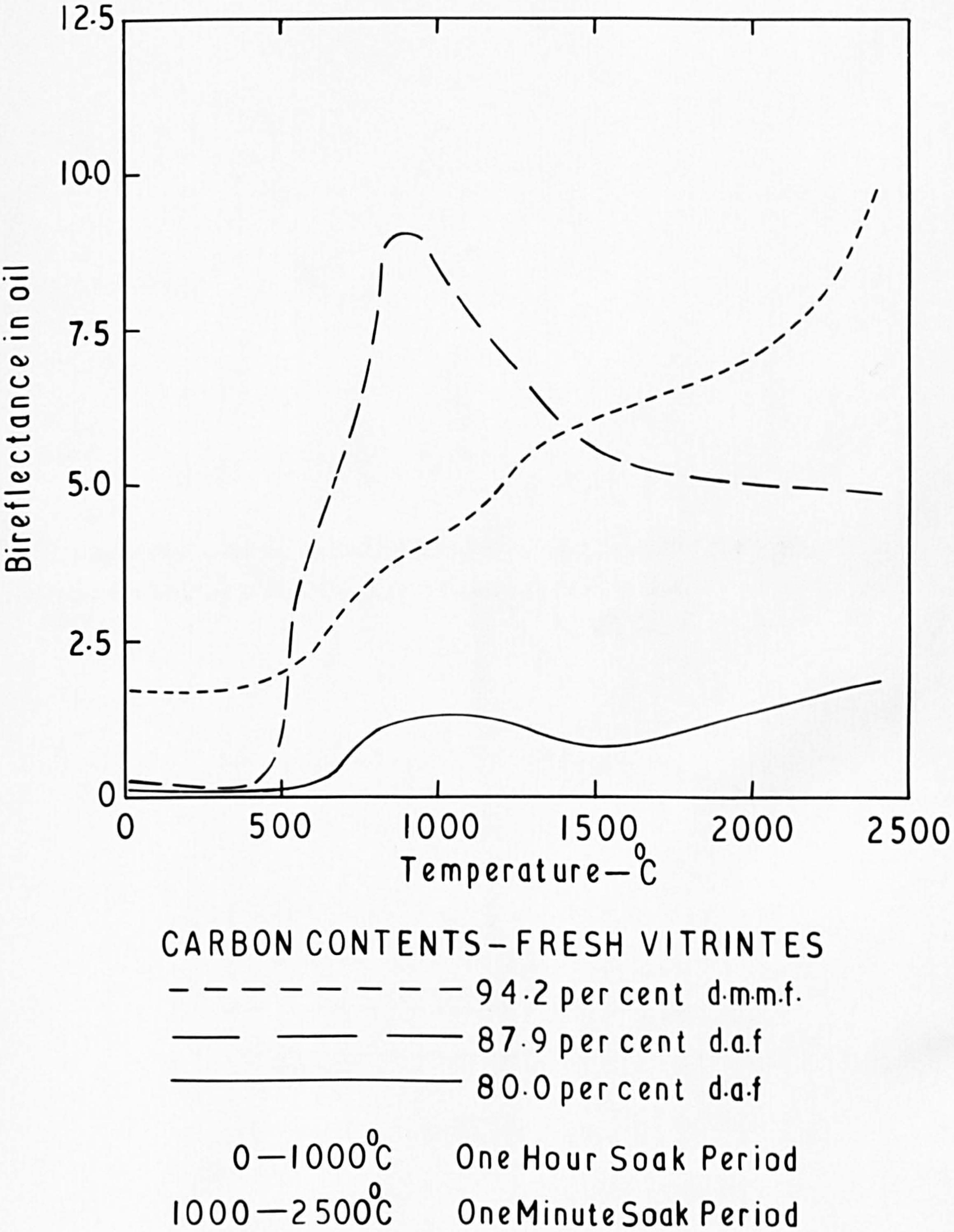
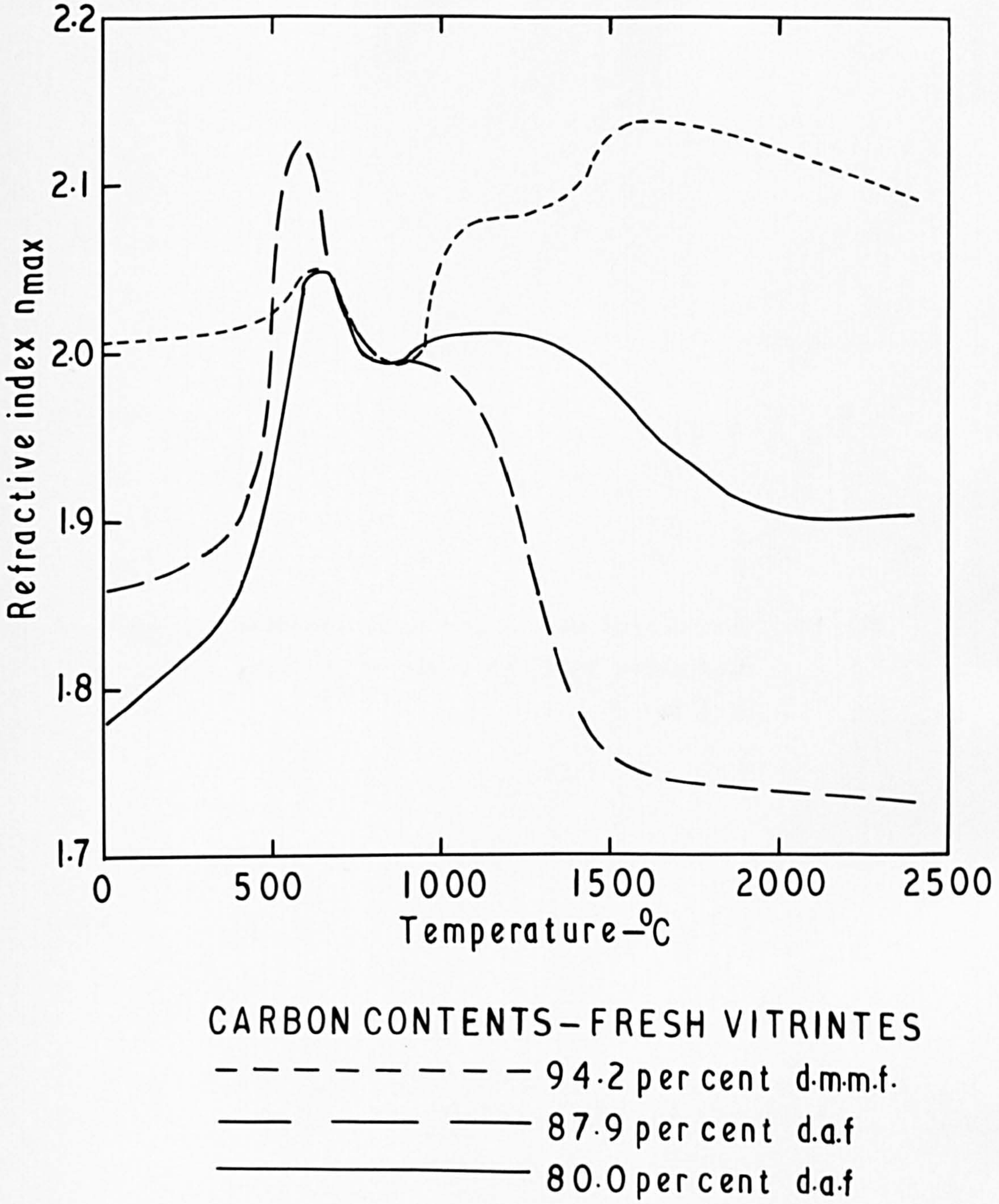

12.5
10.0
7.5
5.0
2.5
0
Bireflectance in oil
0
500
1000
1500
2000
2500
Temperature – °C
CARBON CONTENTS – FRESH VITRINTES
94.2 per cent d.m.m.f.
87.9 per cent d.a.f
80.0 per cent d.a.f
0 – 1000°C One Hour Soak Period
1000 – 2500°C One Minute Soak Period

