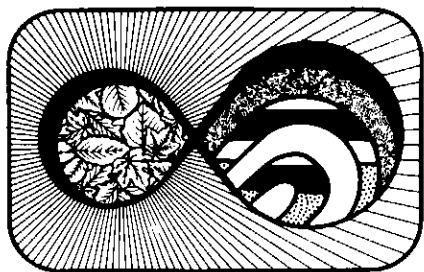


# Articles



## Diagenesis 10. Quantification and Modelling of Organic Diagenesis

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### Introduction

In the first part of our discussion of organic diagenesis (Barnes *et al.*, 1984) we outlined the types of organic matter, their progressive diagenetic transformations, and accompanying chemical reactions and products. In this second part we review some of the more accepted methods of quantifying levels of diagenesis, correlate these different methods with one another, and discuss the application of numerical models in predicting diagenetic state and basin history.

Because of both the complexity of kerogen and its importance in the petroleum and coal industries, considerable research has been directed toward quantifying levels of kerogen diagenesis (Durand, 1980). Organic matter, unlike mineral assemblages, rarely undergoes retrograde diagenesis. The highest level of diagenesis reached is the level observed, regardless of whether the strata have been uplifted and exposed to lower temperatures and pressures or to different groundwater chemistry. The only exception results from the introduction of oxidizing agents, such as molecular oxy-

gen or sulphate, which enable the bacterial degradation and oxidation of organic matter. In as much as the level of organic diagenesis reached has been shown to be almost entirely a product of temperature and time, it follows that if the level of diagenesis is known, the thermal history of the strata may be inferred. In the following sections we summarize the literature on quantification and modelling of organic diagenesis. Recent reviews and books that present the techniques in greater detail include Heroux *et al.* (1979), Brooks (1980), Durand (1980), Staplin *et al.* (1982) and Bustin *et al.* (1983). Some of the more widely applied methods are outlined below.

### Methods of Quantifying Organic Diagenesis

Both petrographic and chemical methods have been used to quantify organic diagenesis (Fig. 1; Tables I and II). The petrographic methods have been developed mainly by coal petrologists and include vitrinite reflectance, liptinite fluorescence, and kerogen colour and translucency.

**Vitrinite Reflectance.** Vitrinite reflectance is not only the most widely used but also the most reliable and precise method of quantifying organic diagenesis. It provides a standard scale against which other diagenetic indicators can be compared. The term "vitrinite reflectance" refers to the amount of light reflected from a polished surface of vitrinite, a common coal maceral.

Vitrinite reflectance measurements are made with a reflected light microscope equipped with a stabilized light source, photometer and digital voltmeter for recording. A narrow band filter centred on 546 nm is placed between the objective lens and the photometer. The optical properties required of the microscope, and necessary accessories, are outlined in Bustin *et al.* (1983). Reflectance is related to the refractive and absorptive indices of the material by Beer's equation:

$$R_o = \frac{(\mu - \mu_o)^2 + \mu k^2}{(\mu + \mu_o)^2 + \mu^2 k^2}$$

where  $\mu$  and  $k$  are the refractive and absorptive indices, respectively, of the vitrinite, and  $\mu_o$  is the refractive index of the immersion oil. In practice, this relationship is seldom if ever used, but a standard of known reflectance is compared to the vitrinite. With increasing levels of diagenesis (and aromatization) of organic matter, vitrinite reflectance increases regularly from a minimum of 0.15% (0.2% according to Middleton, 1982), to greater than 5.5% at a level equivalent to the lower greenschist metamorphic facies. As diagenesis increases, vitrinite becomes progressively more anisotropic, and thus the standard deviation of measurements increases. Typically, the mean maximum vitrinite reflectance for each grain is recorded, which requires using polarized light and rotation of the microscope stage. Random (unpolarized light) reflectance is much quicker to measure and is related to the mean maximum reflectance by

$$R_o = 1.06 R_e$$

where  $R_o$  is the mean maximum reflectance and  $R_e$  is the mean random reflectance (Ting, 1978). The mean is typically determined from measurements on 50 or 100 particles.

Vitrinite is derived from cellulose, lignin and tannins, and is an abundant constituent of continental sedimentary rocks (Stach *et al.*, 1982). Even clastic marine rocks contain sufficient fine dispersed vitrinite (phytoclads of Bostick, 1979) to enable analysis after concentration by demineralization (using HCl followed by HF) or light liquid methods. Thus, vitrinite reflectance is applicable to most sedimentary rocks, the principal exceptions being coarse grained, permeable rocks in which the percolation of oxygenated groundwater may lead to the oxidation of the vitrinite, carbonates, evaporites and bitumen impregnated rocks.

Vitrinite reflectance offers a number of advantages as a measure of organic diagenesis: (1) it is a broadly accepted and standardized procedure (Ting, 1978; Davis, 1978; ASTM, 1980); (2) vitrinite is sensitive to minor changes in the level of diagenesis and matures in a regular manner; (3) it is a microscopic method, so determinations are always made on the same physical compo-

nent; (4) vitrinite is a common constituent of many rocks or can readily be concentrated and isolated; and (5) the method is applicable throughout the entire range of diagenesis, from recent sediments to metamorphic rocks of lower greenschist facies.

Some of the limitations of the technique are (1) recycled vitrinite may be present, so that care must be taken to discriminate between separate populations; (2) oxidation may reduce vitrinite reflectance (Bustin, 1982) or, in rare instances, increase reflectance (Marchioni, 1983); and (3) vitrinite is rare in Devonian and older strata because of the absence of higher plants. In pre-Devonian strata attempts have been made to measure the reflectance of pyrobitumens

with some success (Ogunyami *et al.*, 1980).

**Fluorescence Microscopy.** Fluorescence microscopy is based on the premise that the liptinite component of organic matter, derived from algae, spores, pollen, resin and cutin, autofluoresces when irradiated by ultraviolet light. The intensity and fluorescent colours of the liptinite, although not well understood, are thought to result from excitation of pi electrons in conjugated systems (Cook, 1980). Fluorescent intensity and colour vary with the type of liptinite and the level of diagenesis. Studies by Ottenjahn *et al.* (1975), van Gijssel (1979), Teichmuller and Durand (1983) and others have demonstrated that with increasing level

of diagenesis the fluorescent intensity decreases and there is a shift in colour from lower to higher wavelengths. Relative to vitrinite reflectance, the changes in fluorescence are somewhat irregular. At a reflectance between 0.35% and 0.5% the fluorescence changes rapidly. The most rapid shift to higher wavelengths and loss of fluorescent intensity occurs at a level of diagenesis equivalent to a vitrinite reflectance of 0.8% to 0.9% (Teichmuller and Durand, 1983). Above a level of diagenesis equivalent to a vitrinite reflectance of 1.2%, fluorescent intensities are so low as to be unmeasurable.

