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D. G. Murchison, A. C. Cook, Anne C. Raymond, B. Durand, A. C. Cook, D. P. McKenzie and B. Sellwood

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Optical properties of organic matter in relation to thermal gradients and structural deformation

By D. G. Murchison[1], A. C. Cook[2] and Anne C. Raymond[1]

[1] *Department of Geology, University of Newcastle, Newcastle upon Tyne NE*1 7*RU, U.K.*
[2] *Department of Geology, University of Wollongong, New South Wales, Australia* 2500

The general response of macerals to the coalification process, the effectiveness of organic geochemical and petrological parameters as estimators of coalification and the applicability of different microscopical parameters in the assessment of rank are reviewed. The central role of vitrinite reflectance as the most widely used estimator of coalification from brown coals to the low-grade metamorphic zone is established on the basis of its relatively uniform variation with rank, specificity, ease and rapidity of measurement and cheapness. Factors influencing the optical properties of vitrinites are considered. Temperature has the dominant influence in modifying optical properties with rank, but time, static pressure and stress can all have significant influences upon the course of optical properties, depending upon particular geological conditions. Static pressure has a retarding effect on the coalification process, but it is also responsible for creating increasing anisotropy within the condensing aromatic structures as rank rises. Hydrostatic pressures and pore pressures can contribute to the overpressuring of sediments, thus affecting their thermal conductivities and consequently the rate of coalification. Stress is responsible for the development of biaxicity in the reflectance indicatrix. Fast and high levels of heating from igneous bodies cause textural effects on vitrinites as a result of carbonization that are quite different from those of coalification. Recognizing these different influences upon the optical properties of vitrinites, examples are given of the use and application of vitrinite reflectance in the preparation of rank maps, in the burial histories of basins, in the timing of coalification in relation to orogenesis and igneous activity and in the zones of anchimetamorphism and low-grade metamorphism. Consideration is also given to the problem of 'provincialism' in correlations between chemical and physical parameters and to the future development of optical studies in organic petrology and their relation to organic geochemical investigations.

1. Introduction

Organic matter of great diversity in both content and maturity is widespread in sediments. While the differences between the concepts of type and rank (coalification, maturation, catagenesis, etc.) have perhaps been laboured excessively in recent years by organic petrologists, a clear distinction between the concepts is absolutely necessary. This contribution to the geochemistry of organic sediments is essentially concerned with rank and, in particular, the way in which petrological parameters have been applied to the assessment of rank in relation to thermal and tectonic events affecting buried sediments. Relatively recently, Teichmüller & Teichmüller (1981) presented an extensive review of the significance of coalification studies to geology. This paper, while covering some of the same ground as this review, is equally concerned with examining certain factors which may influence the accepted generalized variation of petrological parameters with rank but which still require further study to establish just how significant these may be in affecting coalification trends.

Two essentially different and largely independent stages of coalification are recognized. The first, the peat or biochemical stage, together with the nature of the organic matter contributed to a coal or other sedimentary rock, controls the organic constituent (maceral) composition and organic matter type. The second, the physico-chemical stage, commences when the coal or sedimentary rock is buried by subsequently deposited strata and is a response of the organic matter to elevated temperatures acting under confining pressures and sometimes stress over long periods of time. The response of organic matter to physico-chemical coalification is essentially metamorphic in nature. It results in the development of the coal-rank series, peat-anthracite (and their rank equivalents in the case of the organic matter in other sedimentary rocks) and at more extreme levels, in the development of meta-anthracites, semi-graphite and some forms

TABLE 1. MACERAL TERMINOLOGY (AFTER I.C.C.P. STOPES–HEERLEN SYSTEM MODIFIED BY SMITH 1981) AND MACERAL ORIGINS (PARTIAL LIST)

maceral group	maceral	origin
vitrinite	telovitrinite	humified plant remains typically derived from woody, leaf or root tissue with well to poorly preserved cell structures
	detrovitrinite	humified attrital or less commonly detrital plant tissue with particles typically being cell fragments
	gelovitrinite	humified material showing no trace of cellular structure, probably colloidal in origin
liptinite	sporinite	outer casing of spores and pollens
	cutinite	outer waxy coating from leaves, roots and some related tissues
	resinite	resin filling in cells and ducts in wood; resinous exudations from damaged wood
	fluorinite	essential oils in part; some fluorinite may be produced during physico-chemical coalification and represent non-migrated petroleum
	suberinite	cork cell and related tissues
	bituminite	uncertain but probable algal origin
	alginite	tests of some groups of green algae; material referred to alginite shows moderate to strong fluorescence
	exsudatinite	veins of bitumen-related material expelled from organic matter during coalification
inertinite	fusinite	pyrofusinite originates from wood and leaf tissue in forest fires
	semifusinite	wood or leaf tissue weakly altered by mouldering or by biochemical alteration
	inertodetrinite	similar to fusinite or semifusinite but occurring as small fragments
	macrinite	humic tissue probably first gelified and then oxidized by processes similar to those producing semifusinite
	sclerotinite	moderately reflecting tissue of fungal origin – largely restricted to Tertiary coals
	micrinite	largely of secondary origin formed by disproportionation of lipid or lipid-like compounds to fluid hydrocarbons and a high reflecting granular residue of micrinite

of graphite. Figure 1 shows diagrammatically the development of the maceral groups and certain macerals in the peat stage and their evolution through the rank series.

The term maceral is used as an analogue of the term mineral in that coals are composed of a range of macerals. Because each maceral can have a range of origins (for example, different woods or other structural tissues for vitrinite, or different spores or pollens for sporinite (table 1)), data relating to the mixtures show variations due to type as well as to rank. Rank assessment can be made on the basis of the properties of any of the macerals or maceral groups, but in practice, most rank assessments are based on measurements made on vitrinite (figure 1 and see also §2*b*).

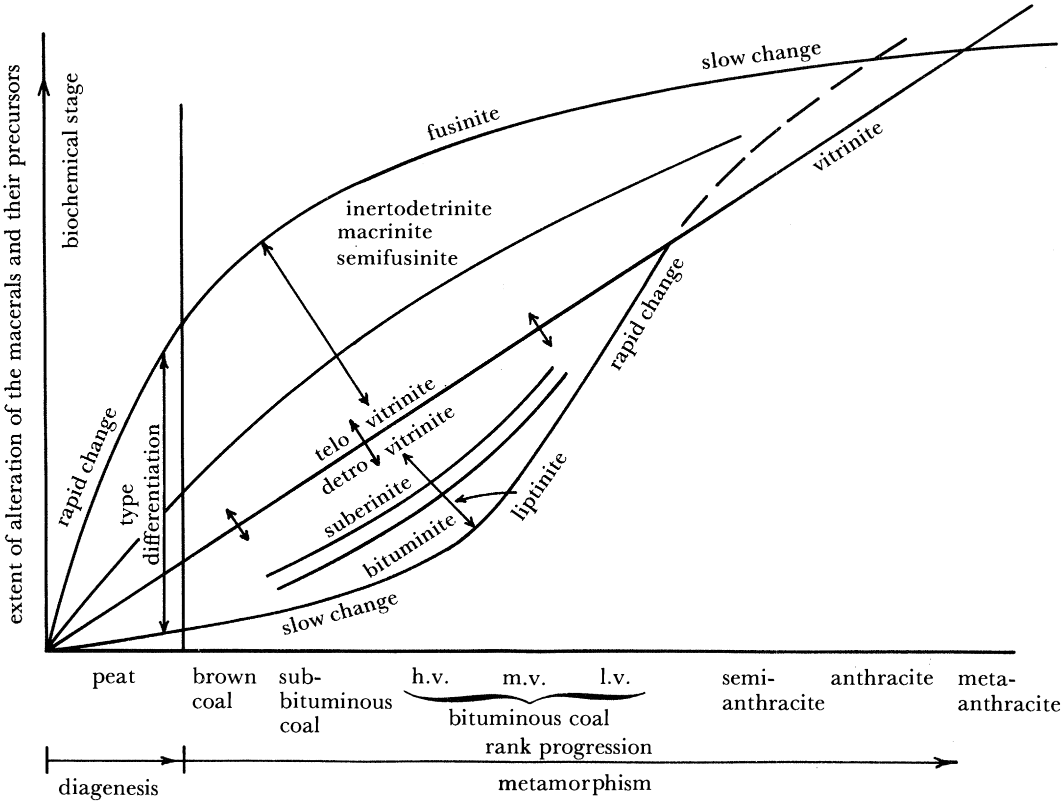

Figure 1. A modified Schopf diagram illustrating the variation in rates of coalification between individual macerals and maceral groups. The approximately linear change in the properties of vitrinite macerals throughout the rank series is important in their use in rank assessments. (Note that h.v., m.v. and l.v. represent high-, medium- and low-volatile respectively.) (Redrawn, with permission, from Cook 1982; data from Smith & Cook 1980.)

Petrographic techniques provide a method of determining the properties of organic matter so that corrections for mineral matter do not have to be made. Type and rank can be evaluated as largely independent variables. Organic matter type and abundances are a major input into any organic petrological study, but because of the particular emphasis of this contribution, these will have to be largely ignored. Although sample sizes of several grams are desirable, measurements, particularly those leading to rank assessment, can be made on microgram quantities of organic matter. Thus the techniques developed for petrological study of coals have, with relatively little modification, been applied in the more general study of dispersed organic matter in sedimentary rocks. A summary of the aims of and the results from organic petrological investigations are given in table 2.