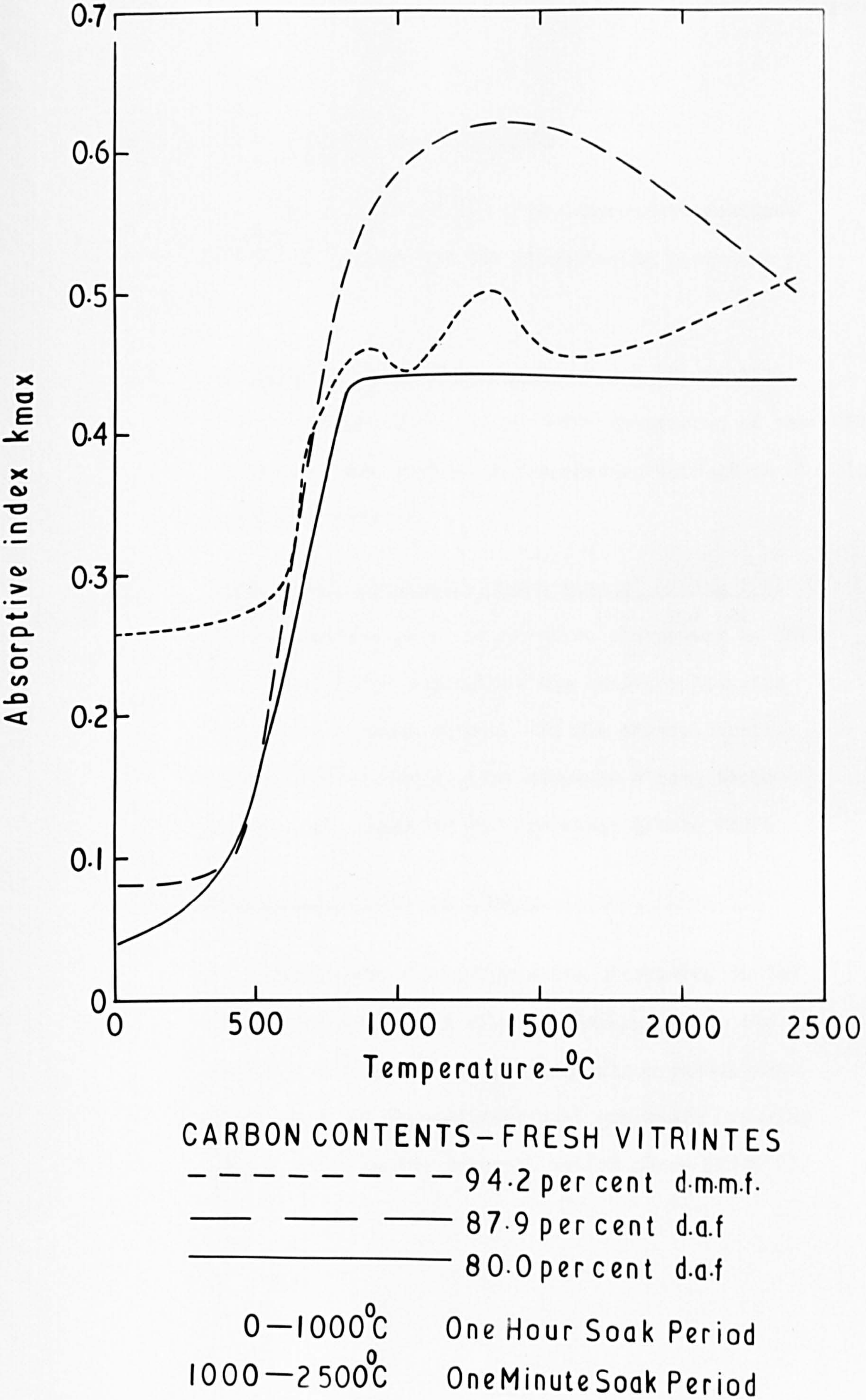
Fig 142 Generalised curves for variation with temperature of refractive index of three vitrinites, heated up to 2400°C.



0—1000°C One Hour Soak Period

1000—2500°C One Minute Soak Period

Fig 143 Generalised curves for variation with temperature of absorptive index of three vitrinites, heated up to 2400°C.


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Absorptive index k_{max}
0
500
1000
1500
2000
2500
Temperature—°C
CARBON CONTENTS—FRESH VITRINTES
94.2 per cent d.m.m.f.
87.9 per cent d.a.f
80.0 per cent d.a.f
0—1000°C One Hour Soak Period
1000—2500°C One Minute Soak Period

X-Ray diffraction (Plates 127 to 129)

X-Ray powder photographs of the high-temperature residues of the three vitrinites demonstrate the graphitising behaviour of each vitrinite.

(a) Low-rank vitrinite (non-graphitising) (Plate 127)

The photographs show progressive sharpening of the (002) reflection with rising of temperature throughout the high-temperature phases.

(b) Coking coal vitrinite (graphitising) (Plate 128)

The photographs show progressive sharpening in the (002) reflection throughout the semi-graphisation and graphitisation phases. In the crystallisation phase (2400°C) the residue displays strong three-dimensional graphitic (hkl) ordering (Plate 129).

(c) Anthracitic vitrinite (intermediate) (Plate 129)

The photographs show progressive sharpening in the (002) reflection with rise of temperature in the semi-graphitisation and graphitisation phases and development of three-dimensional graphitic ordering (Plate 128c) in the crystallisation phase (2400°C).

Fig 127 X-ray diffraction photograph of high temperature residues of low-rank vitrinite (carbon = 80.0% daf), showing non-graphitic behaviour

(a) 1100°C semi-graphitised, showing diffused (002) reflection

(b) 1800°C graphitised, showing sharper (002) reflection

(c) 2400°C crystallised, showing intense (002) reflection and almost no three-dimensional (hkl) graphitic ordering