Quantifying the fluorescent properties of liptinite entails exciting the sample with ultraviolet light and recording the intensities

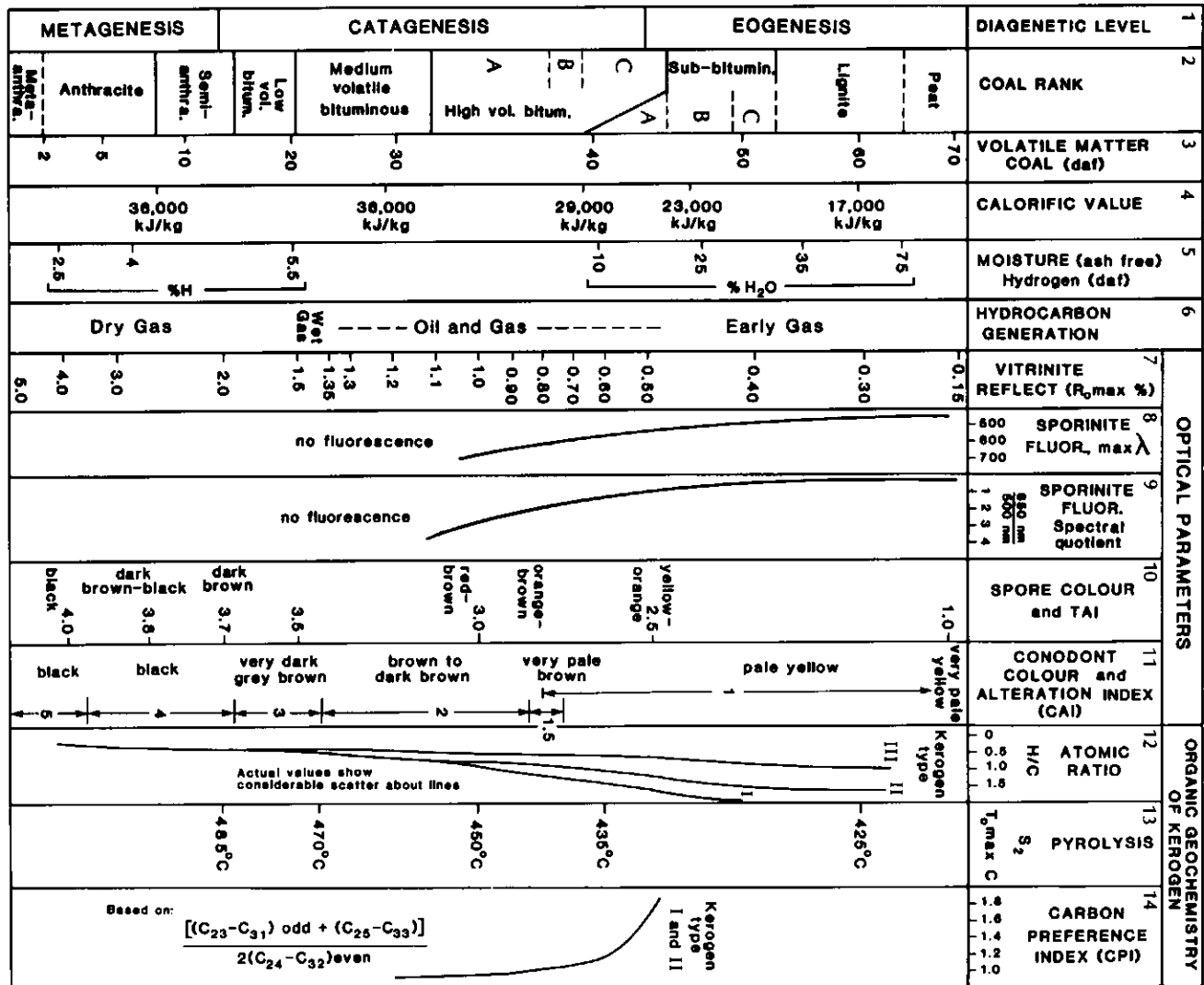


Figure 1 Correlation of major organic maturation indices. The correlations shown are based on vitrinite reflectance. Modified from (1) Barnes *et al.* (1984); (2, 3, 4, 5, 7) Teichmüller and Teich-

müller in Stach *et al.* (1982; p. 45, 47); (6) Dow (1977); (8, 9) van Gijssel (1979) and Teichmuller and Durand (1983); (10) Jones and Edison (1978);

(11) Epstein *et al.* (1977); (12) Durand and Monin (1980); (13) Espatallé *et al.* (1977b); (14) Allan and Douglas (1977)

of the fluorescent colours emitted in the range between 400 and 700 nm. The wavelength of maximum intensity shifts progressively with increasing levels of diagenesis and can be correlated with vitrinite reflectance. An alternative method now widely employed is measurement of the red/green ratio, *Q* (Stach *et al.*, 1982):

$$Q = \frac{\text{relative intensity at 650 nm}}{\text{relative intensity at 500 nm}}$$

The use of fluorescence microscopy to quantify diagenesis has both advantages and disadvantages. In samples where vitrinite is absent, it provides an alternative to vitrinite reflectance, and in samples from rocks of low diagenetic level ( $R_o < 0.3\%$ ) the vitrinite reflectance is low, whereas fluorescent intensity is high. In addition, measurements are actually performed on that part of the kerogen that can generate liquid hydrocarbons, rather than on the vitrinite, which is not considered to be a source of liquid hydrocarbons and which may be reworked. The disadvantages of fluorescence microscopy include (1) the method is only applicable to rocks of low

diagenetic level; (2) there are no widely accepted standards; (3) for interlaboratory correlation of results corrections must be made for differences in microscope optics and sample background; (4) with prolonged exposure to ultraviolet radiation, fluorescent intensity may either decline or increase; and (5) the precision of the method is less than that for measurements of vitrinite reflectance.

For quantitative fluorescence microscopy a microscope equipped with a photometer, similar to that described for reflectance measurements, is required. In addition, a stabilized high pressure mercury lamp, ultraviolet filter, barrier filter (to prevent scattered ultraviolet radiation from entering the eye) and variable grating filter (to enable intensity measurements to be made on individual wavelengths) are required.

**Kerogen Colouration.** With increasing levels of organic diagenesis the colour of kerogen observed in transmitted white light changes progressively. Such studies originated with palynologists, who observed changes in the colour of pollen and spores from translucent and nearly colourless to greenish

yellow, yellow, amber, brown and, finally, to black and opaque with increasing diagenetic level (Gutjahr, 1966; Correia, 1967; Staplin, 1969). An arbitrary numeric scale has been applied to these colour changes (Staplin, 1982) and has been standardized by use of a series of reference samples. One widely adopted scale is the "thermal alteration index" (TAI) proposed by Jones and Edison (1978; Fig. 2).

The use of kerogen colour as an index of diagenesis has the advantage that only standard palynological preparation techniques and microscopic observation are required. Palynomorphs occur in most fine grained sedimentary rocks, so that recovery of sufficient material for analysis is seldom a problem. The technique is applicable to levels of diagenesis equivalent to vitrinite reflectances from 0.15% to about 2.4%, and thus covers the range of petroleum generation and cracking. The major disadvantage of the method is that it is subjective and only semi-quantitative. Palynomorph colour is influenced by particle thickness and initial pigmentation. Standardization of sample processing, microscope light source and reference samples are required. Re-

**Table I** Relative Value of Organic Diagenetic Indicators

Class	Technique	Analysis Required	Precision	Range of Application
Optical	- vitrinite reflectance	- microscopic	- excellent (standard)	- complete range of diagenesis
	- Fluorescence	- microscopic	- moderate (requires further study)	- up to $R_o = 1.2\%$
	- Palynomorph color	- microscopic	- moderate	- up to $R_o = 2.4\%$
	- Conodont color	- microscopic	- moderate	- complete range of diagenesis
Organic Geochemistry	- Extractable organic matter	- extraction-gas chromatography	- moderate (?)	- to above zone of wet gas generation
	- Carbon preference index	- extraction-gas chromatography	- moderate	- diagenesis to zone of hydrocarbon generation where CPI $\rightarrow$ 1
	- % Paraffins, aromatics, & polar compounds	- ext. -liq. chromatography	- good within stratigraphic sequence see Table II	- diagenesis to zone of hydrocarbon cracking see Table II
	- Gic profiles paraffins	- ext. -gas chromatography (Gic)		
	- GC-MS profiles biological markers	- ext. -gas chromatography-mass spectrometry		
	- Light hydrocarbon analysis	- extraction or head-space gas samples-Gic	- poor	- complete range
	- Pyrolysis	- heating and/or extraction and gas chromatography	- moderate at low levels of diagenesis	- complete range
	- Ultimate analysis	- separation and various chemical analysis	- good at low levels of diagenesis	- complete range
- Proximate analysis	- heating in-different atmospheres	- good at low levels of diagenesis	- complete range	
Physiochemical	- Infrared Spectroscopy	- separation and infrared spectrometry	- moderate-insufficient data	- unknown
	- Electron Paramagnetic Resonance	- separation and EPR	- insufficient data	- unknown
	- C,H,S Isotopes	- separation and mass-spectrometry	- insufficient data	- up to $R_o \sim 1.5$
	- Caloric value	- separation and calorimetry	- moderate-good at low levels of diagenesis	- complete range

working of kerogen from older rocks or caving of boreholes may complicate the analysis.