Table 2. Organic petrology: aims and results

aims		geological	industrial
	A	organic matter: type and abundance	coal type, source rock potential for hydrocarbons
	B	level of organic metamorphism: pressure, temperature and time dependent properties may be assessed separately	coal rank, maturation and carbonization data
results	A	organic matter: type	
	A1	qualitative and quantitative data (visual estimates, point counts, image analysis) on the nature, distribution and abundance of organic entities, with data summarized in table, diagram and map form (aspects of inorganic petrology may also be observed and are commonly reported to link organic and inorganic petrology)	
	A2	interpretation of data in terms of facies (in the general sedimentological sense and in terms of organic facies); relation of organic matter to facies data from clastics and other rock types	
	B	level of organic metamorphism: rank	
	B1	typically vitrinite reflectance and exinite fluorescence data, but desirably optical orientation data and information on as many other rank-sensitive variables as possible to allow inferences about provincial factors: data summarized as well profiles for boreholes, as 'fence' diagrams for sets of surface samples or boreholes: mapping of properties dependent upon level of metamorphism	
	B2	thermal histories inferred from reflectance profiles and isoreflectance surfaces: timing of coalification events from spatial distribution of rank and from the use of coalification models, typically in conjunction with present-day subsurface temperatures	
	B3	testing of hypotheses on basin histories with evidence provided by rank distribution: use of organic matter type and rank to predict utilization behaviour of coals and to compare inferences on hydrocarbon generation with direct evidence, e.g. location of hydrocarbon reservoirs, hydrocarbon properties and bitumen paragenesis	

2. Petrographic assessments of rank

Petrographic characterization of organic matter in coals and sediments can involve the integrated use of transmitted-light, reflected-light and fluorescence microscopy. Each of these methods contributes different data that, when combined, will allow an assessment of the quality, type and maturity of the organic matter, but not necessarily over the entire rank range.

(a) *Transmitted light*

Examination of coals in transmitted light requires the preparation of thin sections. This preparative method, which is difficult, coupled with the rise in absorption and therefore decreasing translucency of organic matter with increasing rank, means that sections of coals higher than coking rank cannot be made sufficiently thin to transmit light. These factors, coupled with the failure of transmitted-light microscopy to allow a ready distinction between liptinitic constituents and mineral matter, has led to the almost exclusive use of reflected-light microscopy for rank determination of coals. With lower rank organic sediments, however, valuable information about maturity may be gleaned through transmitted-light studies, a prerequisite being the concentration of the kerogen component by using the standard palynological technique of digesting the mineral matrix with hydrochloric and hydrofluoric acids. The separated organic material is then strewn onto a glass slide and viewed in transmitted light for 'kerogen typing' on a qualitative or semi-quantitative basis. The morphology and translucency of the components allows the distinction between structured humic, liptinitic material and amorphous (often sapropelic) organic matter. The juxtaposition of microfossils and tissue-remains on the slide means that transmitted-light microscopy is also well suited to environmental interpretations and the construction of palynofacies.

Information on maturity is gained by observing the colour of the organic matter. With increasing maturation, there is a progressive darkening of the kerogen, although the colour of the various components at a given maturation level may differ. For this reason, observations are restricted to spores and pollen assemblages because their size and translucency generally remains uniform. Palynomorphs are initially pale yellow, but with increasing organic metamorphism they become successively deep yellow, orange, red and finally black. This thermally induced discoloration has been the foundation of a number of semi-quantitative maturation scales (see, for example, Barnard *et al.* 1976; Batten 1976; Correia 1967, 1971; Correia & Peniguel 1975; Staplin 1969, 1977). Attempts to quantify spore colour have been undertaken by Grayson (1975), who used a photomultiplier linked with a fibre-optic probe to measure the translucency of palynomorphs and by Smith (1983), who has produced spectral correlations between sets of standards used by Barnard *et al.* (1976) Batten (1976) and Staplin (1969, 1977).

Care must be taken with transmitted-light determinations in successions penetrating unconformities and red beds, because these frequently contain thin and bleached palynomorphs which yield anomalously low maturation indices. High values are derived from thick, reworked or stained assemblages, the latter often found in source and reservoir rocks. Although the perception of colour is highly subjective, an advantage of the spore-coloration method over other parameters such as vitrinite reflectance is that changes in palynomorph colour over a given temperature range are more rapid than is the increase in vitrinite reflectance in the lowest part of the rank range. Furthermore, the composition of sporopollenin is closer to that of hydrocarbon-rich material than is vitrinite and thus liptinite may therefore be better suited as a hydrocarbon maturity indicator, although further investigation is necessary.

(*b*) *Reflected light*

Reflected-light microscopy finds its greatest application in the differentiation of the humic constituents vitrinite and inertinite and in assessing the rank (maturity) of samples through measurement of the reflectance of the vitrinite components. The macerals respond differently to coalification, initially showing a divergence and then a convergence of optical properties with increasing rank (figure 2). The reflectance of vitrinite, however, increases more uniformly through the rank range than does the reflectance of any other maceral. The uniform reflectance increase of vitrinite and its persistence over a wide range of organic metamorphism, its distribution in many facies and its unwillingness to suffer retrograde alteration, in addition to the ease, accuracy and precision of the measuring procedure, have made vitrinite reflectance probably the most satisfactory and certainly the most widely used optical parameter for determining the rank of coals and organic matter in sediments. Yet a further asset is the simplicity of sample preparation. Rock chips or organic matter concentrates are embedded in

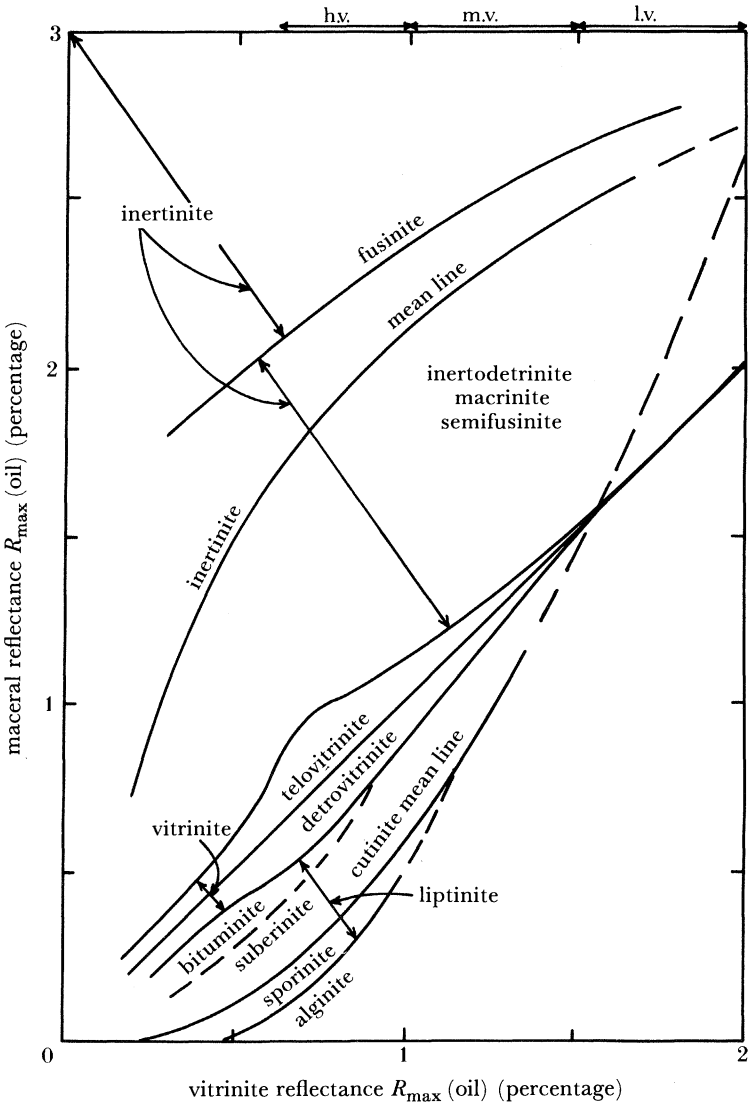

Figure 2. Relation between the reflectances of individual macerals and maceral groups and the reflectance of vitrinite (see figure 1). (Data from Smith & Cook 1980.)

synthetic resin and then ground and polished, the resulting high-quality surface being ready for examination by using oil-immersion objectives.

Vitrinite is usually represented as a pseudo-crystalline material, normally possessing a uniaxial negative indicatrix with the optic axis perpendicular to the sedimentary bedding. Under these circumstances:

(i) a surface cut perpendicular to the bedding will display maximum reflectance when the incident light is polarized parallel to the bedding and a true minimum reflectance when polarized perpendicularly to it;

(ii) a surface cut parallel to the bedding is isotropic and displays maximum reflectance in all directions, and

(iii) an oblique-section cut will show a true maximum parallel to the bedding and an apparent minimum perpendicular to it. With coal samples the maximum reflectance is obtained by rotating any coal particle until the stratification is parallel to the plane of vibration of the polarized incident light. For dispersed organic matter in sediments the small size of the vitrinite particles means that they often tend to move away from the microscope measuring aperture on rotation of the microscope stage, which has led to the use of 'random' or 'average' reflectance when readings are taken; i.e. by using a fixed-stage position with the polarizer out of the optical train (random), or in the optical path (average). The distinction between random, average or maximum reflectance measurements is particularly important at higher rank levels when vitrinite becomes markedly anisotropic and when only maximum reflectance should be used (or on occasions minimum reflectance; see, for example, Ragot 1977).

Reflectances are calculated by comparing the light intensity reflected from the unknown sample, as shown by a digital or analogue voltmeter or pen recorder, with that reflected from a standard of known reflectance. Substitution of the relevant values into a simple equation allows the calculation of reflectance. Unless otherwise noted, the term 'reflectance', when used here, refers to reflectances measured at a wavelength of 546 nm in an immersion oil with a refractive index of *ca.* 1.520 at 20 °C.

(*c*) *Bireflectance*

The rise of reflectance with increasing coalification can be correlated with the increasing condensation and aromatization undergone by the vitrinite molecular units principally in response to thermal stress. Physical modification of vitrinite occurs as a result of the increase in confining pressure exerted by overlying strata. On a molecular level the pressure increase promotes the progressive alignment of the aromatic lamellae to give a preferred orientation which is reflected in the development of optical anisotropy. A quantitative evaluation of this anisotropy is given by measuring the bireflectance, determined by taking the numerical difference between the maximum and minimum reflectances, preferably on an oriented surface. This parameter also increases with rising rank, reflecting a higher degree of molecular ordering within the vitrinite matrix.

(*d*) *Refractive and absorptive indices*

Although vitrinite reflectance is perhaps the most satisfactory single parameter for defining coal rank, reflectance *per se* is not an inherent property of organic matter because its value depends on the properties of the measuring medium. The fundamental optical parameters are the refractive index and the absorption index (or absorption coefficient), which can be derived from reflectance measurements made in two media of different refractive index. In certain circumstances these parameters can be helpful in allowing an understanding of the molecular structural changes taking place in organic matter in relation to thermal and tectonic events.