(d) natural graphite

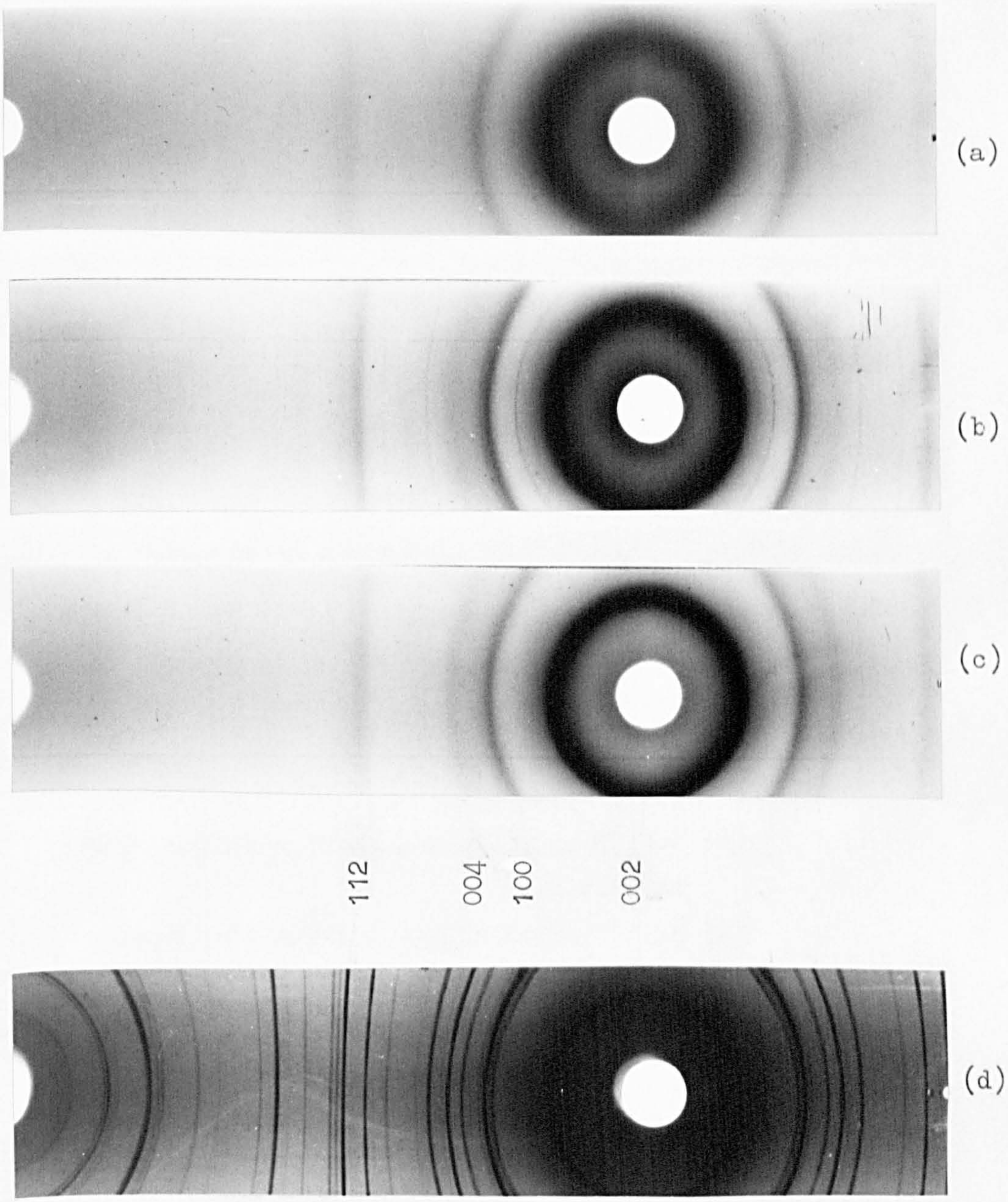
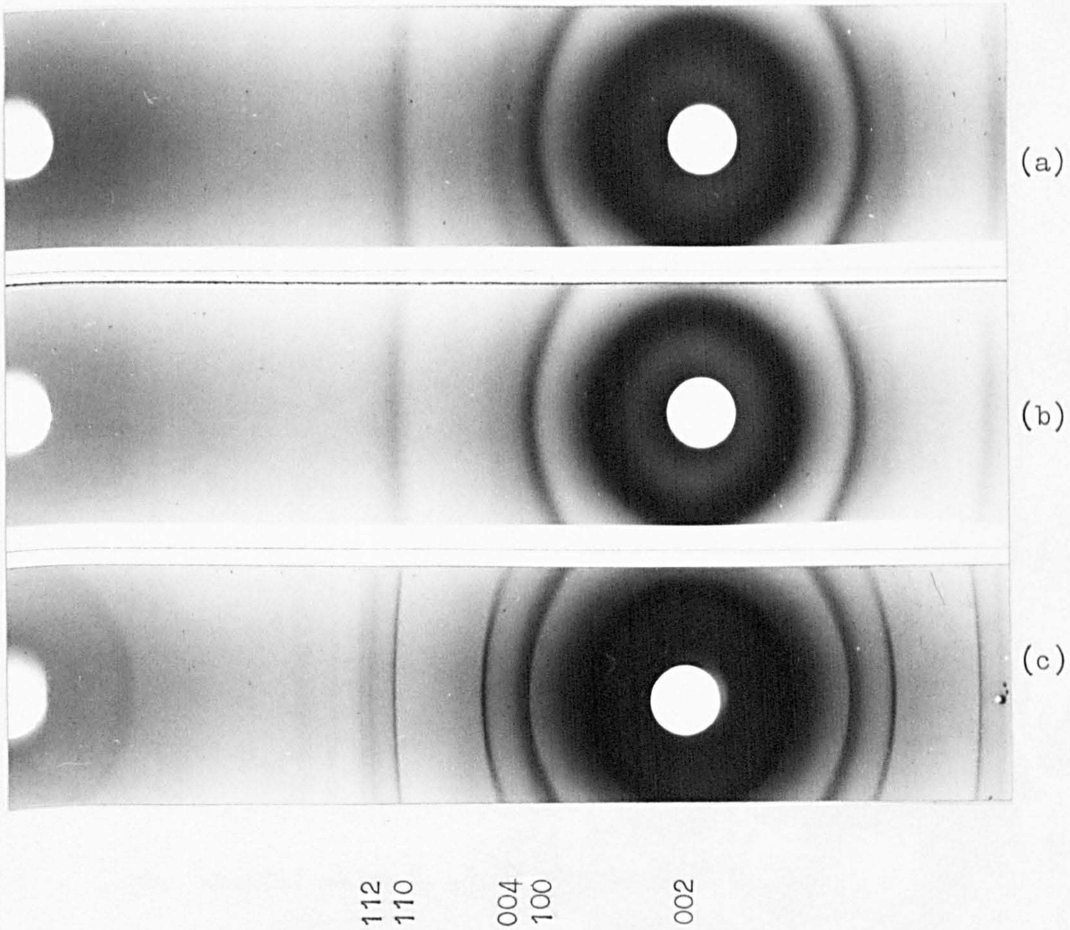

(a)
(b)
(c)
112
004
100
002
(d)

Plate 128 X-ray diffraction photograph of high-temperature residues of high-rank bituminous vitrinite (carbon = 87.9% daf) showing graphitising behaviour

(a) 1100°C semi-graphitised, showing diffused (002) reflection
(b) 1800°C graphitised, showing intense (002) reflection
(c) 2400°C crystallied, showing very sharp (002) reflection and also (hkl) three-dimensional graphitic ordering
(d) natural graphite


(a)
(b)
(c)
112
110
004
100
002

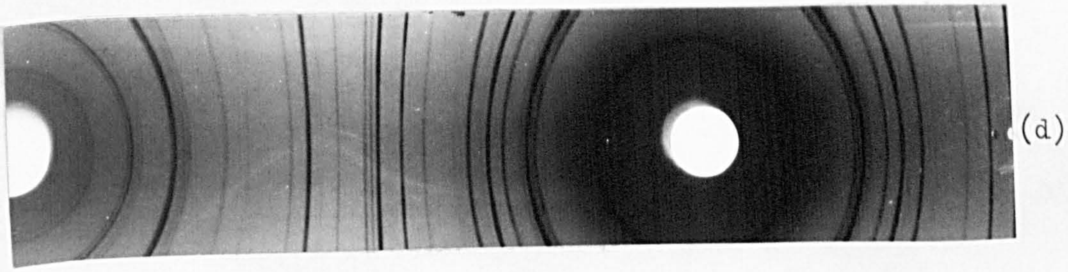

(d)