The only equipment necessary for TAI determination is a transmitted light microscope and a series of reference samples. In an attempt to refine the method, Staplin (1982) suggested the use of a light source illuminating at 3200 K and a "daylight" filter. An alternative method of determining palynomorph colour is the measurement of their translucency. Measurements of translucency are made on specific taxa; at least thirty measurements must be made and averaged (Grayson, 1975).

In addition to palynomorphs, other forms of kerogen display progressive changes in colouration with increasing diagenesis. Of particular importance are colour changes in conodonts. Conodonts, although composed mainly of apatite, contain organic matter which changes sequentially from pale yellow to black (Epstein *et al.*, 1977; Harris, 1979) with increasing levels of diagenesis, in a manner analogous to palynomorphs. At the highest temperatures

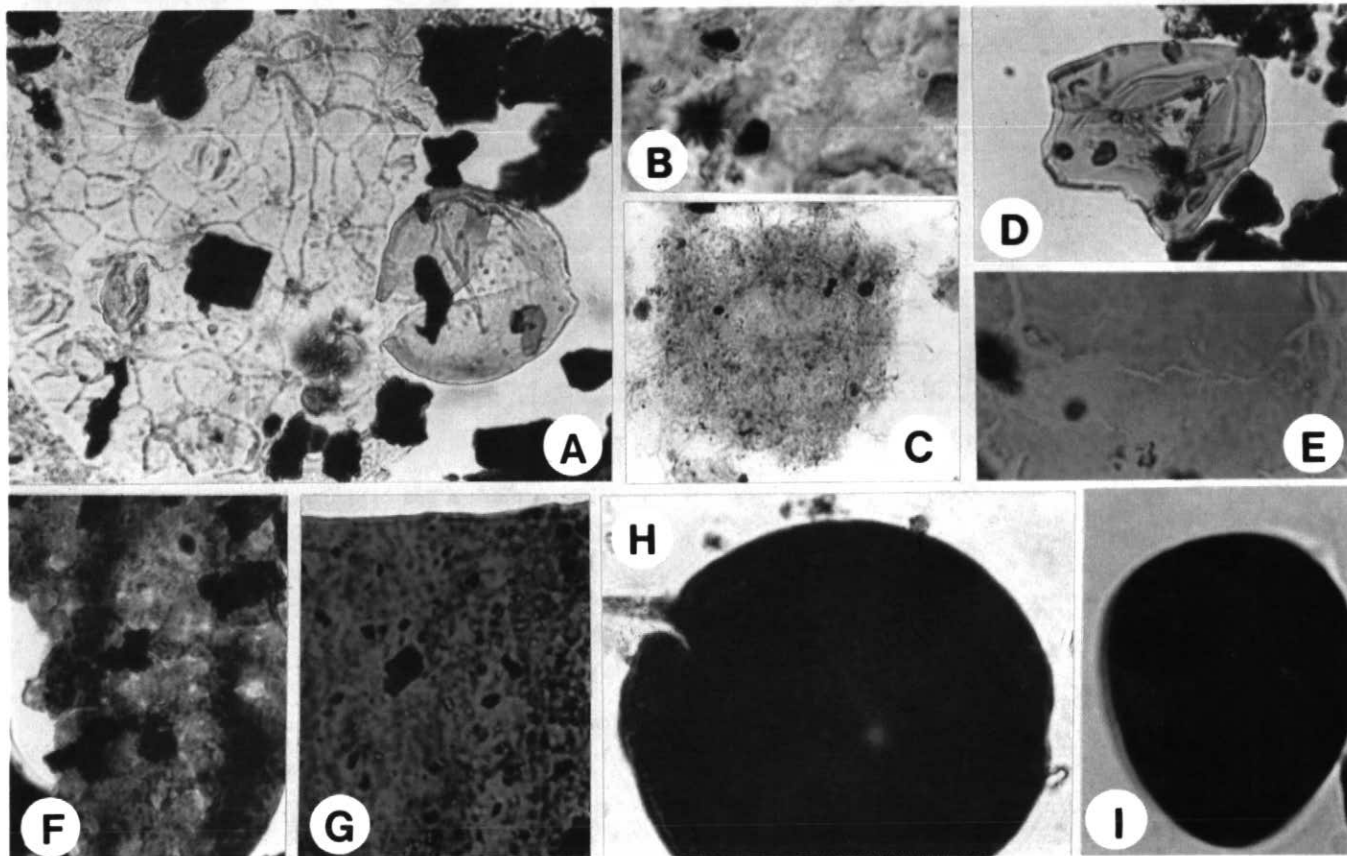
of diagenesis or metamorphism, the colour may change to an opaque white if the partial pressure of oxygen is high enough to permit oxidation of the graphite (Harris, 1979). The progressive colour changes have been divided into eight visually determined levels, giving a conodont alteration index (CAI) scale. CAI can be correlated with vitrinite reflectances from  $R_o < 0.8\%$  to  $R_o > 3.6\%$ .

Conodonts can be recovered from carbonates or shales by acid treatment and heavy liquid or magnetic separation methods (Harris, 1979). The conodont alteration index has the advantage that the method can be used over a wide diagenetic range (up to and including the greenschist metamorphic facies), and conodonts can be recovered from pre-Devonian rocks where vitrinite is rare or absent. Conodonts are, however, restricted in their stratigraphic range from the Cambrian to the Triassic, and the technique, like palynomorph colouration (TAI), lacks the refinement, precision and acceptance of vitrinite reflectance as a diagenetic indicator.

### Geochemical Methods

Organic geochemistry has also been used to determine the degree of organic diagenesis. A variety of geochemical methods have been developed to isolate and investigate the soluble and insoluble fractions of organic matter in sediments and sedimentary rocks. Petroleum geochemists (Durand, 1980, p. 24; Waples, 1981, p. 2) define as bitumen the fraction soluble in organic solvents. Kerogen is defined by some as all organic matter that is not soluble in organic solvents (Durand, 1980, p. 27; Waples, 1981, p. 20) and by others as organic matter which is insoluble in both organic solvents and in aqueous bases (Tissot and Welte, 1978, p. 123). As a great many methods have been developed, only the most widely used will be discussed here.