(*e*) *Fluorescence and emission spectra*

Fluorescence microscopy permits rapid identification of liptinitic material in the lower part of the rank range and is a useful complement to vitrinite reflectance measurements, which are less well suited to the discrimination of highly hydrogenated matter. Reflectance and fluorescence parameters overlap considerably in the lower rank scale, the reliability of one group improving as the other falls.

Liptinitic materials fluoresce through exposure to ultraviolet or blue light. When their emission spectra are plotted, there is a shift of the spectrum peaks towards longer wavelength with increasing rank. The colour and intensity of the emission also change with increasing rank. Sporinite fluorescence has hitherto proved to be the most reliable rank estimator in fluorescence studies, showing a progressive change in colour from green through yellow to orange and finally to red with rising rank, after which fluorescence in the visible spectrum ceases. Attempts have been made to quantify emission spectral data, for example the wavelength of maximum intensity, the half-peak width and a 'red:green' spectral quotient. Teichmüller (1982) has reviewed fluorescence investigations of vitrinites and liptinites in relation to rank and coking behaviour and concludes that fluorescence parameters can be used up to a vitrinite reflectance level of $R_{\max}(\text{oil}) \approx 1.5\%$.

(*f*) *Textural properties*

The textural features developed in vitrinites of certain rank as a consequence of rapid heating through igneous activity can afford a valuable indication of rank within a succession before pronounced thermal alteration occurs. When heating is sufficient to carry vitrinites and certain other macerals through their decomposition zones, this process is called carbonization to distinguish it from coalification, which takes place at lower temperatures. Vitrinites in the medium- to low-volatile bituminous coal range, particularly with oil reflectances in the range of *ca.* 1.2–1.5% ('highly coking' vitrinites), undergo extensive devolatilization and condensation reactions with concomitant fluidization at appropriate temperatures. In this state, the enhanced molecular mobility promotes a much increased degree of ordering of the aromatic lamellae, which is expressed by the development of coarse granular to flow mosaic textures in these vitrinites. The texture forms through a 'mesophase' consisting of optically anisotropic droplets from an isotropic matrix (Brooks & Taylor 1965). Each droplet represents a sphere of aromatic lamellae with the same orientation. With increasing temperature, the droplets coalesce to form a granular texture (a 'mosaic'), with juxtaposed units lying in optical discontinuity.

Vitrinites in coals or sediments of medium-volatile bituminous rank with oil reflectances of *ca.* 0.80–1.20% do not become sufficiently fluid to allow the development of a well formed pronounced mosaic texture. As best, a poor to fine granularity may form. Even 'caking' vitrinites do, however, become sufficiently fluid to allow the agglomeration of particles.

Vitrinites, other than those referred to above, do not form mosaics under 'normal' heating conditions of igneous activity. The rigidity of the cross-linked aromatic structures at higher ranks (semi-anthracites and beyond) is inimical to fluidization, while the limited preferred orientation of aromatic lamellae at lower ranks also hinders the attainment of a highly ordered molecular state. The reflectance boundaries for the onset of fluidization in coking and caking vitrinites are not rigid, because mosaics can develop in vitrinites encompassing a wider rank range when subjected to high rates of heating (Goodarzi & Murchison 1978).

Liptinitic material may also show mosaic structures when heated. Although the initial reflectance of liptinitic macerals is lower than that of the vitrinite of the same coal, the higher hydrogen contents of these macerals promote fluidization and often lead to the formation of much larger mosiac units after carbonization.

(*g*) *Selection of parameters for rank assessment*

Table 3 shows that vitrinite reflectance is a variable that can be used over a wide rank range and one that is relatively insensitive to type effects and to interference from mineral matter. Other advantages of vitrinite reflectance measurements were noted earlier (§2*b*). Figure 3, based on data from Kantsler *et al.* (1978) and Smith & Cook (1984), illustrates the variation

TABLE 3. ASSESSMENT OF RANK

major methods	selectivity in avoiding effects of:		precision at different levels of rank			
	sample type	mineral matter	low $R_v = 0$–$0.5\,\%$	medium $R_v = 0.5$–$1.3\,\%$	high $R_v = 1.3$–$4.0\,\%$	very high $R_v = 4.0\,\%$
light microscopy						
reflectance (oil)	high	high	moderate–high	high	high	high–moderate
translucency (spores, pollen)	high	high	moderate	high–moderate	low–zero	zero
fluorescence (liptinite)	high	high	moderate	moderate–low	zero	zero
X-ray diffraction	low	high	zero	low	low–high	high
chemical analysis (proximate and ultimate)	low	low (except for atomic ratios)	highly variable depending on parameter, but only carbon high throughout rank range			
organic geochemical methods	low	low–high	typically low except for certain biomarkers	moderate for some parameters	low except for T_{max} of coals	very low to zero

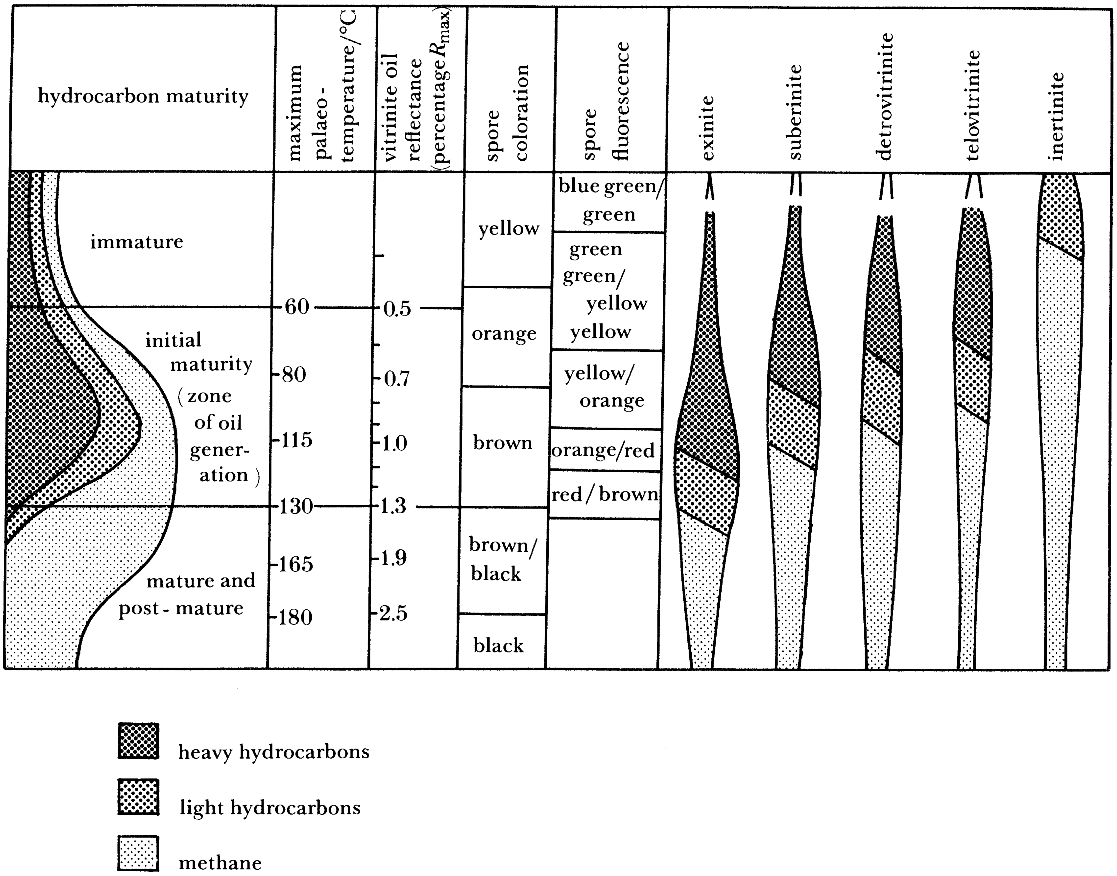

FIGURE 3. Generalized zones of petroleum generation and an approximate correlation with maximum palaeotemperatures, vitrinite reflectance, spore coloration and fluorescence. The maximum widths on the generation envelopes are not to scale. (After Kantlser *et al.* 1978; Redrawn from Smith & Cook 1984 with the permission of the Australian Petroleum Exploration Association Limited.)

of several microscopical parameters over a restricted portion of the rank range. The parameters are related to palaeotemperatures and to the generation of hydrocarbons, including the probable times when heavy and light hydrocarbons as well as methane gas are generated by individual macerals or maceral groups. The use of petrographical parameters other than virtrinite reflectance to assess rank or maturation has been mainly in the province of organic petrologists working in the petroleum field. There is still, however, a considerable range of coalification (vitrinite reflectance R_{max}(oil) $> 2.5\%$) where vitrinite reflectance and related optical parameters are virtually the only quantitative microscopical parameters available for the measurement of rank.

Other variables used to assess rank, of which there are many, tend to have greater limitations than reflectance, although some are useful in certain parts of the rank range, such as moisture content. Total carbon content, a widely used rank parameter for coals in the past, is strongly dependent upon corrections made for moisture and mineral matter contents; it is probably also more sensitive to type effects and is more restricted in the kind of sample that can be used. Where a number of rank-sensitive variables can be used simultaneously to assess rank, this practice affords the possibility of regarding rank as a complex response to a number of different factors rather than as a simple response to a single factor.

3. The influence of temperature, time, pressure and stress on coalification

The temperature level and duration of exposure to maximum temperature (most probably at the time of maximum burial) are widely regarded as the dominant influences in the coalification process. There is no doubt about the central role of temperature in inducing rise of coalification, but the effect of time has almost certainly been oversimplified. The influence of other factors such as the thermal conductivity of sediments and different forms of pressure has probably received insufficient consideration, but as the results of an increasing number of investigations are reported, their greater importance is becoming evident.