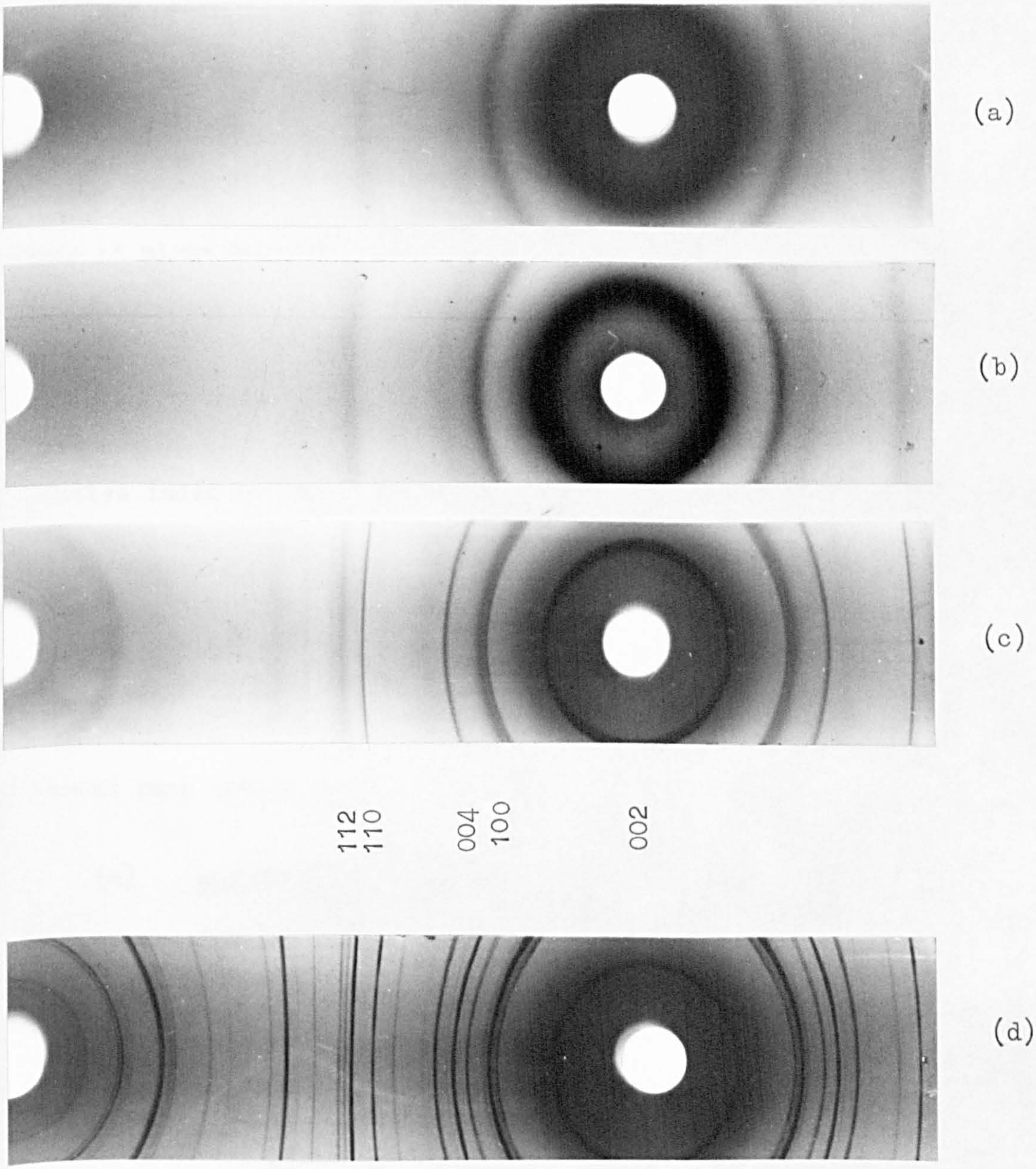
Fig 129 X-ray diffraction photograph of high temperature residues of anthracitic vitrinite (carbon = 94.2% dmmf), showing graphitising behaviour

(a) 1100°C semi-graphitised, showing diffused (002) reflection

(b) 1800°C graphitised, showing intense (002) reflection

(c) 2400°C crystallised, showing sharp (002) reflection and also (hkl) three-dimensional ordering

(d) natural graphite


(a)
(b)
(c)
112
110
004
100
002
(d)

D. Discussion

1. Introduction

The results presented here are in some respects unexpected, because it might be anticipated that the trends of optical properties of residues of vitrinite heat-treated at high temperature would continue the trends shown by carbonised residues at lower temperature, i.e. above 1000°C reflectivity, bireflectance, refractive index and absorptive index would rise continuously (possibly with some local interruptions) with increase of temperature, finally approaching the properties of graphite. This explanation is only partially incorrect (see Figs 133 to 135). For discussion of the high-temperature work the vitrinites of different rank can be placed under three headings:-

(a) non-graphitising (hard carbon), which includes the low-rank vitrinites, does not truly soften during low-temperature carbonisation. The aromatic structure of the carbonised residues are disordered and strongly cross-linked, remaining disordered on heating up to the end of the graphitising stage (about 2100°C), when a partially graphitic structure develops (see Franklin 1951; Warren 1956 and Loebner 1956).

(b) intermediate carbon, which includes the anthracitic vitrinite, does not soften during the early stages of the carbonisation process (in the plastic phase), keeping its original well-ordered but strongly cross-linked aromatic structures, but with rise of temperature, the cross-linking starts to break down at about 2000°C, resulting in a highly graphitic structure (see for example Franklin 1951), and

(c) graphitising carbon (soft carbon), including the coking coal vitrinite, which softens during the early carbonisation process producing a mosaic structure and a highly ordered molecular structure with loose cross-linking. Graphitisation of this carbon is fairly easy and does not require as high a temperature as is necessary for hard or intermediate carbon. The mosaic structure shrinks preferentially with rise of temperature.

2. Morphology

(a) Non-softening vitrinites

Development of high-reflecting, isotropic material with high relief during the semi-graphitisation phase (1000° to 1400°C) on the residues of the low-rank bituminous (Plates 104 and 105) and the anthracitic vitrinites (non-graphitising) (Plates 112 and 113) is probably due to devolatilisation and the deposition on the surface of particles of pyrolitic carbon. The results of Alpern and Chauvin (1957) suggest that if non-graphitising vitrinite is subjected to predistillation before heating at about 1000°C, the amount of this bright, vesiculated material with relief, decreases. Similar structures also develop from non-reactive components (non-granular) during high-temperature coking (Plate 13) (Marsh, private communication 1975). However, the above substances are present only superficially, because their amount greatly diminishes if the time of polishing is increased (compare Plate 105a and Plate 105b). These bright isotropic materials are considerably harder than the less bright, anisotropic particles, on which they are deposited. With approach towards the grpahitisation phase (above 1400°C), this material disappears rapidly, giving further support to the opinion that the material is due to evolution and deposition of volatile matter which ceases to evolve at about 1500°C (see Blayden 1969).

The non-graphitising vitrinites, after becoming harder with rising temperature between 1000° and 1250°C (apparent by length of time required to prepare a suitable polished surface, and which is probably due to an increase in two-dimensional bonding between the crystallites - see Ouchi 1955), become softer with further rise of temperature. The anthracitic vitrinite becomes softer than does the low-rank vitrinite, probably because anthracitic vitrinite develops a graphitic structure at higher temperatures, whereas low-rank vitrinites does not (see Franklin 1951). At 2400°C the anthracitic vitrinite develops almost similar 'macro-properties' to graphite, i.e. soft and silky to touch.

The continuous increase in the intensity of anisotropy of the low-rank bituminous vitrinite towards the end of the semi-graphitisation phase indicates better ordering of molecular structure, which is also evident in X-ray diffraction diagrams (Plate 127), which show a gradual sharpening of the 002 band with rise of temperature. At about 2400°C the low-rank vitrinite develops anisotropy that appears similar to that of fresh vitrinite of high-rank anthracite. Development of botryoidal structure in this vitrinite, evident from 'Stereoscan' micrographs (Plate 117) probably indicates softening of the low-rank bituminous vitrinite.

The devolatilisation vacuoles in anthracitic vitrinite, which disappear with rising temperature (see Goodarzi 1971 and results in Part III of this Thesis), towards the end of the carbonisation process, i.e. 900° to 950°C, appear once again during the semi-graphitisation phase (1000° to 1400°C). Comparison should be made between Plate 112a at 1000°C and Plate 113 at 1200°C.

The above phenomena suggest that anthracitic vitrinite undergoes at a much higher temperature the same mechanism as softening vitrinite undergoes at an earlier temperature, viz. during the carbonisation process, development of primary vacuoles (in the plastic phase) and secondary vacuoles (during resolidification phase). The development of perforated edges on particles in the semi-graphitisation phase (Plates 113 and 114) is a further indication of the formation of hard residues in this temperature range. However, the devolatilisation vacuoles and perforated edges in heat-treated anthracitic residues disappear at about 2000°C (Plate 115b) and the residues develop a similar appearance to that at 1000°C (Plate 112a), probably due to softening and expansion of the residues towards the ends of graphitisation-crystallisation range.