**Extractable Organic Compounds.** The chemical composition of sedimentary organic matter, including petroleum, reflects both source material ("biological marker" compounds) and the level of diagenesis. Ultrasonication or soxhlet extraction with



**Figure 2** Examples of kerogen, illustrating the progressive change in colour with increasing level of diagenesis. Samples were prepared using standard palynological techniques (HCl followed by HF) by G.E. Rouse. Photographs were taken in transmitted light. (A) Sheet of leaf epidermis, on the left, with stomata and cuticle (colourless; TAI = 1). On the right is a reworked smooth

walled spore (yellow; TAI = 2). Magnification 600 x. (B) Fragments of leaf, showing cell outlines. TAI = 2; magnification 1000 x. (C) Mass of amorphous granular plant debris, slightly darker than (B). TAI = 2; magnification 1000 x. (D) Smooth walled spore with yellow brown colour. TAI = 2.5; magnification 1000 x. (E) Fragment of waxy leaf cuticle, amber-brown. TAI = 2.5;

magnification 1000 x. (F) Leaf fragment with brownish yellow colour. TAI = 2.75; magnification 1000 x. (G) Leaf cuticle showing reddish brown colour. TAI = 3.0; magnification 1000 x. (H) Mesozoic pollen grain with dark brown wall. TAI = 3.8; magnification 1000 x. (I) Same pollen type as (H), but completely carbonized. TAI = 4; magnification 1000 x

organic solvents (such as chloroform/methanol, benzene/methanol or dichloromethane) is used to isolate extractable organic matter (EOM), the quantity of which is used as a bulk parameter. Because of the complexity of the extract and the large number of organic compounds present,

extensive chemical separations are necessary to isolate and identify specific organic compounds which are used as molecular parameters. Column chromatography, thin-layer chromatography and adduction as clathrates are used prior to analysis by high performance liquid chromatography

(HPLC), gas-liquid chromatography (GLC) or computerized on-line gas chromatography-mass spectrometry (GC-MS). The small amounts of the compounds present, coupled with the extensive chemical separation procedures employed, can lead to a loss of material, oxidation or a chemical

**Table II** Changes in Biological Markers with Increasing Diagenesis

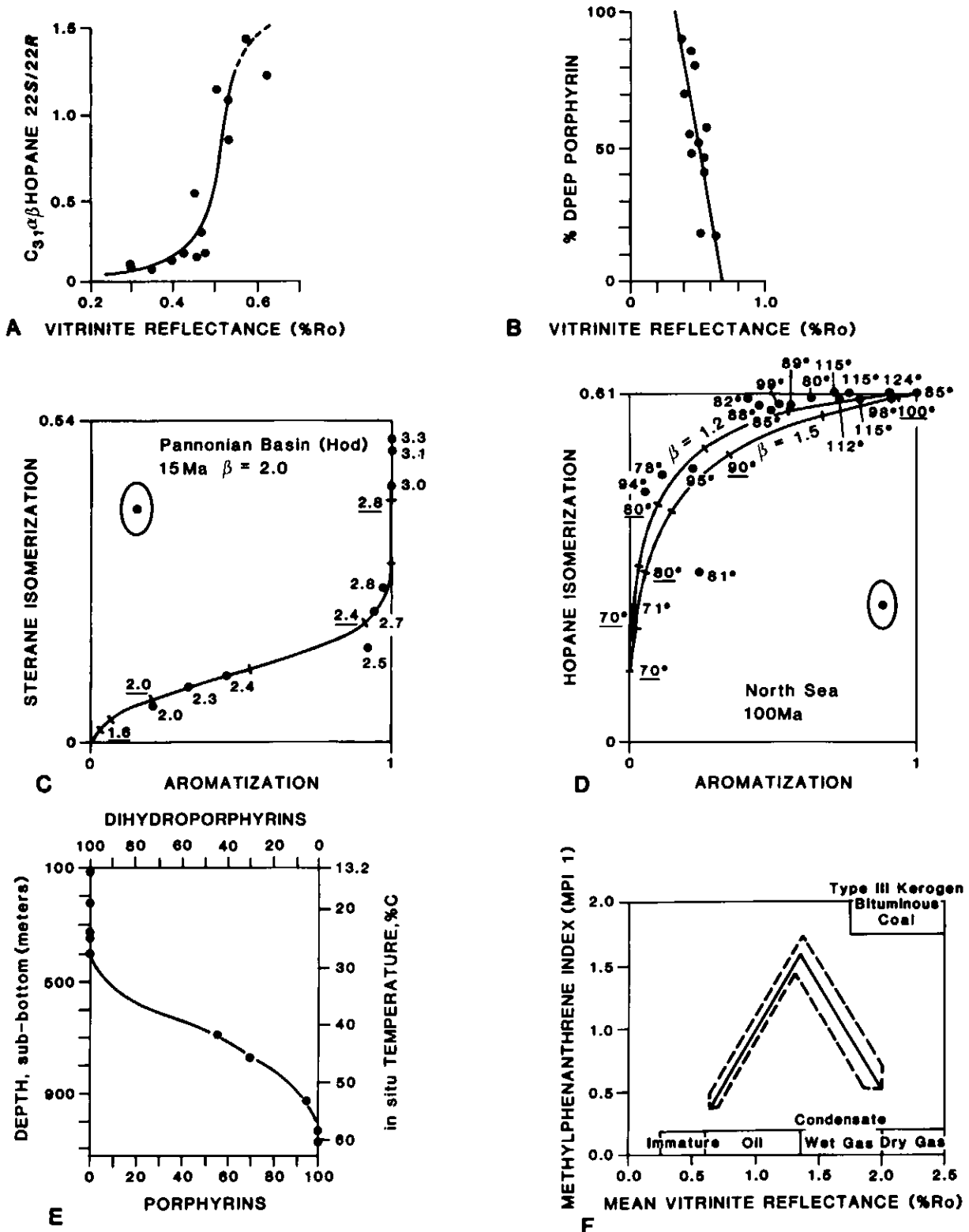
-----> Increasing maturity, as measured by increasing vitrinite reflectance or burial depth ----->		
Biological Configuration	Geochemical Fossil	Changes in Ratio (with increasing maturation)
<b>STERANES</b>		
<i>Ring alteration:</i>		
5, 14, 17 $\alpha$ H (20 <i>R</i> )-sterane (see Fig. 4: 2a-e, h, i)	5 $\alpha$ H, 14 $\beta$ H, 17 $\beta$ H(20 <i>R</i> )-sterane <sup>2</sup> (Fig. 4: 3a-e, h, i)	(20 <i>R</i> )-sterane: $\beta\beta/\alpha\alpha$ increases (Mackenzie and others 1980; 1983; McKirdy and others 1983; Seifert and Moldowan 1981)
5, 14, 17 $\alpha$ H(20 <i>R</i> )-sterane (Fig. 4: 2a-e, h, i)	13 $\beta$ H, 17 $\alpha$ H(20 <i>R</i> )-rearranged sterane (diasterane) <sup>1 2 3</sup> (Fig. 4: 6a-e, h, i)	((20 <i>R</i> )-rearranged sterane)/5 $\alpha$ -sterane increases (Pym and others 1975; Seifert and Moldowan 1978; Seifert and others 1983)
5, 14, 17 $\alpha$ H-sterane (Fig. 4: 2g) Monoaromatic steranes (Fig. 4: 9g) (Fig. 4: 4f)	Monoaromatic steranes (Fig. 4: 9g) <sup>2</sup> Triaromatic steranes (Fig. 4: 10g) (Fig. 4: 5f)	MA/5 $\alpha$ -steranes increases (Seifert and others 1983) TA/MA increases (Seifert and others 1983) (Mackenzie and others 1982; 1983a; 1983b)
Monaromatic diasteranes (Fig. 4: 7g)	Triaromatic diasteranes <sup>2</sup> (Fig. 4: 8g)	TA/(MA + TA) increases (Mackenzie and others 1981)
<i>Side chain isomerization:</i>		
5, 14, 17 $\alpha$ H(20 <i>R</i> )-sterane <sup>1</sup> Fig. 4: 2a-f)	5, 14, 17 $\alpha$ H(20 <i>S</i> )-sterane <sup>2</sup> (Fig. 4: 2j-l)	20 <i>S</i> /20 <i>R</i> increases in $\alpha\alpha\alpha$ -steranes (Mackenzie and others 1980, 1981, 1982, 1983a; McKirdy and others 1983; Seifert and Moldowan 1978, 1981; Seifert and others 1983)
5, 14, 17 $\alpha$ H(20 <i>R</i> )(24 <i>S</i> )-sterane (Fig. 4: 2b, d)	5, 14, 17 $\alpha$ H(20 <i>R</i> )(24 <i>R</i> )-sterane <sup>2 3</sup> (Fig. 4: 2c, e)	24 <i>R</i> /24 <i>S</i> increases in $\alpha\alpha$ (20 <i>R</i> )-steranes (Mackenzie and others 1980, 1981, 1983a)
5 $\alpha$ H, 13 $\beta$ H, 17 $\beta$ H(20 <i>R</i> )-diasterane <sup>1</sup> (Fig. 4: 6a)	5 $\alpha$ H, 13 $\beta$ H, 17 $\beta$ H(20 <i>S</i> )-diasterane <sup>2</sup> (Fig. 4: 6j)	20 <i>S</i> /20 <i>R</i> increases in $\beta\alpha$ -diasteranes (Mackenzie and others 1980; Pym and others 1975)
<b>HOPANES</b>		
<i>Ring alteration:</i>		
17 $\beta$ H, 21 $\beta$ H(22 <i>R</i> )-hopane (Fig. 4: 11m-q)	17 $\alpha$ H, 21 $\beta$ H(22 <i>R</i> )-hopane (Fig. 4: 12m-q)	$\beta\beta$ -hopanes / (total hopanes) decreases to 0 (Mackenzie and others (1980, 1981; Seifert and Moldowan 1980)
17 $\beta$ H, 21 $\alpha$ H(22 <i>R</i> )-moretane (Fig. 4: 13m-q)	17 $\alpha$ H, 21 $\beta$ H(22 <i>R</i> )-hopane (Fig. 4: 12m-q)	$\beta\alpha$ -moretane/ $\alpha\beta$ -hopane decreases (Mackenzie and others 1980, 1981; Seifert and Moldowan 1980)
17 $\alpha$ H-22, 29, 30-trisnorhopane (Tm shown in Fig. 4: 14m)	18 $\alpha$ H-C <sub>27</sub> hopane (Ts shown in Fig. 4: 15m)	C <sub>27</sub> Tm/Ts decreases (Seifert and Moldowan 1978, 1980, 1981; McKirdy and others 1983)
<i>Side chain isomerization:</i>		
17 $\alpha$ H, 21 $\beta$ H(22 <i>R</i> )-hopane for C <sub>31</sub> - C <sub>35</sub> (Fig. 4: 12q)	17 $\alpha$ H, 21 $\beta$ H(22 <i>S</i> )-hopane (Fig. 4: 12r)	22 <i>S</i> /22 <i>R</i> increases in $\alpha\beta$ -hopanes (Mackenzie and others 1980, 1981, 1983a; McKirdy and others 1983; Seifert and others 1979; Seifert and Moldowan 1980)
<b>PORPHYRINS</b>		
Free base C <sub>28</sub> - C <sub>32</sub> DPEP (Fig. 5: 17)	C <sub>28</sub> - C <sub>32</sub> ETIO porphyrin (Fig. 5: 18)	DPEP/ETIO decreases (Mackenzie and others 1980, 1981; Baker and Louda 1983; Barwise and Park 1983)
C <sub>28</sub> - C <sub>32</sub> Ni-DPEP C <sub>27</sub> - C <sub>34</sub> VO-DPEP <sup>4</sup>	C <sub>28</sub> - C <sub>32</sub> Ni-ETIO C <sub>27</sub> - C <sub>34</sub> VO-ETIO	Ni-DPEP/Ni-ETIO decreases VO-DPEP/VO-ETIO decreases and C <sub>27</sub> - C <sub>34</sub> shifts to C <sub>30</sub> - C <sub>50</sub>
<b>ISOPRENOIDS</b>		
(6 <i>R</i> , 10 <i>S</i> ) pristane (Fig. 5: 22)	(6 <i>R</i> , 10 <i>R</i> ) pristane + (6 <i>S</i> , 10 <i>S</i> ) pristane (Fig. 5: 23)	( <i>RS</i> pristane)/(total pristane) decreases to 50% (final mixture: <i>RS</i> : <i>RR</i> : <i>SS</i> = 2 : 1 : 1) (Mackenzie and others (1980, 1981, 1983a)
(C <sub>15</sub> 3 <i>R</i> , 7 <i>R</i> )-isoprenoid acid (Fig. 5: 26)	C <sub>15</sub> (3 <i>S</i> , 7 <i>R</i> ) + (3 <i>R</i> , 7 <i>S</i> ) acids (Fig. 5: 27)	<i>RR</i> /(total isoprenoid acids) decreases to 0 as acids isomerize and then decarboxylate to hydrocarbons
C <sub>16</sub> (4 <i>R</i> , 8 <i>R</i> )-isoprenoid acid (Fig. 5: 28)	C <sub>16</sub> (4 <i>S</i> , 8 <i>R</i> ) + (4 <i>R</i> , 8 <i>S</i> ) acids (Fig. 5: 29)	