(a) *Temperature and time*

The reflectance attained by vitrinite (or other macerals) is regarded as being principally governed by the length of time to which the vitrinite was exposed to maximum temperature. It is thus not surprising that many correlations between vitrinite reflectance and palaeotemperature have been attempted. Crucial to such correlations is an accurate knowledge of the burial history of the sedimentary succession. If this is known, then estimates of the palaeogeothermal gradient and the maximum temperatures to which the vitrinite has been exposed are possible, by using the determined coalification gradient based on reflectance measurements. The higher the coalification gradient, the higher the palaeogeothermal gradient will have been. This latter gradient depends principally upon heat flow and upon the thermal conductivity of the sediments in the section. Thermal conductivity can obviously have an important bearing on reflectance because the geothermal gradient is inversely proportional to the thermal conductivity.

The more satisfactory correlations between vitrinite reflectance and palaeotemperature have been made for the younger Tertiary basins. This is understandable because estimates of the duration of erosional breaks, thicknesses of missing strata, rates of sedimentation, maximum depth of burial and other relevant details can be made with greater confidence than for older buried sediments. Present-day geothermal gradients in such situations are also more likely to be representative of relatively recent palaeogeothermal gradients. Even when geological control is favourable, however, reflectance–temperature correlations differ considerably (see, for example, table 4, based on data from Ammosov *et al.* (1975), compared with the data of figure 3). Ammosov & Utkina (1975) suggest that time has an important influence on reflectance–temperature correlation: Neogene samples consistently display lower reflectances at the same depth than do Palaeogene and Cretaceous samples of the same area.

Despite the widespread enthusiasm to produce temperature–time correlations, caution must be exercised. Figure 4 illustrates the variation of vitrinite reflectance in two deep petroleum exploration boreholes. The sections for both wells range from Cretaceous to Permian in age, but well A (left ordinate) is from the Perth basin with a low geothermal gradient, whereas well B (right ordinate) is from the Cooper basin with a much higher gradient. At total depth the vitrinite reflectance for well A is just over 1 %, while that for well B reaches approximately 5 % at 3812 m. The bottom-hole well temperatures were 120 and 216 °C respectively, but the well temperatures at the 1 % reflectance level are similar for both wells, even although the ages of the sequences are quite different at this level (Permian in well A, Jurassic in well B). Although both of these wells occur in Australian basins with relatively simple sedimentation and

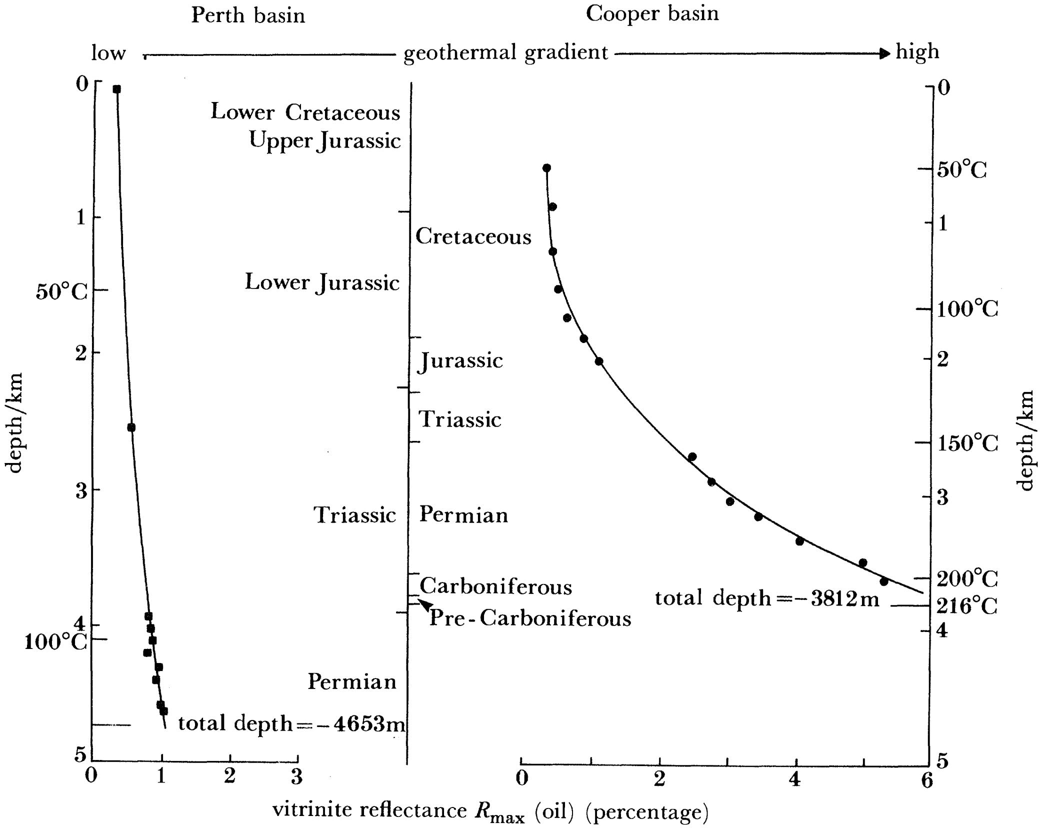

FIGURE 4. Variation of reflectance with depth in two petroleum exploration boreholes from different Australian basins with similar stratigraphic successions but different present-day geothermal gradients.

TABLE 4. MINIMUM BURIAL PALAEOTEMPERATURES REQUIRED TO ATTAIN A GIVEN VITRINITE REFLECTANCE LEVEL†

vitrinite reflectance R(oil) (percentage) (from R(air))	palaeotemperature/°C (minimum)
0.48	100
0.59	125
0.72	145
0.86	165
1.00	180
1.16	195
1.42	210
1.50	220
1.70	230
1.92	235
2.14	240

† From Ammosov *et al.* 1975.

structural histories, careful analysis of a large number of wells in these basins suggests that the thermal histories for both sequences have been relatively complex (Cook & Kantsler 1980; Kantsler *et al.* 1984). Thus, present-day temperatures are only one of the factors controlling the rank distribution. Even relatively young basins typically show complex thermal histories (Smith & Cook 1984), so that the relation of rank to temperature can often only be shown in a generalized manner.

Many attempts have been made to determine temperature–time relations by using samples of known rank and making assumptions about the burial and thermal histories of a basin or a number of basins. The approaches used in 'thermal modelling' vary considerably. Karweil (1956) measured rate constants associated with coalification and correlated these with the presumed geothermal history of the sequence or sequences. Bostick (1973) modified and improved on Karweil's work by correlating temperature and time with reflectance as a measure of coalification, with the recalibration being partly controlled by data from artificial coalification experiments and from contact-altered zones near igneous intrusions. Lopatin (1971, 1976) assumed the form of the rate-determining equation for coalification and then correlated temperature–time integral values for a number of basins with 'known' geothermal histories. More recently, Waples (1980, 1981) has evaluated Lopatin's method. Waples maintains that there is generally good agreement between Lopatin's 'time–temperature index' of maturity and other geochemical–petrological parameters, particularly vitrinite reflectance, in predicting, for example, the timing of oil generation, although he also admits some discrepancies.

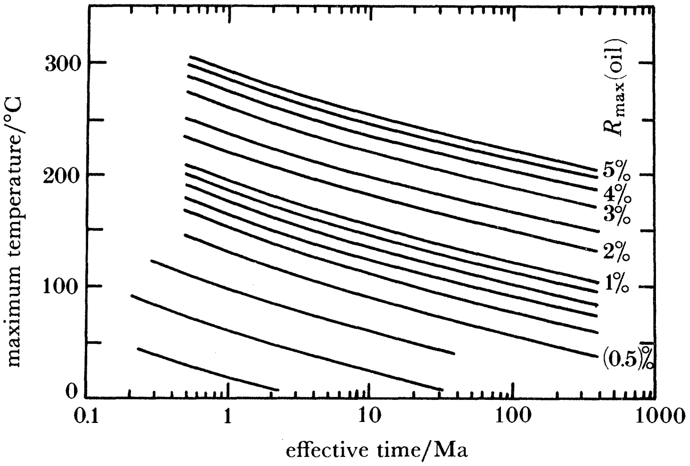

FIGURE 5. A modified Karweil diagram allowing the determination from reflectance measurements of the maximum temperature to which organic matter (vitrinite in this case) has been exposed if the age of the sediment is known. (Redrawn, with permission, from Bostick *et al.* (1979), with acknowledgement to A. Hood of Shell Oil.)

Figure 5 presents a version of the Karweil–Bostick nomogram (Bostick *et al.* 1979), replotted with temperature and time as orthogonal axes and vitrinite reflectance contoured on the diagram. At low temperatures, this variable is the controlling factor, but as temperature increases, time becomes of greater importance. However, geological time, even over very long periods, cannot compensate for low temperatures because a certain minimum temperature is required to achieve the activation energy necessary to initiate chemical coalification reactions. Lopatin (1976) suggests that this minimum temperature is 65 °C, but at this temperature level, long periods of time will still be necessary to reach even low levels of coalification. The time for rank increase to high levels can be radically shortened if temperatures are high enough to overcome large activation energies.

The basis for the Lopatin and other models is the Arrhenius equation, which consequently demands that certain assumptions are made about the level of activation energy necessary at the start of coalification, a topic about which there has been widespread discussion. The matter is, however, more complicated than a simple decision on the actual value of the activation energy that is initially substituted in the Arrhenius equation. Tissot & Espitalié (1975) have proposed a mathematical model for kerogen degradation, drawing attention to the necessity for knowledge of not only the level of activation energy required, but also the distribution of activation energies in relation to kerogen composition during the course of the coalification process. Figures 1 and 2 make it clear that the macerals coalify at varying rates at different stages of the coalification process. Activation energies therefore must be not only rank dependent, but highly type dependent as well; reaction rates will be similarly governed by both type and rank. A model of high accuracy will require a high level of sophistication and data input.

There are models that do not depend upon the Arrhenius equation. Buntebarth (1978) has described an empirical method in which the palaeogeothermal gradient is calculated from vitrinite reflectance, a reconstructed depth of maximum burial and the duration of burial of the organic matter. Within Cainozoic basins of southern Germany Buntebarth (1979) also found that the square of the mean reflectance was related to a function of the temperature gradient and to the burial history. However, great care is necessary, as with other models, in establishing the 'subsidence curve' for burial history from depth and time data from boreholes.