(b) Softening Vitrinite (Plates 108 to 111 and 119 to 123)

In contrast to the non-softening vitrinites, a softened, coherent structure is evident in this vitrinite. There is no trace of bright, isotropic material with relief in the residues of the coking coal vitrinite in the semi-graphitisation stage. The intensity of the anisotropy of this vitrinite also decreases continuously with rise of temperature, which is again a contrast to the residues of low-rank and anthracitic vitrinites. This behaviour is rather strange, because the X-ray diffraction photographs show continuous sharpening of the 002 band up to about 1800°C (Plate 128b), with the development of three-dimensional (hkl) graphitic ordering at about 2400°C (Plate 128c), indicating that an increase in anisotropy should be observable with the optical microscope. However, considering the surface quality of this vitrinite, which shows a marked deterioration (compare Plate 108 and Plate 111) with a reduction in the general reflectivity of the samples, then a reduction in anisotropy can probably be expected, because the mosaic structure (Plates 110 and 111) at 2000°C and particularly at 2400°C shows marked shrinkage, resulting in the development of a system of grooves in the material (Plate 111b). Indeed, the results of Brooks and Taylor (1965) indicate that the mosaic structure shrinks preferentially on heating up to 2500°C. The present results do not agree with the findings of Marsh et al. (1971) who state that there is no morphological change between the mosaic structures formed during the early stages of carbonisation and at high temperatures. The shrinkage of mosaic structure will result in scattering of the light and a reduction in reflectivity observed by optical microscope; the decrease in intensity of anisotropy can partially be due to destruction of two-dimensional order within the crystallites and to the development of three-dimensional graphitic ordering in this vitrinite. The results of Khavari (1975) show a similar drop in the bireflectance of gilsonite and grahamite, which develop mosaic structures during high-temperature heating.

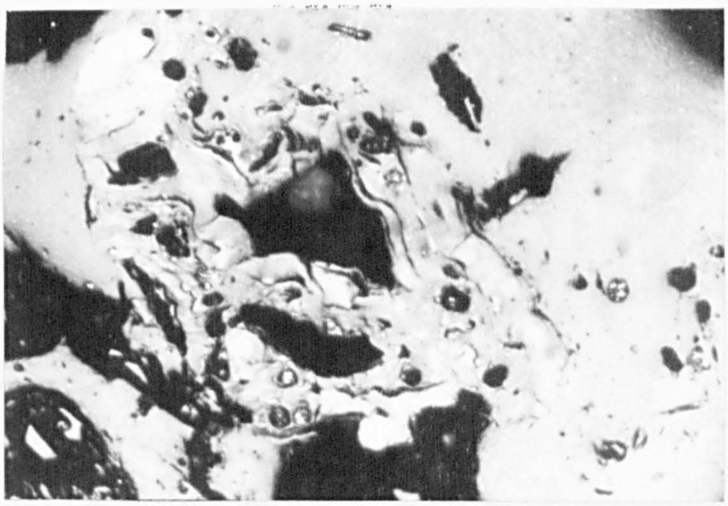
(c) Summary

The continuous increase of anisotropy observable through the reflected light microscope of residues of heat-treated low-rank and anthracitic vitrinites, in contrast to those from coking coal vitrinite, can only be due to differences in morphology, viz. development of a mosaic structure in coking coal and its shrinkage with rise of temperature that results in a decrease of bireflectance. Non-softening or low-softening vitrinite during the semi-graphitisation phase develops an isotropic type of pyrolitic carbon due to thermal cracking (Marsh 1975, private communication), although pyrolitic carbons are generally anisotropic (Plate 130) and it appears that here there is a new phenomenon which has not been reported previously. However, high-temperature coke (1200°C) develops such structure (isotropic and with bright relief), on areas arising from non-softening inclusions (Plate 131).

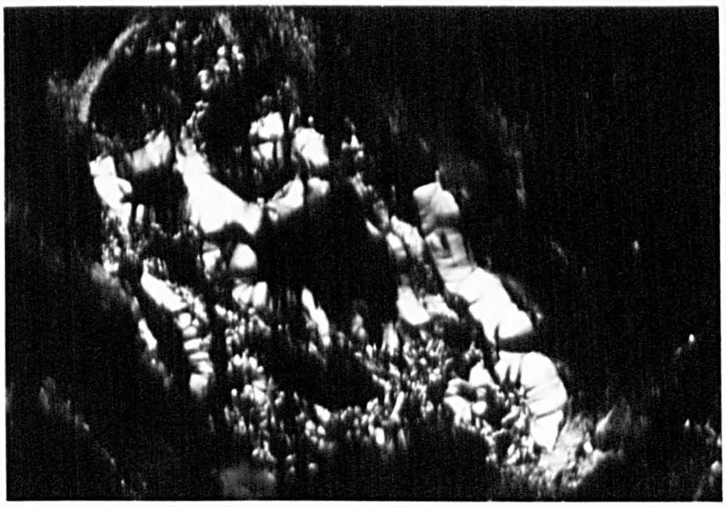
Plate 130 Metallurgical coke, heated at 1200°C, showing pyrolitic carbon x200

(a) (i) plane-polarised light
    (ii) crossed polars
(b) crossed polars

(a) (i)



(a) (ii)



(b)

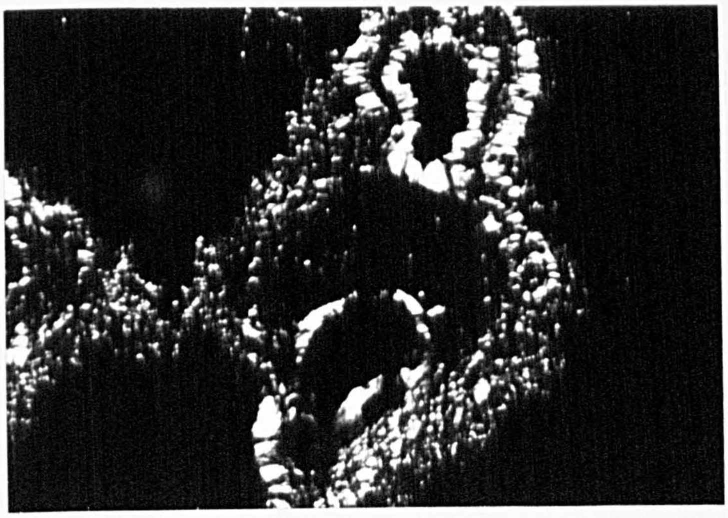
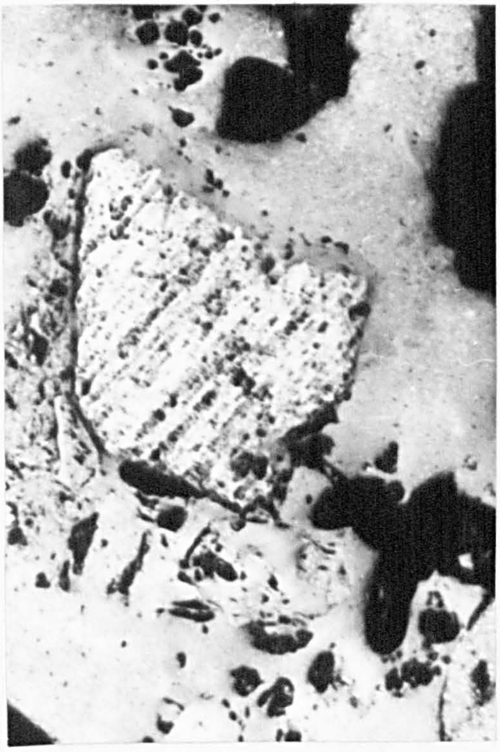


Plate 131 Metallurgical coke, heated at 1200°C, showing non-reactive particle x210