<sup>1</sup> Source parameter for oil/source rock correlation

<sup>2</sup> Maturation parameter

<sup>3</sup> Migration parameter

<sup>4</sup> VO = vanadyl



**Figure 3** Changes in biological markers with increasing diagenesis. (A) Changes in side chain isomerization at C-22 for the C<sub>31</sub> αβ-hopanes in Jurassic Kimmeridge oil shales (Douglas et al., 1983); (B) Decrease in ratio of DPEP to total porphyrins in gilsonite with increasing reflectance (Barwise and Park, 1983); (C) Changes in size chain isomerization at C-20 for the C<sub>29</sub> steranes for Pannonian Basin sediments relative to the shift from mono- to triaromatic steranes. The Pannonian Basin is assumed to have formed by

rapid extension 15 Ma ago. Solid dots are observed values, with depths shown in km; underlined values were calculated from Mackenzie and McKenzie (1983; extension factor (β) = 2.0); (D) Changes in side chain isomerization at C-22 for the C<sub>32</sub> hopanes from North Sea sediments relative to the shift from mono to triaromatic steranes; theoretical curves for two extension factors (β = 1.2 and 1.5) are shown; solid

dots are observed values; underlined values at intervals of 5°C were calculated from the model (Mackenzie and McKenzie, 1983); (E) Aromatization of dihydroporphyrins to DPEP with increasing depth and temperature in Black Sea sediments (Baker and Louda, 1983); (F) Methylphenanthrene index first rises and then falls with increasing reflectance; dashed lines represent one standard deviation (Radke and Welte, 1983)