A substantial number of contributions using Buntebarth's method have been made by German petrologists and geologists over the past five years. Thus, a high palaeogeothermal gradient with an extensive heat source at depth was established by Buntebarth *et al.* (1979) in the Urach district of south west Germany. More recently Buntebarth & Teichmüller (1982) have estimated the palaeoheat-flow density of the same district – the temperature gradient is proportional to the heat-flow density – and have found that it is similar to present-day heat flow. It is concluded that the heat source was in existence before uplift in the Cretaceous took place. Buntebarth *et al.* (1982*a*) have also shown by examination of a large number of boreholes from the Ruhr basin (the molasse on the southern margin of the Subvariscan foredeep), that high thermal gradients (60–80 °C $\mathrm{km^{-1}}$) existed during the Westphalian, implying a much thinner crust in late Carboniferous times than at present. In the structural analogous northern foredeep (the molasse trough) of the Alps, geothermal gradients are low (*ca.* 23 °C $\mathrm{km^{-1}}$), but it is known that the crust in the S1 Alpine foredeep is especially thick, probably because of subsidence of the upper mantle within the subduction zone, thus accounting for the low levels of coalification in the molasse. Buntebarth (1983) has also discussed the palaeogeothermal history of the Saar-Nahe basin (the back deep of the Rhenish Variscan), in which the coalification gradients (Teichmüller *et al.* 1983) are rather similar to those of the foredeep (Ruhr basin). His method has also been applied to examine the relation between coalification gradients and the probable temperature distribution during the cooling of a probable Permo–Carboniferous basic intrusion, almost centred below Krefeld, identified on the basis of magnetic anomaly distributions (Buntebarth *et al.* 1982*b*).

Buntebarth's modelling approach certainly seems to have advanced our knowledge of past temperature distributions and heat flows in the German area particularly. As with other models, it is dependent upon the quality of the data input. Thus, palaeotemperature and palaeoheat-flow determinations are dependent upon the quality of the vitrinite reflectance data. A discussion of these and other points can be found in Lerche *et al.* (1984). Guidish *et al.* (1985) believe that vitrinite reflectance is the most satisfactory method available at the present time to determine heat-flow history. These authors have also discussed several proposed geological models for basin formation in which predictions for both heat flow and subsidence with time vary, so much so that the models disagree even on the sign of the derivative of heat flow. There is therefore a strong case for using independent estimators of heat flow. Guidish *et al.* feel vitrinite reflectance to be the most important and they are currently testing how well the geological models fit available vitrinite reflectance data.

Finally, little has been said about the behaviour of bireflectance in response to rise of temperature. Bireflectance is a parameter that has not received the attention it warrants in relation to different thermal and stress environments in the crust. High values of bireflectance can generally be expected where organic sediments have been affected by thermal metamorphism. Thus, Jones & Creaney (1977) have reported values as high as 0.9 for the ratio of bireflectance to the maximum reflectance of thermally metamorphosed vitrinites in coals of the Alston Block, northern England. Raymond & Murchison (1985) have obtained similar data for vitrinite particles in sediments heated by a thick quartz dolerite sill in the Rashiehill borehole in the Midland Valley of Scotland. In both these cases, despite the very high degree of ordering, the vitrinite maximum reflectance did not approach that of graphite ($R_{\max}(\mathrm{oil}) \approx 17.80\,\%$ at 546 nm) (Kwiecinska *et al.* 1977). Optical strain shown by the organic constituents suggests imposition of stress as well as strong heating, despite the undisturbed nature of the strata. The heating rate, which increases the degree of ordering as it rises (Goodarzi & Murchison 1978), may have played a part in both phenomena. Generalized relations between the reflectance and bireflectance of thermally metamorphosed coals have been produced (Chandra 1963, 1965*a*).

(*b*) *Static pressure*

Pressure has been widely regarded by many geologists as having little influence on the coalification process. Its retarding role has been widely stressed, but few attempts to quantify its effects have been made. Huck & Patteisky (1964), in artificial coalification experiments, concluded that coalification was delayed by high mechanical pressures; Bostick (1973) is dismissive of pressure as playing more than a minor part in relation to the influence of temperature and time; while Davis & Spackman (1964), although acknowledging pressure as an important secondary factor in their artificial coalification experiments in retaining water vapour and volatiles within the system for reactions, state that no differences could be observed in the infrared spectra of woods heated at different pressures over the same wide temperature range. Chandra (1965*b*) found that pressure raised reflectance in his experiments and both he and Hryckowian *et al.* (1967) saw bireflectance changes with increasing pressure, although the results were not simple (figure 6).

To regard pressure purely as having a retarding effect on coalification is almost certainly an oversimplification – overburden pressure does, of course, produce orientation of the aromatic lamellae to induce reflectance anisotropy. The distinction between ‘physical’ and ‘chemical’ rank was recognized by Dulhunty (1954), who identified variables that are especially sensitive to pressure (such as moisture content) from those more strongly influenced by temperature level and duration of heating (such as carbon content). The relation between these physical and chemical processes, however, has also to be recognized, but for bireflectance, both physical and chemical aspects of rank imposition are involved.

Although reasonable correlations of reflectance against present-day temperatures have been obtained (see, for example, Teichmüller 1979), there are anomalies for which explanations must be found. McTavish (1978) shows that the explanation may not lie solely in the difference of past geothermal conditions from the present. He acknowledges that while the temperature–time

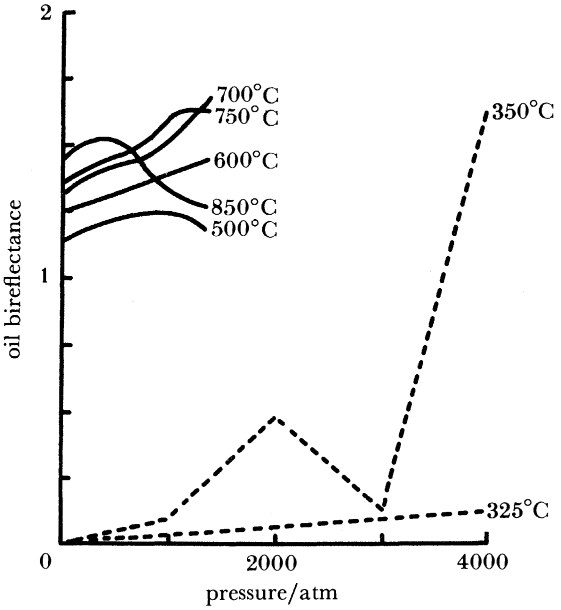

Figure 6. Variation with pressure and different preparation temperatures in laboratory experiments of the oil bireflectances of a high-volatile bituminous coal and an anthracite. Data from Chandra (1965 *b*) shown as broken line; Hryckowian *et al.* (1967) shown as solid line. 1 atm = 101 325 Pa. (Redrawn from Murchison (1978) with the permission of Economic Geology Publishing Co. and Academic Press, Inc.)

factor is of importance in coalification, high formation pressures can retard the progress of vitrinite coalification and these may well be a significant factor in determining the course of vitrinite reflectance levels below $R_{\max}$(oil) ≈ 1.50%. Furthermore, a much improved mean vitrinite reflectance–temperature correlation is obtained (for offshore wells from northwest Europe) if the behaviour of pore pressure is taken into account; the geostatic pressure is the sum of the pore pressure and the effective overburden pressure. In some sections samples used for vitrinite reflectance measurement may have come from overpressured sections, i.e. where pore pressures are abnormally high; in others the vitrinite has been taken from a sediment with normal pore pressures. McTavish (1978) maintains that differing levels of pore pressure affect the development of vitrinite reflectance because of the influence pore pressure has upon thermal conductivity, a factor previously shown to affect the progress of vitrinite reflectance (Teichmüller & Teichmüller 1968; Damberger 1968; Jones *et al.* 1972). He states that in overpressured shales, thermal conductivities will be abnormally low as such shales will act as heat insulators compared with normally pressured shales, which are heat conductors. He also suggests that on a geological scale the time factor is of little consequence in relation to these particular data. Further development of this approach with the use of optical–geophysical data from the younger sedimentary basins would be useful.

(*c*) *Stress and the development of biaxicity*

When reflectance measurements are made under the appropriate optical conditions by using plane polarized light, most vitrinites display anisotropy. The aromatic molecules of the vitrinite are not randomly ordered and they are widely assumed to have taken up an arrangement so that the reflectance anisotropy is in the form of an oblate spheroid with its short axis normal to the bedding (i.e. uniaxial negative so that the maximum reflectance lies in the isotropic plane of the bedding; but see §2*b*).

Departures from this condition are becoming increasingly noted. Initially the anomaly appeared to be confined to high-rank coals or organic sediments that were associated with regional stress fields and it is likely that a preponderance of cases will continue to arise in such situations (see §5). Dahme & Mackowsky (1951) reported the existence of significant bireflectance in the plane of the bedding of anthracitic vitrinite. In a more extensive study, Cook *et al.* (1972*a*) reported similar findings which were supported by further optical data from a British meta-anthracite (Cook *et al.* 1972*b*), suggesting that the vitrinite reflectances had assumed an oblate triaxial ellipsoid with an elliptical section in the plane of the bedding. What were regarded as exceptional cases of departures from the uniaxial condition in lower-rank bituminous coals (see, for example, Jones *et al.* 1973) seem now to be much more widespread. Indeed Stone & Cook (1979) maintain that the biaxial condition is the norm for the optical properties of vitrinite rather than the exception. They have also suggested that if triaxial stress during some stages of coalification has imposed biaxial properties as a result of asymmetric development of the molecular structure, then vitrinite reflectance measurements are a potential method of determining strain orientations. Hower & Davis (1981) have also made use of biaxial optics of vitrinite as a stress indicator in Pennsylvanian anthracites and similarly Levine & Davis (1984) have employed reflectance anisotropy of lower rank coals from the Broad Top Coal Field, Pennsylvania, as a finite strain marker. Although Hevia & Virgos (1977) have argued that when vitrinites are biaxial, measurements of mean maximum reflectance will be invalid, the departures so far reported from the uniaxial condition are known to be relatively small and therefore mean maximum reflectance can be countenanced.