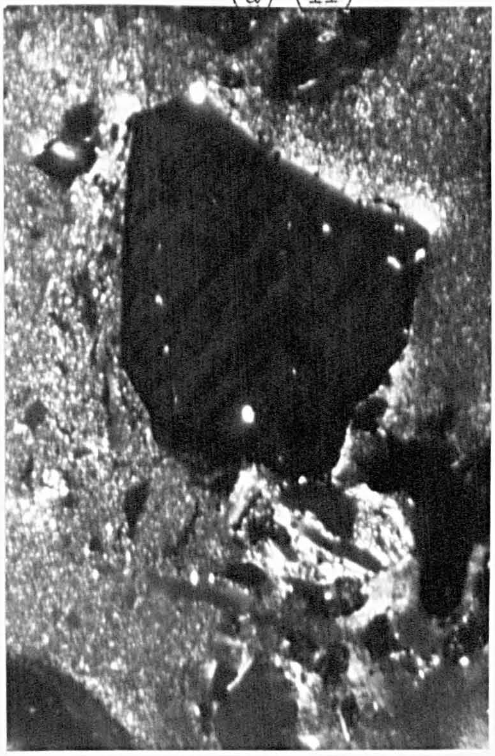
(a) particle is almost covered by a shell of highly reflecting material
   (i) plane-polarised light
   (ii) crossed polars

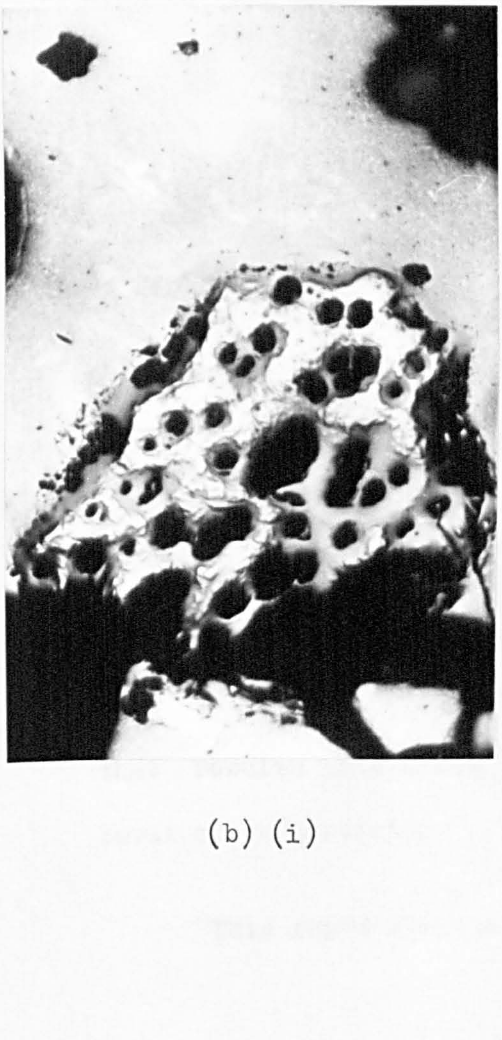
(b) particle is partially covered by highly reflecting material
   (i) plane-polarised light
   (ii) crossed polars

(a) (i)



(a) (ii)





(b) (i)

(b) (ii)

3. Optical Properties

(a) Reflectivity (a and b Figs 133 to 135 and 139, 140)

The explanation for the fall of the reflectivity curves with temperature of the heat-treated bituminous vitrinites, in contrast to the anthracitic vitrinite, might be sought in changes occurring in their molecular structure, changes which may also have an influence on the character of the polished surfaces.

The reflectivity curves of the two bituminous vitrinites, both of which soften during carbonisation, fall continuously with rising temperature above approximately 1000°C. This reflectivity drop is very sharp for the coking coal vitrinite which truly softens and develops a mosaic structure. In contrast, the fall is only slight for the low-rank bituminous vitrinite, which softens much less and probably only develops a very fine mosaic structure, that is observable by 'Stereoscan' microscopy (Plates 117a and b). In the discussion on morphology, attention has already been drawn to the changes in the appearance of the coking coal vitrinite at high temperature, namely the development of a rough surface and an apparent shrinkage of the mosaic units. It appears that the pronounced decrease of the reflectivity curve for this vitrinite is at least partially caused by the non-coherent surface and the preferential shrinkage of the mosaic units (Brooks and Taylor (1965) that results in a partial scattering of light and a decrease in the level of reflectivity.

This rapid decrease of reflectivity may also be due to other changes in the molecular structure of the heated vitrinite. The possible relationship between crystallite diameter (L_a) and reflectivity was discussed in Part III, but it appears that this relationship does not hold in the high-temperature residues of vitrinites of bituminous rank. According to Franklin (1951) and Loebner (1956), the crystallite diameters increase continuously (see a sharpening of 100 band) (Plate 127), while reflectivity falls rapidly. The results of Ouchi (1955), however, indicate that the crystallite diameters (L_a) of carbonaceous materials decrease slightly with rise of temperature between 1000° and 1400°C, due to a breakdown in two-dimensional bonding of the aromatic structure. If Ouchi's findings are true, then a more noticeable change in the reflectivity of heat-treated high-rank than low-rank bituminous vitrinite might be expected, because there is a less strongly-bonded aromatic structure in the high-rank bituminous vitrinite than in the low-rank bituminous vitrinite, which appears to be what happens in the reflectivity-temperature curve (Figs 138 and 140).

The smaller decrease in the reflectivity of the residues of the low-rank vitrinite indicates that the molecular structural changes are not as drastic as in those of the coking coal vitrinite, presumably because the low-rank vitrinite only becomes partially plastic and does not develop a large mosaic structure (see ' Morphology '). Also the rate of increase in the crystallite diameter (L_a) is slower than in the coking coal vitrinite (graphitising). The continuous rise of the reflectivity curve of the anthracitic vitrinite with temperature suggests a progressive increase in crystallite diameter (L_a) with rise of temperature (see Franklin 1951) but still the level of reflectivity, even at 2400°C, the 'crystallisation temperature' (Honda 1959) is much lower than that of graphite (see Table 13). Thus the relatively low level of the reflectivity of heat-treated anthracitic vitrinite (Figs 133a and b, 137 and 138) is probably due to surface deterioration, possibly compounded by the polishing technique applied. A comparison between the results of McCartney and Ergun (1959) and Kwiecinska et al. (1975) (see Table 13) shows the importance of surface preparation in reflectivity measurements applied to graphites.

TABLE 13

Graphite Basal Face	%R air max	%R oil max	RI	k	Wavelength
McCartney and Ergun (1959)	27.7 28.0	15.1 16.1	2.15	0.66	Filtered to pass only in range 500-570nm maximum at 550 nm
Kwiecinska et al. (1975)	31.29	17.92	2.43	0.63	546 nm

(b) Bireflectance (Figs 136 to 138; 141)

The bireflectance-temperature curves of carbonised vitrinites increase continuously with rise of carbonisation temperature, the rise being related to greater ordering of the molecular structure within the crystallites (see Part III of this Thesis). As pointed out earlier, the term 'bireflectance' used here, when a mosaic is present, can only be a generalised bulk measurement of degree of ordering and probably does not represent the same type of measurement on coals with a smooth unstructured surface. The bireflectance-temperature relationship for the heat-treated vitrinites above 1000°C is probably the easiest to assess.

The slight decrease of bireflectance with temperature of the low-rank vitrinite (hard carbon) within the semi-graphitisation phase (up to about 1400°C) is probably due to partial destruction of the turbostratic bonding, which is also evidenced by progressive softening of this vitrinite (hard carbon (see for example Ouchi 1955 and Honda and Sanada 1957). The continuous rise of bireflectance between 1400° and 2400°C is due to increasing ordering of the molecular structure within the crystallites and to the partial development of three-dimensional graphitic ordering within the crystallites during heating at graphitising stage and during the crystallisation stage. Indeed the morphological observations show development of a strong basic anisotropy at about 1800°C (see'Morphology'), which further indicates an increased degree of ordering of the molecular structure within the crystallites. Plate 127 shows an X-ray powder photograph of this vitrinite; the better ordering of molecular structure is evident in the sharpening of the 002 band with rise of temperature.