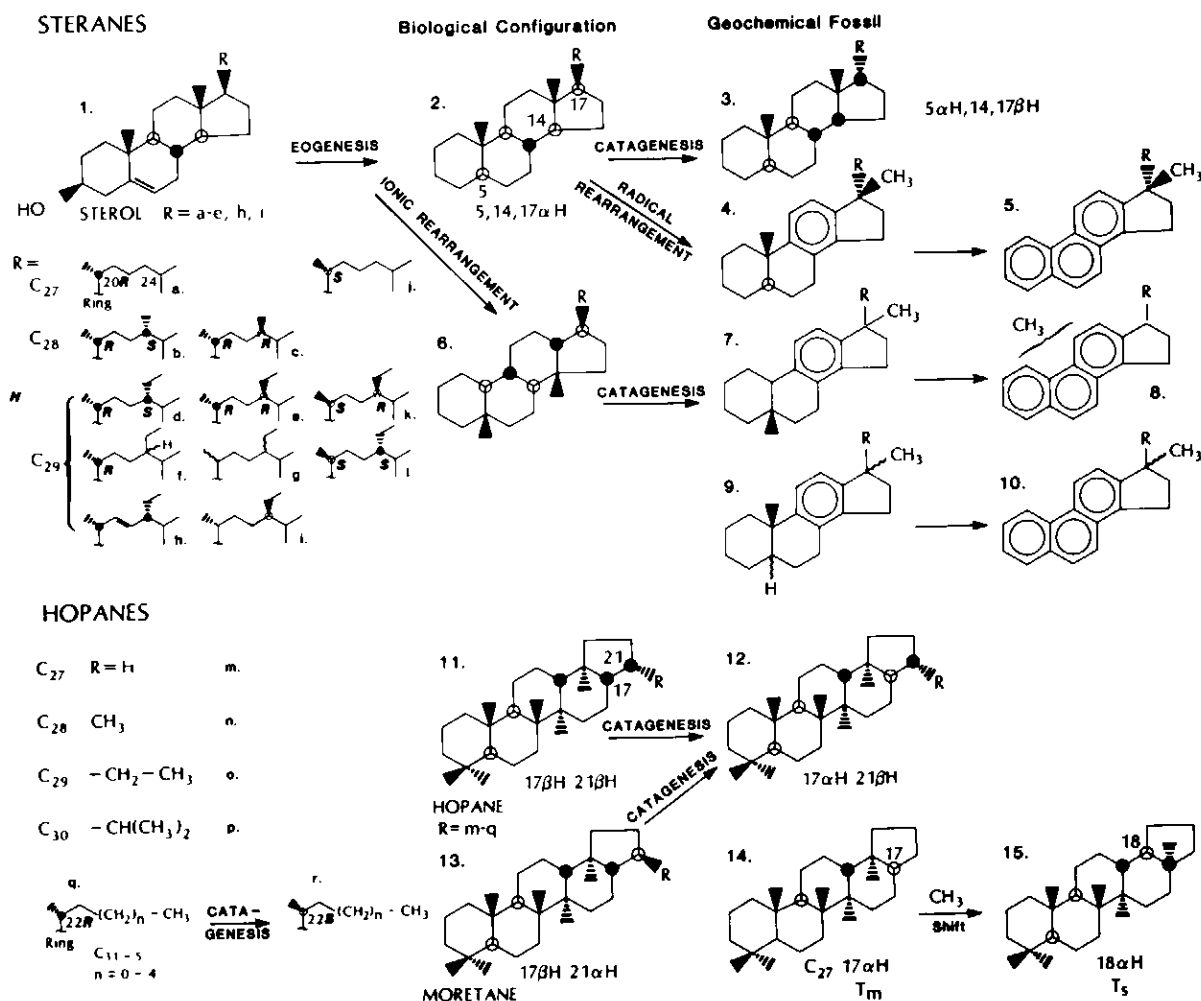
change in the individual compounds. Phthalates, which are used as plasticizers, and naphthenic compounds, from greases used in drilling, are common contaminants (Powell, 1978). Biological markers are especially useful in oil-source rock correlation. Although the isolation and identification of individual organic compounds are both more expensive and time consuming than measurement of vitrinite reflectance, they too can be used for assessment of the degree of diagenesis, particularly at very low and intermediate levels of maturity.

**Biological Markers.** The terms "biological marker" (Eglinton, 1969) and "geochemical fossil" (Tissot and Welte, 1978) have been used to refer to organic compounds in

sediments which reflect the chemistry of the contributing organism, the effect of depositional environment and the effect of burial and subsequent maturation. The carbon skeletons of the compounds show little or no alteration from the precursor forms; however, the effects of eogenesis and catagenesis are reflected in changes which may include (1) an alteration in the stereochemistry; (2) a loss or change in functional groups; (3) reduction and saturation; or (4) aromatization. Changes in the distribution and structure of biological markers are used to (1) correlate oils with their source rocks; (2) evaluate the degree of maturation; and (3) identify migration or biodegradation that may have occurred during the diagenetic conversion of biological lipids to

petroleum (Meinschein, 1983; see references in Table II).

Generally, thermal alteration of biological markers increases with burial depth and with increasing vitrinite reflectance values (Fig. 3, a and b). Commonly used are a combination of parameters determined for compounds whose structures differ in thermal stability. This permits a more sensitive discrimination of degrees of thermal maturation between samples in a stratigraphic sequence than is possible using reflectance data alone. Because of their widespread occurrence, structural specificity and stability, steranes, hopanes, porphyrins and isoprenoids are commonly used as biological markers. Eogenetic and catagenetic changes that result in ring alteration



**Figure 4** Eogenetic and catagenetic changes in steranes and hopanes. Note the use of both the Roman font R and the italic font R on this diagram. R refers to alkyl side chains, whereas R and S refer to the stereochemistry of the alkyl side chains. See Figure 7 for definitions of R and

S. The ring systems lie approximately in the plane of the page. The tilde symbol (~) indicates the point of attachment of R groups to the ring. Solid triangles indicate groups above the plane of the rings (in front of the page); broken triangles indicate groups below the plane of the

rings (behind the page). If an "R" is not shown, the group is a methyl. A solid circle indicates a  $\beta$  hydrogen above the plane of the rings; an open circle indicates an  $\alpha$  hydrogen below the plane of the rings;  $\mu$  indicates undefined stereochemistry