Severe stress must also be imposed on organic matter in the neighbourhood of large thrusts or shear zones and it might be expected that striking optical changes would occur under these circumstances. The evidence produced so far is equivocal. Bustin (1983) reports anomalously high reflectances of vitrinites arising only from very thin films within the shear zones of thrusts in the Rocky Mountains and little, if any, increase in reflectance elsewhere that would not be expected during the course of normal organic maturation. Bustin concludes that there is little evidence for extensive frictional heating, but states that temperatures between 350 and 650 °C were developed locally during thrusting. In contrast, there is other evidence of graphitization due to shearing at unexpectedly low temperatures. Taylor (1971) suggests a temperature as low as 300 °C for graphitization in the presence of shearing and refers to work by Hamilton *et al.* (1970) in which graphitization of *Glossopteris* leaves must have occurred at temperatures below *ca.* 650 °C, the probable intrusion temperature of an adamellite that provided the heat for the graphitization. Taylor (1971) suggested that the shear might be on a molecular scale. Teichmüller & Teichmüller (1981) comment on the stepwise progression of optical properties in the coalification range above meta-anthracitic level. Further discussion of graphitization will be found in §5.

4. Timing of coalification in relation to temperature and tectonics

Optical properties (notably reflectance) and textural properties are now most helpful in elucidating the relation between the occurrence of coalification and thermal and structural events in buried sediments. Simple bulk physical and chemical properties of coals served a similar purpose before optical parameters were thoroughly established. A frequently quoted early example, illustrating the timing of coalification in relation to folding, is given by Böttcher *et al.* (1949), who showed that 'isovols' (lines of equal volatile-matter yield) of the Sonnenschein seam in the Bochum megasynchline of the Ruhr, broadly ran parallel with the folds: coalification was completed before the Asturian folding although, as a result of differential subsidence, coals in the megasynclines became slightly higher in rank than in the mega-anticlines. German workers continued to be assiduous in examining such relations. For example, Damberger *et al.* (1964) illustrated post-coalification thrusting in the Saar through a pronounced interruption of coal-seam calorific values with depth in the coalification curve of the Krughütte borehole.

Optical properties of organic matter now allow a greater refinement in the relative timing of geological events in relation to coalification. Examples of the disturbance of reflectance trends downhole by faulting and thrusting, or by major erosional breaks in sedimentary successions, are numerous. A recent paper by Pearson & Grieve (1984) illustrates the timing of coalification in relation to faulting , thrusting and folding. Following the work of Teichmüller & Teichmüller (1966), figure 7*a* shows the relation of isoreflectance lines to fold patterns in the three situations

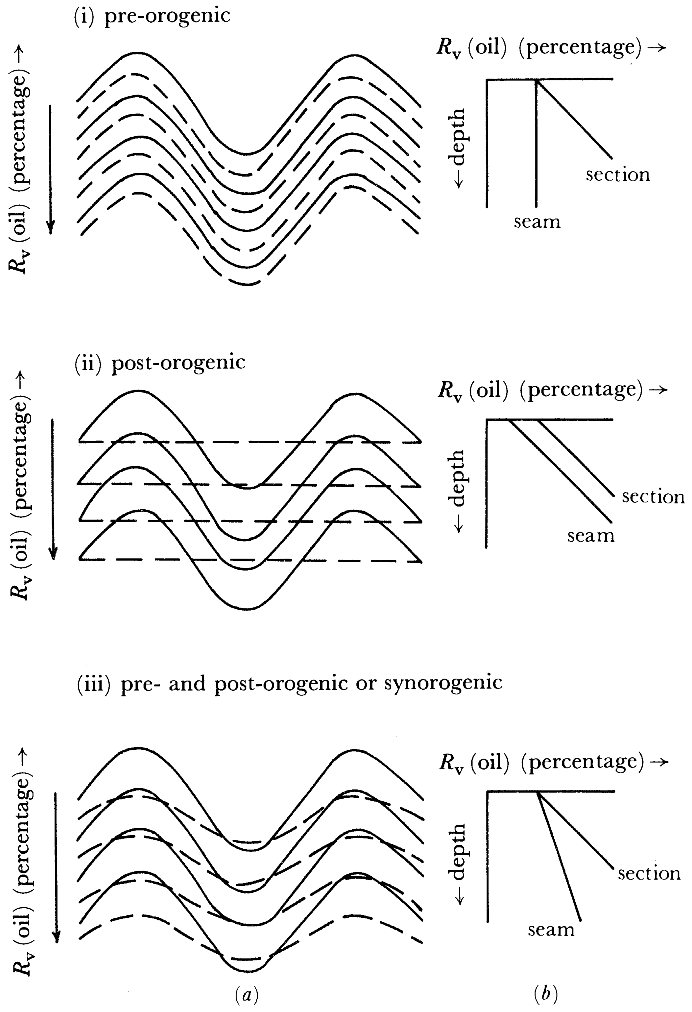

FIGURE 7. Timing of coalification in relation to orogenesis: (*a*) lines of equal reflectance in relation to folding and (*b*) reflectance variation with depth within seams ('seam') and in borehole sections penetrating seams at right angles to the sedimentary bedding ('section'). Pre-, post- and total coalification gradients can be calculated from these relations. Broken lines show isoreflectance lines. (Redrawn from Pearson & Grieve (1985), with the permission of the Canadian Institute of Mining and Metallurgy.)

when coalification is pre-orogenic, post-orogenic and either pre- and post-orogenic or synorogenic, the latter being more likely. Figure 7*b* illustrates the relation between the variation of reflectance within a single seam ('down-dip rank gradient' of Hacquebard & Donaldson 1970) and the reflectance variation that occurs in a stratigraphically vertical succession ('total rank gradient' of Hacquebard & Donaldson 1970) in the same tectonic situations. If the relation of figure 7*b* (iii) holds, the amount of coalification that occurred before and after folding can be calculated. With sufficiently good borehole control, pre-, post- and total coalification gradient maps can be prepared for an area. While clearly simpler for a coal-seam situation, in stratigraphically well controlled successions where reflectance measurements are being used for maturation purposes, gradient maps of this kind can be prepared for successive stratigraphic horizons and compared with temperature data.

In severely folded and overthrust successions, studies of the relations between structural events and coalification will have a greater chance of success in the less eroded mountain regions of the world, as in the Rocky Mountains and their Inner Foothills and in the intermontane belt of the Canadian cordillera (see Hacquebard & Donaldson 1974; Bustin 1984; Pearson & Grieve 1984). In the Alps, Frey *et al.* (1980) have demonstrated through inversion of the reflectance data the transport of the Axen nappe with higher reflectance values to a position above the North Helvetic Flysch, which contains vitrinite particles of much lower reflectance levels. Considerable precision in determining the sequence of thermal and structural events is possible in these younger mountain ranges. Reutter *et al.* (1983) identified both pre- and post-orogenic thermal events in the northern Apennines. However, the principal coalification was shown to be late syn-orogenic, occurring after the emplacement of the nappes in the nappe pile (Miocene Apenninic orogeny), but earlier than the youngest thrusting and tensional structures that affected the internal zones of the mountain chain.

Precise coalification–tectonic timing relations have by no means been solely confined to Tertiary orogenic zones. For example, Kalkreuth (1979), building on work by Wolf (1972) in the northern part of the Rhenish massif, showed through the use of trend surface analysis of reflectance data that in the Ostsauerland anticline (eastern Rhenish massif), pre-orogenic coalification had occurred to the west of the Altenbüren disturbance zone; while to its east, the coalification was syn- and post-orogenic with the isorank lines running transverse to the tectonic structures. Teichmüller & Teichmüller (1979) have demonstrated pre-, syn- and post-orogenic coalification within the Venn anticline (Westphalia), which contains semi-graphites in the Lower Emsian of its southern limb, but a much lower rank level (*ca.* $R_{\max}(\text{oil}) = 2.5\,\%$) to the north in the Lower Emsian of the 'north–south' zone crossing the Eifel.

In many of the studies where successful relations between imposition of coalification and occurrence of folding have been established, high ranks have been reported (see also §5). The optical properties of the vitrinites have almost certainly become sensibly biaxial, but this has not prevented an accurate determination of either the rank distribution or the tectonic–coalification relation. Indeed the biaxicity can be usefully employed in establishing such relations. Levine & Davis (1984) have shown through reflectance measurements on vitrinites of coals of the Broad Top Coal Field, Pennsylvania that oblate biaxial indicatrices are associated with gently deformed strata, while prolate indicatrices are associated with the more intensely folded strata. These indicatrices are elongated parallel to the fold axes and are the result of strong lateral compression; they display consistent orientation regardless of structural dip. The conclusion from the structural–optical evaluation was that maximum coalification (and thus maximum burial) occurred after most of the folding was completed.

The combined use of optical properties and textural features of organic matter in coals and sediments affords a valuable means of deciphering geothermal histories of areas, particularly when the background temperature gradients have been further influenced through igneous activity. Ridd *et al.* (1970), in a study of coals from the Harton borehole, Durham which penetrated three leaves of the quartz dolerite Whin Sill, described well developed granular mosaic textures in coals of that part of the succession close to the upper and middle leaves, but failed to observe such textures in the vicinity of the lower leaf. The conclusion was that the lower coals had attained a rank that was sufficiently high, before the emplacement of the Whin Sill, to preclude the formation of mosaic units characteristic of coals of caking and coking rank ($R_{\max}$(oil) ≈ 0.8–$1.7\,\%$) (see §2*f*).

This work was amplified in a regional assessment of optical properties of organic matter of the Alston Block, northern England by Creaney (1980), who established that the rank of much of the organic matter had been elevated to anthracitic levels during the Carboniferous. The concentric rank zonation, long known to exist on the Alston Block (Trotter 1954), was explained in terms of heat flow associated with postulated renewal of magmatic activity within the Devonian Weardale granite basement, but before the intrusion of the Whin Sill in Stephanian times (295 ± 6 ma) (Fitch & Miller 1967). The thermal overprint caused by emplacement of the sill induced the formation of mosaic units in vitrinites whose rank had been elevated to the coking coal rank range. Those vitrinites of higher or lower ranks could not become sufficiently fluid to develop mosaics, although those of higher rank invariably developed a severe strain anisotropy. The overprint also fixes the time of attainment of high rank by the organic matter to be before Stephanian igneous activity in the attenuated succession of the Alston Block, reflecting the influence of a geologically 'hot' basement, a conclusion that would not otherwise have been possible.