The continuous increase of the bireflectance-temperature curve of anthracitic vitrinite (intermediate carbon) up to 2400°C also illustrates progressively better ordering of the molecular structure within the crystallites. Indeed, the results of Franklin (1951) show that anthracitic vitrinite at about 2500°C (crystallisation temperature) develops a better graphitic structure than does soft carbon (coking coal) due to the initially better ordering of the molecular structure of fresh anthracite. This better ordering is due to rigid cross-linking between the aromatic lamellae, which are not able to form into a graphitic structure at temperatures lower than the 'crystallisation temperature'. A greater level of thermal energy is required to break down these cross-links and when the transformation from two-dimensional turbostratic to three-dimensional graphitic structure takes place, it does so without breakdown of the initial ordering. The present X-ray diffraction photographs of the heated anthracitic vitrinite also show a continuous sharpening of the 002 band with rise of temperature (Plate 129).

The steep fall of the bireflectance-temperature curve of soft carbon (coking coal vitrinite) with rising temperature is very unexpected, because X-ray diffraction photographs (Plate 128) show a progressive increase in the ordering of the molecular structure within the crystallites (002 band). The two-dimensional ordering (turbostratic ordering) within the molecular structure of soft carbons is slowly transormed to the three-dimensional graphitic ordering. This transformation is fairly easy for soft carbon compared with the hard or intermediate carbons, because of the initially looselv-linked aromatic layers in fresh samples (see for example Franklin 1951). This weak cross-linking is destroyed in the early stages of carbonisation, resulting in temporary loss of molecular ordering and optical anisotropy (Goodarzi and Murchison 1972). Then the reordering of the molecular structure commences, resulting in an enhancement of the two-dimensional ordering within the crystallites up to about 1000°C, seen in the continuous rise of bireflectance (see Goodarzi and Murchison 1972 and the results in Part III of this Thesis).

The transformation of molecular structure from two-dimensional ordering to three-dimensional ordering is rather severe in soft carbons and once again is apparent in the progressive softening of the residues (see for example Ouchi 1955). Since the loss of molecular ordering during the early stages of carbonisation (softening stage) is accompanied by a decrease of bireflectance, which is observed in the softening carbons, then a more drastic change in the behaviour of the bireflectance may be expected when a more severe reordering takes place, e.g. transformation from two to three-dimensional ordering. The morphological changes do not appear to be great enough alone to be the cause of this drastic change, although their influence cannot be ruled out, because surfaces of soft carbons are difficult to prepare. The preferential shrinkage of the mosaic structure (see Brooks and Taylor 1965) at high temperatures may be another cause of the decrease in bireflectance. The decrease of the bireflectance curve is thus probably due to a combination of molecular and morphological deterioration.

In summary, the increase of the bireflectance-temperature curves of hard and intermediate carbons appears to be due to their rigid cross-linking, which preserves their two-dimensional or turbostratic ordering up to very high temperatures (about 2000°C). When the transformation from turbostratic to graphitic ordering occurs, it is accompanied by displacement of whole layer planes, or even groups of layers, which come into parallelism with the layer planes. In contrast, the continuous decrease of bireflectance of soft carbons is probably due to more extensive and severe molecular changes than in the hard and/or intermediate carbon and is facilitated by their weakly bonded, highly reordered (turbostratically) layers. It is interesting to observe the changes in the trends of the bireflectance-temperature curves of hard and soft carbons at about 1500°C (Fig 141). The trends are in accordance with the statement of Blayden (1969), who indicates that the thermal reorganisation of carbons commences at about 1500°C, where in the present study the bireflectance of the heat-treated hard carbons starts to increase once more and the sharp decrease of the bireflectance of the soft carbon is at least arrested.

(c) Refractive Index (Figs 133d, 134c, 135c and 142)

The behaviour of the refractive index-temperature curves of carbons during the carbonisation process has been related to changes in (L_c), i.e. changes in crystallite height, improvement in ordering and packing of aromatic lamellae within crystallites and of the amount of buckling in the turbostratic crystallites (see Goodarzi and Murchison 1972, 1973). The results of Franklin (1951); Ouchi (1955); Warren (1956) and Loebner (1956) show that the increase of (L_c) is greater after carbonisation above 1000°C (see Figs 24 and 25). Thus, these results indicate that the refractive index of the heat-treated vitrinites should also rise with increase of temperature, at least to the level of the refractive index of graphite, and then remain stable there. But refractive indices of the residues of all vitrinites decreases with increase of temperature above 1000°C at some stage. Why is this? There seem to be two possible principal explanations.

The surfaces of the heat-treated carbons at temperatures above 1000°C show a gradual deterioration in surface quality with the polishing method employed. This deterioration would produce a drop in reflectivity that would be accompanied by a fall in the derived parameter of refractive index. Whether or not the deterioration in surface quality is sufficient to produce the falls in refractive index observed is conjectural. A further factor may be the changes in molecular structure occurring when two-dimensional alters to three-dimensional ordering. What will happen if the two-dimensional turbostratic crystallites are replaced by three-dimensional graphitic ordering; would the relationship between (L_c), refractive index and temperature still apply or not? The present results suggest that the relationship does not hold at least when the semi-graphitisation temperature is approached (1000° to 1400°C) and this is particularly shown by the trend of the refractive index of the heat-treated soft carbon which is a graphitising carbon. Since the turbostratic bonding in these carbons is weak, with progressive increase of temperature, the turbostratic ordering transforms to graphitic ordering and at about 1700°C the three-dimensional graphitic relation is formed (see Loebner 1956). The sharp decrease of refractive index from 1000° to about 1800°C of the soft carbon could be assisted by this structural transformation. Since the changes from the turbostratic to the graphitic structure takes place at high temperature (above 2000°C) for hard carbons (low-rank vitrinite), it is not surprising that the refractive index only starts to decrease once the temperature of graphitisation is approached, i.e. the refractive index remains at a high level to a higher temperature than with soft carbons.

The trends of the refractive index for the heat-treated anthracitic vitrinite is interesting because it indicates that (L_c) increases irregularly with rise of temperature from 500°C to 1600°C, probably because the cross-linking between aromatic lamellae is strong and resists the thermal energy up to about 1500°C (see Franklin 1951), if not to higher temperatures. Then the cross-linking starts to break down and the transformation of turbostratic crystallites to graphitic ordering commences; the decrease of refractive index at temperatures higher than 1600°C can be related to this transformation.

(d) Absorptive Index (Figs 133c, 132d, 133d and 144)

As stated earlier, the increase of absorptive index of naturally coalified vitrinites and heat-treated vitrinites with rise of rank is related to increase of layer diameter (L_a) and to the number of the mobile electrons present. Thus, decrease of absorptive index should indicate a fall in the number of the mobile electrons and a lessening crystallite diameter (L_a). The results of Franklin (1951), however, indicate that the crystallite diameters of carbons increase with rise of temperature and that the soft carbons, on heating, develop larger crystallite diameters than hard carbons heat-treated at the same temperature. If the rise in absorptive index is related to increase in (L_a), then a continuous increase of absorptive index with temperature should be expected. The present results are contradictory, at least for the absorptive index curves of heat-treated, low and high-rank bituminous vitrinites. A possible explanation, besides surface effects on reflectivity determination (see 'Morphology' and Reflectivity of this Part), could be the transformation of turbostratic ordering to graphitic ordering which is greater for soft carbons (coking coal) than for relatively harder carbons (low-rank bituminous and anthracitic vitrinite). The pattern of the absorptive index change would support this view, viz. a sharp decrease of the absorptive index curve for the coking coal vitrinite, a slight decrease for low-rank bituminous vitrinite and a continuous rise for the anthracitic vitrinite. It is more likely, however, that the fall in absorptive index is mainly due to the reduced reflectivity produced by poor surface quality.