PORPHYRINS

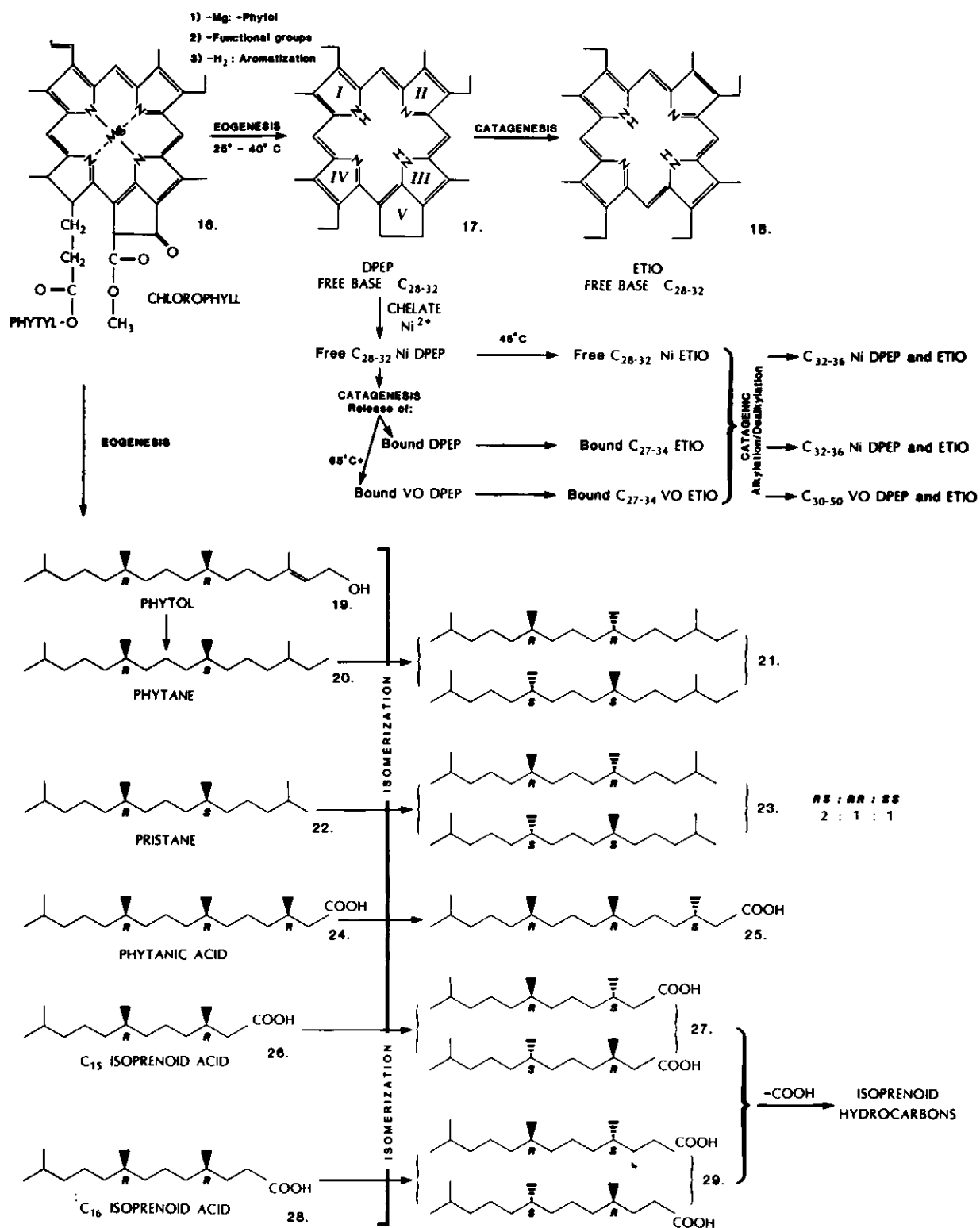
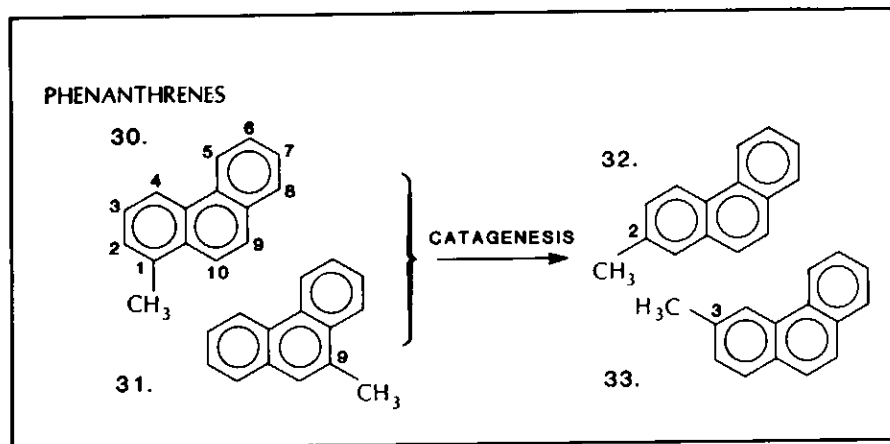


Figure 5 Eogenetic and catagenetic changes in porphyrins and isoprenoids. Symbols are defined in Figure 4





**Figure 6** Catagenetic changes in phenanthrenes

and side chain isomerization are summarized in Table II and Figures 4, 5 and 6.

During early eogenesis, sterols [Fig. 4: compound 1, side chain (R) = a-e, h, i] are converted by biologically mediated processes in the sediment to the corresponding stanols, which in turn form steranes (Fig. 4: 2, R = a-e, h, i); the  $\alpha\alpha$ -steranes retain their original biological configuration [5, 14, 17  $\alpha$ H (20R)] in both the ring and side chain. Depending on the biological precursor, there can be some variation in the stereochemistry of the alkyl side chain, particularly in marine sources (Scheuer, 1973; Scheuer, 1978), but the more common stereochemistry has the R configuration at C-20 (Fig. 4: R = a-f) and a mixture of R (Fig. 4: R = c, e) and S (Fig. 4: R = b, d) at C-24. The R and S stereochemistry is defined in Figure 7. These are the dominant forms in immature sediments. With increasing maturation there is a shift to thermally more stable geochemical fossils. Isomerization of the alkyl side chain occurs with the shift from S to R at C-24, followed by R to S at C-20. Alteration of the ring occurs with the formation of 5 $\alpha$ H, 14 $\beta$ H, 17 $\beta$ H steranes (Fig. 4: 3). Aromatization occurs with the formation of monoaromatics (Fig. 4: 4, 7, 9) followed by triaromatics (Fig. 4: 5, 8, 10). An increase in rearranged steranes [diasteranes (Fig. 4: 6)] relative to non-rearranged steranes (Fig. 4: 2) reflects both source and subsequent migration and maturation effects (McKirdy *et al.*, 1983; Seifert and Moldowan, 1983); diasteranes are thought to arise from acid catalyzed ionic rearrangement of  $\alpha\alpha$  steranes or sterols and occur more commonly in oil shales than in carbonate-sourced oils (McKirdy *et al.*, 1983). Table II and Figure 4 summarize some of the parameters commonly used in oil-source rock correlations and as measures of thermal maturation, migration and biodegradation.

Seifert and Moldowan (1981) have defined a maturity index for non-migrated oils

(Biomarker I) and a migration index (Biomarker II) from a first order kinetic plot of the side chain isomerization in  $C_{28}$  steranes (Fig. 4: 2l/2f) relative to ring alteration (Fig. 4: 3f/2f).

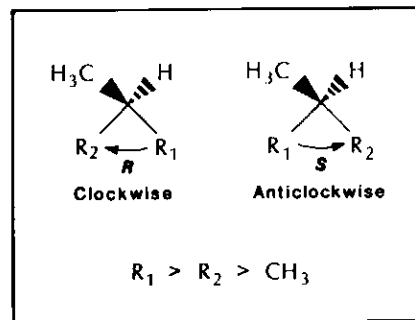
The hopanoic acids and hydrocarbons occur in blue-green algae (cyanobacteria) and bacteria and are commonly used as indicators of microbial sources in sediments (Ourisson *et al.*, 1979). The  $\beta\beta$ -hopanes (17  $\beta$ H, 21  $\beta$ H; Fig. 4: 11, R = m through q) with the R-configuration at C-22 (R = q) are the more common biological isomers; lesser amounts of  $\beta\alpha$ -moretanes occur (17  $\beta$ H, 21  $\alpha$ H; Fig. 4: 13, m through q). With increasing thermal maturity, both the  $\beta\alpha$ -moretanes and the  $\beta\beta$ -hopanes undergo ring alteration and form the  $\alpha\beta$ -hopanes (Fig. 4: 12, m through q); alteration of  $\beta\beta$ -hopanes to  $\alpha\beta$ -hopanes occurs prior to the zone of oil generation (Mackenzie *et al.*, 1980; Seifert and Moldowan, 1980). An increase in the Tm/Ts ratio (Fig. 4: 14, 15) occurs with increasing catagenesis (Seifert and Moldowan, 1978, 1980, 1981; McKirdy *et al.*, 1983; Seifert *et al.*, 1983); the 17 $\alpha$ H- $C_{27}$  hopane (Fig. 4: 14) is altered to the thermally more stable 18 $\alpha$ H- $C_{27}$  hopane (Fig. 4: 15) with the shift of a C-18 methyl group to C-17. Thermal isomerization of the alkyl side chain in  $C_{31}$  to  $C_{35}$  hopanes occurs with the shift in stereochemistry from R (Fig. 4: R = q) to S (R = r) at C-22. The sensitivity of the S/R ratio for the  $\alpha\beta$   $C_{31}$  hopanes to changes in vitrinite reflectance in the region  $R_0$  0.4 through 0.6 is shown in Figure 3: a.