In the Midland Valley of Scotland, a different geothermal régime is evident. A feature common to both provinces, however, is the intrusion of a Stephanian sill complex, the Scottish Midland Valley sill being the consanguineous counterpart of the Whin Sill of northern England. An optical study of sedimentary organic matter from the the Rashiehill borehole, Stirlingshire (Raymond & Murchison 1985), has shown that some of the vitrinite in the succession had attained at least a caking rank ($R_{\max}$(oil) $\approx 0.8\,\%$) before the emplacement of a large sill in the sequence. Poorly formed mosaic textures developed occasionally in the thermal alteration zone of the sill. The results of carbonization experiments by Goodarzi & Murchison (1978) suggest that granular mosaic textures can be induced in vitrinites outside the 'normal' coking range of $R_{\max}$(oil) ≈ 0.8–$1.7\,\%$, under conditions of high heating rates, which must be assumed to exist in the contact zones of a large igneous body of the type present in the Rashiehill borehole.

5. ANCHIMETAMORPHISM AND LOW-GRADE METAMORPHISM

Although several examples of the application of reflectance in high-rank régimes have already been quoted in other contexts in this paper, stress must be laid on the diagnostic potential of reflectance measurements in the anchimetamorphic, low-grade metamorphic zones of buried sediments. Kisch (1974), summarizing earlier work in which he attempted to correlate different aspects of burial-metamorphic facies with coal rank, commented in particular on the replacement of kaolinite in argillites by illite, chlorite, or pyrophyllite or combinations of these (approximately correlating with anthracitic and meta-anthracitic rank levels) and the appearance of the laumontite and quartz assemblage and the albite replacement of analcime and quartz by albite in tuffs and feldspathic lithic rocks (correlating with bituminous-coal rank levels). In extending his work Kisch showed that bituminous-coal ranks could be broadly correlated with the zeolite facies (heulandite–analcime zone and then the laumontite zone); coking coals, anthracites and low-rank meta-anthracites with the prehnite–pumpellyite metagraywacke facies and then with the pumpellyite–actinolite schist facies (or the equivalent glaucophane–lawsonite schist facies); and the higher-rank meta-anthracites with the greenschist facies and the epidote–amphibolite facies.

In an addendum to his paper Kisch (1974) drew attention to the work on the coalification of the Palaeozoic sediments of the Rhenish massif through reflectance measurements by Wolf (1972) and studies in the eastern part of this same area by Weber (1972), in which the distribution of illite crystallinity and other criteria of low-grade metamorphism were examined. Kisch (1974) produced correlations of the reflectance with illite crystallinity based on this area (table 5). Since then, attempts have been made to refine these relations with varying degrees of success. For example, Frey *et al.* (1980) did not find a satisfactory general correlation between reflectance, illite crystallinity and fluid-inclusion data in their studies of regional metamorphism in the Helvetic Alps, although reflectance and illite crystallinity demonstrated similar trends through low-grade metamorphic zones: inverted metamorphism in nappe relations was identified, as well as the importance of post-metamorphic thrusting in the external parts of the Central Alps. The correlations require further refinement, but it is clear that the use of both will be continued and extended with identification of low-grade metamorphic zones (see, for example, studies by Deutloff *et al.* (1980) of the low-grade metamorphic rocks of the Lower Saxony tectogene underlain by the igneous bodies of the Bramsche and Vlotho massifs and the more recent investigation of the Permo–Carboniferous of the Saar-Nahe basin (Teichmüller *et al.* 1983).

TABLE 5. COMPARISON OF REFLECTANCE AND ILLITE CRYSTALLINITY VALUES IN THE NORTHEASTERN RHENISH MASSIF†

R_{max} (oil) (percentage)	R_{rel} (hb)	
> 6	< 115	low
5–6	130–115	↑
		illite crystallinity
4–5	150–130	↓
< 4	> 150	high

† From Kisch 1974.

Other authors have examined the relation between reflectance and metamorphic zones. Diessel & Offler (1975) related reflectance variations and changes in the X-ray diffraction patterns of coalified particles to metamorphic zones, commenting on the difficulty of polishing the organic matter so that its reflectance approached that of graphite when, on the basis of X-ray study, it clearly was approximately of this composition (Kwiecinska *et al.* 1977). These preparation problems were later largely overcome (Diessel *et al.* 1978) in a study of coalification levels in high-pressure schists of New Caledonia in which reflectance levels were also related

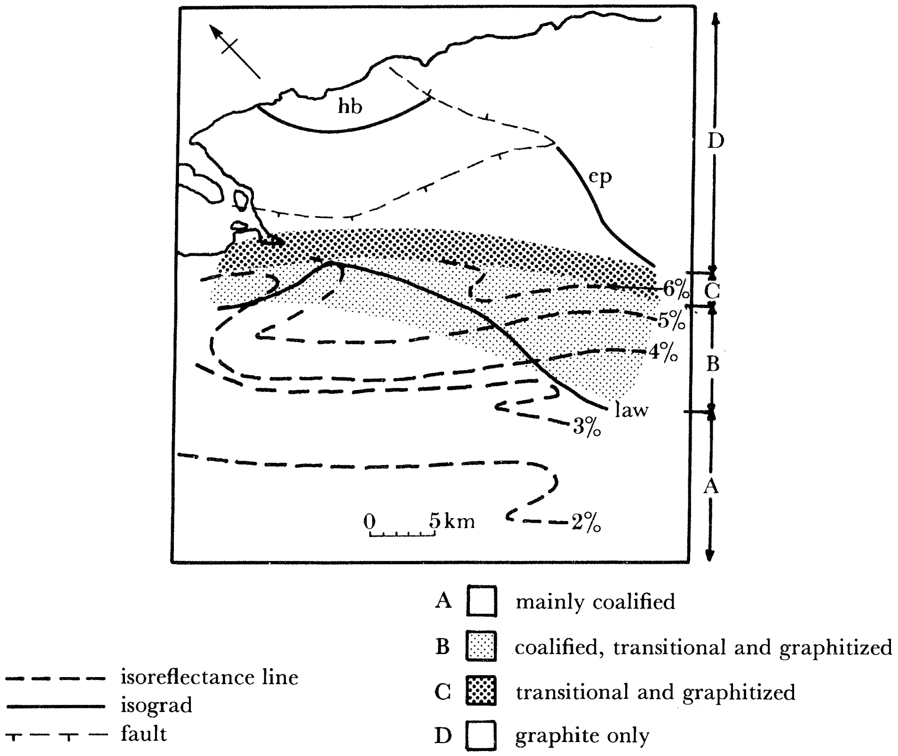

FIGURE 8. Lines of equal oil reflectance in relation to isograds in low-level metamorphic zones of part of New Caledonia. Measurements of reflectance and the appearance of the organic matter in the sediments allows an assessment of the metamorphic grade. Hb, hornblende; ep, epidote, law, lawsonite. (Redrawn from Diessel *et al.* (1978), with the permission of Springer-Verlag.)

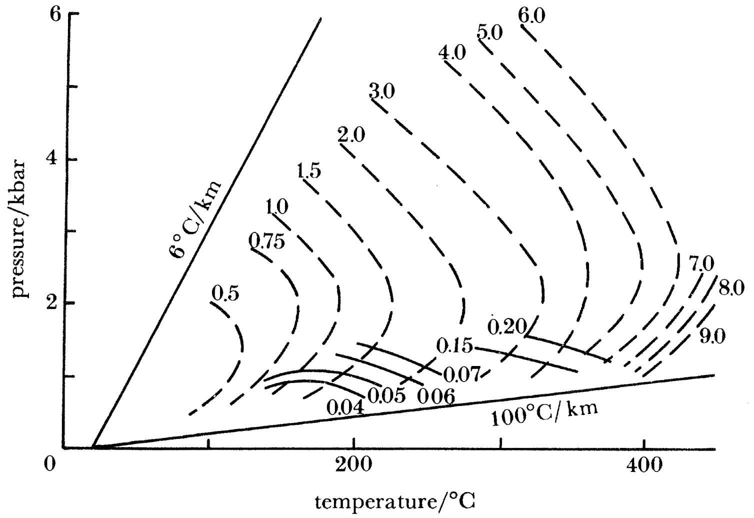

FIGURE 9. Lines of equal percentage oil reflectance and equal bireflectance, based on measurements on coals of the Allegheny Plateau, related to pressure, temperature and temperature gradient. Optical measurements allow an assessment of the pressure–temperature conditions to which the organic matter has been exposed. Isoreflectance lines shown by broken lines; isobireflectance lines shown by solid lines. 1 bar = 10^5 Pa. (Redrawn from Hower & Davis (1981), with the permission of the Geological Society of America.)

to metamorphic zones (figure 8). An interesting approach has more recently been followed by Hower & Davis (1981), who have attempted to relate both reflectance and bireflectance to pressure–temperature conditions in the crust (figure 9). Based on measurements of coals from the Allegheny Plateau, anisotropy is quantified in relation to past depth of burial (3.5–4.0 km with temperature gradients varying from 33–40 °C km^{-1}). Hower & Davis acknowledge that because of the nature of the basins studied figure 9 only refers to shallow depths, but the data would still be appropriate to the burial histories of many of the world's coals and thus helpful in analysing the diagenesis or metamorphism of coal basins.

6. Provincialism

The correlations between properties shown in figure 3 are similar to relations reported by many authors. Some caution may however be necessary in applying these correlations generally without due regard to the thermal and structural histories of the buried organic sediments in question and this may be even more important when optical–chemical relations are involved. Jones *et al.* (1984) have shown that correlations between optical and chemical properties of vitrinites from certain British coalfields may show significant differences. Almost certainly, varying thermal histories are the most probable cause for these differences. The contrast between the products of coalification and carbonization is well known. Coals involved in these processes follow different routes to the end-point of graphite, or a similar but less well molecularly structured chemical equivalent (figure 10).