E. Conclusion

The following conclusions can be drawn from the behaviour of the optical properties of vitrinites heat-treated at temperatures ranging from 1000° to 2400°C.

1. Morphological

(i) At temperatures above 1000°C, the condition of the mosaic structure of truly softening vitrinites deteriorates with rise of temperature.

(ii) The less softening and/or non-softening vitrinites develop isotropic pyrolitic carbon during the semi-graphitisation phase.

(iii) All the vitrinites increase in hardness and then become softer with rise of temperature

(iv) The number of devolatilisation vacuoles decreases with rise of temperature beyond the semi-graphitising phase for anthracitic vitrinite

2. Optical

(i) The decrease of the reflectivity and the absorptive indices of softening vitrinites at high temperatures is most likely due to surface defects brought about because of deterioration of the mosaic and molecular structures. The decrease is less in the low-rank bituminous vitrinite and an increase occurs in anthracitic vitrinite.

(ii) Bireflectance is a function of ordering of molecular structure, but the bireflectance of truly softening vitrinite decreases, whereas the bireflectance of less softening and non-softening increases with rise of temperature. The bireflectance fall is again probably due to deterioration of surface quality.

(iii) The trends of the refractive index-temperature curves may show some effect of the transformation of turbostratic ordering to graphitic ordering but also must reflect the influence of surface defects on the level of reflectivity of the surfaces.

PART VIII CONCLUSION AND PRACTICAL USE OF PRESENT STUDIES

Having considered the influence of various factors on the optical properties of heat-treated macerals, it is now possible to draw some general conclusions and suggest some practical uses arising from the work.

In Part III of this Thesis it was demonstrated that with rising heating rate there is a progressive increase of mosaic size and bireflectance of vitrinites that could be related to increased fluidity. A caking-coal vitrinite (carbon = 85.4% daf) carbonised at a fast heating rate produces a strong coke with similar morphological (mosaic size; apparent swelling) and optical properties to those of a coke produced from low-rank coking coal (carbon = 87.9% daf). Further, it was also demonstrated that by using mosaic size in conjunction with oil bireflectance, it is probably possible to estimate the rank of the original coal forming a coke. Alternatively knowing the initial ranks, the properties of a coke may allow deductions about heating conditions in the coke ovens. Some vitrinites showing cell structure are reactive during carbonisation because of the development of mosaic structure.

The fourth part of the Thesis showed that given a sufficiently long holding time at temperatures below decomposition temperature, viz. 150°C and 350°C, vitrinites, other than those of anthracitic rank, will soften. This is apparent by the increase in the size and number of devolatilisation vacuoles. The normal temperature of formation of mosaic structure (ca. 425°C) and also the fluidity of truly softening vitrinite can be greatly reduced (ca. 350°C) given sufficient time (ca. 32 weeks). This observation may be helpful in estimating the temperature level attained during metamorphism of heat-affected coals from rocks.

Part V dealt with the carbonisation of sporinites, a maceral whose optical properties on carbonisation had not so far been examined. Low-rank sporinite develops mosaic structure, whereas the associated vitrinite does not. This observation may be applicable in the study of particles of these macerals in dispersed sedimentary rocks, because the residues of sporinite can produce a mosaic structure and a higher anisotropy than the vitrinitic particles of the same rank which remain almost morphologically unchanged. The systematic study of carbonised sporinites has given a greater insight into the behaviour of this maceral during coking process. Further, the systematic study of the interaction between carbonised sporinites and vitrinites in blends of the same rank from low- and medium-rank bituminous coals may be helpful for petrologists in analysing industrial cokes, particularly in recognising the parent macerals of coals going to form the coke.

In Part VI useful correlations between pressure levels during carbonisation and the optical properties and morphological changes of carbonised residues from a coking-coal vitrinite were made. These studies may also be helpful in evaluating the conditions under which organic matter has been altered in the crust, as are the results of the previous parts.

The results of Part VII show that in contrast to what might reasonably have been expected, optical properties of bituminous-rank vitrinites heated at temperatures above 1000°C follow an unexpected trend. An explanation was sought using optical and electron-scanning microscopy and X-ray diffraction studies, but the likely explanation lies in an altering molecular structure and poor surface preparation of samples which probably require a different type of surface preparation to overcome this problem. The non and/or less reactive vitrinites develop an unexpected surface phenomenon which was referred to as 'isotropic pyrolitic carbon'. This phenomenon has not been reported previously except for a brief reference by Alpern and Chauvin (1958). The results of this Section suggest at least that until a more satisfactory surface-preparation technique is found, the relationship between optical properties and molecular structural changes in this temperature range will not be easily established.

An estimate of the conditions to which naturally heat-affected coals have been subjected is the subject of many publications. The increase in the optical properties and the development of higher anisotropy have been assumed to be due to the influence of pressure (Chandra 1965) or to pressure and/or heating rate (Brown and Taylor 1965). The present results show that these features, viz. large mosaics, numerous equidimensional vacuoles, high bireflectances, which are observed in thermally metamorphosed coals, can also be observed in residues carbonised at fast rates of heating and/or under hydraulic pressure. Finally, heating at relatively low temperatures (ca.350°C) for long periods of time results in the development of mosaic structure. Thus, in the study of factors causing the thermal metamorphism of coals, the above three factors should be carefully considered.

Throughout this programme the oil bireflectance of residues under different carbonisation conditions seems best to illustrate the molecular changes brought about during carbonisation. A better understanding of the nature of factors influencing the carbonisation process can probably be obtained by a combination of oil bireflectance and morphological changes. It appears that variations in oil bireflectance and morphological changes in the chars also indicate the degree of fluidity of the carbonised residues. The other optical parameters, e.g. reflectivity, refractive and absorptive index, are also indicative of molecular structural changes, but occasionally they do not detect the smaller molecular changes. This is well demonstrated by a comparison between oil bireflectance and the reflectivity-temperature curves of vitrinite carbonised at a rate of heating of 1°C/min (Figs 58 and 61) as well as by a comparison of the oil bireflectance-temperature curves (Fig 104) with the reflectivity curves (Fig 103) of low- and medium-rank sporinites alone and of mixtures of sporinite and vitrinite of corresponding ranks, which further indicates the sensitivity of oil bireflectance. Further reference can be made to Part VII where the bireflectance of low-rank bituminous vitrinite heated at high temperature increases independently of the reflectivity. Finally, the refractive index curve is also very informative about the vertical changes in the crystallite (crystallite heights) and related factors, but the accuracy and length of time required to obtain satisfactory data through the refractive indices are a handicap for speedy determinations. Interpretation of refractive index data is also really only possible from a refractive index curve, not from individual data points, which further hinders rapid practical application of this parameter.

PART IX SOME POSSIBLE SUGGESTIONS FOR FUTURE WORK

A. Heating Rates

(i) Studies of the possible development of improved qualities of coke by carbonisation of less strongly caking coals at fast heating rates.

(ii) Use of mosaic size and texture, in addition to the oil bireflectance, to assess coke quality.

(iii) Possible use of optical properties, particularly oil bireflectance and mosaic texture, in estimating hardness of coke.

(iv) Study of the possible development of a mesophase in British bituminous vitrinites using smaller temperature intervals.

B. Sporinite

(i) Possible development of better quality coke by mixture of sporinite of higher rank (durainous coal) with weakly caking coal.

(ii) Study of the hardness of coke developed from mixtures of sporinite and vitrinite.

(iii) Reactions between sporinite and inertinite and optical effects.

C. Pressure

(i) Study of the optical properties of macerals under shear pressures when carbonised.

(ii) More comprehensive study of the optical properties of vitrinite carbonised under low hydraulic pressure, using lower pressure levels and smaller temperature intervals with and without the presence of water.

D. High-temperature

(i) Development of a polishing technique to improve surfaces of vitrinites heated to high temperatures.

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