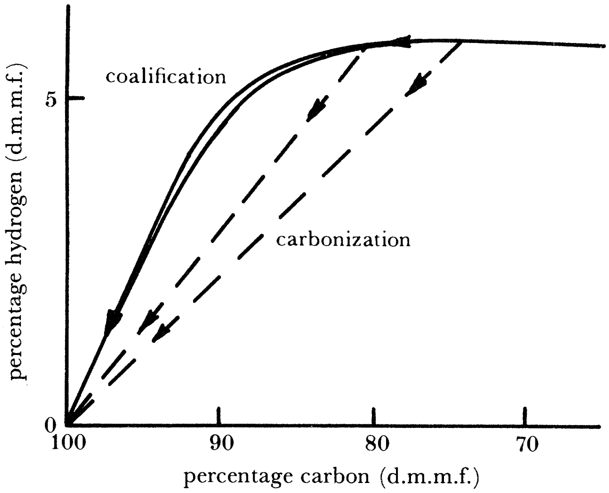

Figure 10. Generalized carbonization and coalification tracks for coals in the rank series in relation to carbon and hydrogen contents. The different tracks reflect variations in such factors as temperature levels, duration of heating and rate of heating. (D.m.m.f. = dry mineral matter free.) (Redrawn, with permission, from Cook (1982).)

In the important temperature–time relations, coalification involves exposure at relatively low temperatures over long periods of time but carbonization occurs when, over a short period, coal is raised to a temperature above its decomposition point. The properties of the carbonization product can be altered by varying such factors as the heating rate or the 'soak period'. It must equally be that vitrinites coalified relatively rapidly may display different optical–chemical relations to vitrinites coalified at much slower rates.

While differing thermal histories may be important in promoting provincialism between coals and other organic matter of different basins, tectonic setting at the time of effective coalification may also be a significant factor in introducing differences in correlations. Jones *et al.* (1984) also showed that vitrinites from the Ruhr displayed markedly lower levels of anisotropy than vitrinites of equivalent rank from British coalfields. Coalification of the German Westphalian coals was early and rapid, but the coalification was accompanied by strong lateral stresses of the pre-Asturian and Asturian fold movements. As suggested in discussion elsewhere in this contribution, these stresses would deform the molecular structure of the vitrinites, lowering the anisotropy compared with that produced by continuing vertical pressure solely due to overburden in the coals of northern England. These observations suggest that single scales correlating chemical and physical properties must be viewed with caution. Provincialism, if it is present, can be established relatively easily for coals of different basins. It may equally exist for dispersed organic matter in sediments, but its occurrence may be much more difficult to demonstrate.

7. CONCLUSIONS AND THE FUTURE

(1) A number of organic geochemical–petrological parameters can be used to assess the level of maturation (rank) reached by buried sediments. Of these parameters, reflectance (principally of the maceral vitrinite) can be used over the widest range of rank (from virtually brown coals into the region of low-grade metamorphism). It is easily and quickly measured and more linear in its variation, compared with other macerals, over virtually the whole of its measured range. The demonstration of 'provincialism' between regions with different geological histories does not diminish the potential and application of reflectance in organic petrology, but merely emphasizes the sensitivity of the parameter. A similar view can be taken of the departure of vitrinite reflectances from a uniaxial to a biaxial condition under stress and certain thermal conditions.

(2) The preparation of reflectance maps to represent rank or maturation variations with depth or laterally in relation to geothermal and structural histories is now commonplace and has proved valuable at all levels of rank. Reflectance has been most helpful, sometimes in conjunction with other textural or optical properties, in demonstrating the timing of thermal and structural events and there is little doubt that it will have a continuing significant role in basin history studies.

(3) Organic matter in marine sedimentary rocks has traditionally been considered as the main source for liquid hydrocarbons, although coaly material and coals themselves have been accepted as a source for dry gas at high rank. Recently it has become clear that terrestrial organic matter and possibly the coals themselves are the source of the oil in some major oilfields. In spite of the large amount of work published on coal chemistry, the nature of the chemical and physical changes occurring in coaly material are still not understood well enough to allow modelling of the results of the disproportionation reactions that take place during coalification. Recent work suggests that the organic geochemical and petrological approaches can be useful in a complementary manner to answer problems associated with the specific oil and gas generation capacities of all of the macerals, the maturation profiles over which this generation takes place, and the migration mechanisms associated with coals and coal-related organic matter.

(4) A number of important lines of development seem necessary for the future and could greatly improve our understanding of crustal processes. Those listed below will require continued and increasing cooperation of earth scientists of different disciplines for their success.

(i) Integration of organic matter type and abundance data with conventional facies mapping to refine the knowledge of the biological input to sedimentary sequences.

(ii) Systematic rank mapping in both basins and geosynclinal sequences to provide data on the thermal and tectonic evolution of continental masses, widening our knowledge, based on stratigraphic, sedimentological and structural studies, which should be extended to the use of patterns of rank variation to infer the burial and thermal histories of sedimentary sequences.

(iii) Examination of the possibility of using other forms of organic matter for reflectance studies in sediments containing no input from terrestrial land plants. Graptolites, for example, were first successfully used in reflectance studies by Kurylowicz *et al.* (1976) to define the level of organic metamorphism in the Cambro–Ordovician Larapinta Group of the Amadeus Basin in Central Australia and, more recently, Clausen & Teichmüller (1982) have used graptolite fragments to demonstrate the high rank of Palaeozoic rocks in the Soest-Erwitte 1/1a borehole in the Rhenish-Westphalian basin.

(5) Petrological- and organic geochemical-based concepts have for some time been partly in conflict. Stress has been laid here upon the value of petrographic parameters, particularly reflectance and its related properties, in assessing the burial history of sedimentary basins, without any intention of disparaging or diminishing the value of other parameters used appropriately in such assessments. Christie *et al.* (1984) point out that different types of data, such as organic geochemical and organic petrological, may have different types of structure which interfere and that the most constructive approach would be to study the relations between such data. Multivariate statistical methods, particularly principal components analysis, have been widely applied in the field of inorganic geochemistry, but hitherto relatively little in organic geochemistry. Such methods have, however, been employed to denote organic affinities in studies of the major- and trace-element geochemistry of coals in relation to their sedimentary histories (Gluskoter *et al.* 1977; Asuen 1984) and to Lower Palaeozoic marine shales (Stephens *et al.* 1975). A generalization of principal-components analysis termed the partial least-squares strategy (Wold *et al.* 1980, 1983), is suggested by Christie *et al.* (1984) as having great potential in the fields of organic geochemistry and organic petrology. Two sets of variables, for example, biomarkers and reflectance, can be treated independently by principal components analysis and then any correlation between the two models examined by using linear partial least-squares analysis. Before multivariate methods can be usefully applied, however, a greater understanding needs to be developed of the nature of the relations between pairs of rank-sensitive variables. The recognition of provincial effects emphasizes the need for a greater depth of knowledge about these relations. Very few organizations systematically measure more than two or three rank-sensitive variables, either because of cost or because the additional data are considered (incorrectly) redundant. This attitude should change.

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Discussion

B. Durand (*Institut Français du Pétrole, Rueil Malmaison, France*). One of the major problems in using vitrinite to study the thermal history of a rock is that we do not have a good physical model for its behaviour. Another is the level of reproducibility of the results. We sent some sediment samples to a number of different laboratories and the standard deviation of the resulting measurements was at least four times greater than a similar study on coals.

D. G. Murchison. I am also unaware of anyone who has produced a successful scheme that can relate vitrinite reflectance dependence to the temperature history. However, because the reflectance of vitrinite is a good estimator of the extent of aromaticity it should be possible to construct such a model. Though vitrinite reflectance may have problems, in my view it remains the most useful guide to maturity which is available during exploration. I also believe it can be widely used to investigate geological processes in sediments. With regard to the intercomparison experiment you described, our experience is similar. We find that the repeatibility of a reflectance measurement performed in the same laboratory is better than the agreement between different laboratories.

A. C. Cook. Precision between laboratories can be a problem for vitrinite reflectance measurements on dispersed organic matter but it generally appears to be as good or better than for other parameters. In sequences where coal is present, vitrinite reflectances have a precision better than that obtainable from any other variable. Nevertheless, vitrinite reflectance techniques do demand a considerable amount of experience, or at the very least, close supervision by an experienced petrologist.

A number of Australian sedimentary basins contain thick sequences of coal measures. Studies of rank variation in these basins indicate that the problems of correlating vitrinite reflectance relate to the inaccuracies in understanding the subsidence and thermal histories of the basins rather than to problems of reflectance or temperature measurement. These inaccuracies are much greater than is conceded in most descriptions of the stratigraphic history of sedimentary basins. To obtain an understanding of reflectance–temperature relations, the level of understanding of basin history will have to be vastly improved. In many cases, vitrinite reflectance provides significant information that is not available from conventional stratigraphic studies.

D. P. McKenzie (*Department of Geology and Geophysics, University of Cambridge*). What evidence is there that the change in vitrinite reflectance is associated with changes in aromaticity?

D. G. Murchison. The main evidence comes from studies by van Krevelen (1961) and by Hirsch (1954), who examined the molecular structure of coals by using X-ray diffraction. Later work has largely supported their conclusions. Much aliphatic material can be extracted without affecting the reflectance. Oxidation of vitrinite increases both the reflectance and the aromaticity.

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B. Sellwood (*Department of Geology, University of Reading*). How quickly does vitrinite reflectance cease to change when the material is held at a constant temperature?

D. G. Murchison. In the Gippsland Basin the thermal histories onshore and offshore are different. Onshore, the reflectance is about 0.45 % at a temperature of 80 °C. Offshore the same reflectance is found at a temperature of 110 °C. But there is no reliable method to estimate the time which will elapse before these two regions have the same reflectance at a given temperature.

B. Sellwood. If the temperature was increased for a short period of time would this event be recorded by the vitrinite?

D. G. Murchison. The reflectance will certainly change, and irreversibly. The main problem with vitrinite reflectance comes at temperatures associated with low-grade metamorphism, where it can be a very useful parameter, but there are surface problems when the organic matter is in the so-called 'semi-graphite' phase.