Mackenzie and McKenzie (1983) have used side chain isomerization in steranes and hopanes, and the shift from monoaromatic to triaromatic steranes, to model the thermal, subsidence and uplift histories of stretched basins. Their ideas are discussed here in the section on numerical methods.

Early in eogenesis, porphyrins arising from chlorophyll (Fig. 5: 16) lose magnesium and the phytol side chain (Fig. 5: 19);

phytol, in turn, may be oxidized to the corresponding acid (Fig. 5: 24), reduced to the  $C_{28}$  isoprenoid phytane (Fig. 5: 20) or shortened to pristane (Fig. 5: 21) in the guts of zooplankton. In each case the original biological configuration is retained. With thermal maturation both pristane and phytane isomerize from RS (Fig. 5: 20 and 22) to a mixture of the RS, RR and SS isomers (Fig. 5: 21 and 23). Similar thermal isomerization of the biological configuration to an isomeric mixture occurs in the isoprenoid acids (Fig. 5: 24 goes to 25; 26 goes to 27; 28 goes to 29); with increasing burial depth the  $C_{15}$  and  $C_{16}$  acids (Fig. 5: 26 and 28) disappear as they decarboxylate to the corresponding hydrocarbons.

After the successive loss of magnesium and of phytol and other functional groups from the porphyrin ring, hydrogen is lost and the free base is aromatized under anoxic conditions to DPEP (Fig. 5: 17) with a range in carbon number from  $C_{28}$  to  $C_{32}$ . The aromatization of the porphyrin ring system with the formation of DPEP takes place in the temperature range of 30°C to 60°C for samples taken from the Black Sea (Fig. 3E). Baker and Louda (1983) also suggest that rechelation with Ni to form Ni-DPEP occurs between 30°C and 60°C. DPEP is thermally altered to the ETIO form (Fig. 5: 18) with the loss of ring V. As a result, increasing thermal maturation is evident and can be measured by decreases in the DPEP/ETIO ratio, which occur first for the free bases and then for their Ni chelates. The decrease in the DPEP/ETIO ratio for porphyrins isolated from gilsonite is shown in Figure 3B. Barwise and Park (1983) suggest porphyrins are a sensitive index to maturation in the region  $R_0$  0.4 to 0.6, and



**Figure 7** R and S stereochemistry for a tetrahedral carbon atom with four different groups attached. Alkyl groups  $R_1$  and  $R_2$  lie in the plane of the page; the methyl group lies in front of the page and hydrogen behind. Group  $R_1$  is larger than group  $R_2$ , which in turn is larger than a methyl group. Size is defined by the total atomic number of the attached groups. Thus,  $-\text{COOH} > -\text{CH}(\text{CH}_3)_2 > -\text{CH}_2\text{CH}_3 > -\text{CH}_3$ . In R stereochemistry, group size decreases in a clockwise direction; in S stereochemistry, it decreases in an anticlockwise direction

can be used in algal rich samples that commonly lack vitrinite particles. Finally, kerogen-bound DPEP and its vanadyl chelates are released, and subsequently altered to the ETIO form; with both the addition and loss of alkyl side chains, a series of C<sub>30</sub> to C<sub>36</sub> porphyrins is produced.

A methylphenanthrene index (MPI) has been developed to measure increases in coal rank and thermal maturation in sediments (Radke *et al.*, 1982a, 1982b; Radke and Welte, 1983). Methylphenanthrenes (MP) and naphthalenes, and dimethylphenanthrenes are extracted and separated by liquid chromatography. The quantity and distribution of methyl homologues of phenanthrene (P) and naphthalene in the C<sub>15+</sub> soluble organic fraction are strongly controlled by changes in rank. At R<sub>o</sub> = 0.9, the liptinite fluorescence ratio (Q) shows a sharp increase; a corresponding shift occurs in the structure of the methyl homologues. Methyl groups adjacent to the ring junction [1-methylphenanthrene (Fig. 6: 30) and 9-methylphenanthrene (Fig. 6: 31)] are thermally less stable than methyl groups in non-adjacent positions [2-methylphenanthrene (Fig. 6: 32) and 3-methylphenanthrene (Fig. 6: 33)], which are subject to less steric hindrance. Two MPI indexes are defined:

$$\text{MPI 1} = 1.5(2\text{-MP} + 3\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})$$

$$\text{MPI 2} = 3(2\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})$$

A strong positive correlation with reflectance is observed for MPI 1, which increases within the oil window but then decreases abruptly with the onset of the wet gas zone below (Fig. 3: F). A "calculated reflectance" for coal and kerogen extracts can be derived from the MPI (Radke and Welte, 1983):

$$\text{For } R_o < 1.35\%: R_c = 0.6(\text{MPI 1}) + 0.4$$

$$\text{For } R_o > 1.35\%: R_c = -0.6(\text{MPI 1}) + 2.3$$

The "calculated reflectance" shows a linear correlation with R<sub>o</sub> and makes it possible to compare the thermal maturity of sediments with their extractable organic content.

**Total Extractable Organic Matter.** The ratio of the total amount of extractable organic matter (EOM) to total organic carbon (TOC) is related to the level of diagenesis attained by sedimentary rocks (Tissot and Welte, 1978). Although the EOM/TOC ratio is high in immature surface sediments, it decreases rapidly during early eogenesis as humic substances form, then increases during catagenesis with the formation of hydrocarbons from the cracking of kerogen. At higher diagenetic levels the loss of aliphatic, alicyclic and low molecular weight aromatics and the formation of the relatively less soluble large, multi-ring aromatic compounds results in the progressive decline of EOM/TOC. The method is limited by the dependence of the EOM/TOC ratio

not only on the level of diagenesis but also on the type of organic matter present. In addition, the ratio will decrease during catagenesis if hydrocarbons migrate out of their source rocks. To compensate for some of these problems, the ratios of aromatics to saturated hydrocarbons and of aromatics to total EOM have been used (Albrecht *et al.*, 1976); both ratios increase with increasing levels of diagenesis, but are affected by the type of kerogen present. These ratios are most significant if used in a sequence of strata of constant kerogen type, where values from different stratigraphic levels, or from a given stratigraphic unit down into or across a basin, can be compared.

**Carbon Preference Index.** Carbon preference index (CPI) is the ratio of odd carbon number to even carbon number n-alkanes in extractable organics. During eogenesis CPI is controlled by the alkane ratio present in precursor organisms (Barnes and Barnes, 1978). While most higher plants and algae have a large odd CPI, some marine sponges, freshwater aquatic plants, ferns, lycopods, fungi, yeasts and bacteria have small odd carbon preferences. Hydrocarbons from the cuticles of higher plants range from n-C<sub>23</sub> to n-C<sub>28</sub>, with n-C<sub>25</sub> or n-C<sub>27</sub> dominant; ferns, lycopods, fungi, yeasts and bacteria commonly have a broader carbon range. Algae have major components at n-C<sub>17</sub>, n-C<sub>17:1</sub> (heptadecane with one double bond), n-C<sub>15</sub> or n-C<sub>13</sub> (Gelpl *et al.*, 1970). Fungi have n-C<sub>25</sub> dominant, while yeasts and bacteria show both unimodal and bimodal distributions with both n-C<sub>19</sub> and n-C<sub>27</sub> as dominant hydrocarbons (Weete, 1974; Bird and Lynch, 1974). During eogenesis, the CPI approaches unity in hydrocarbons altered by the aerobic and anaerobic decay of algae (Cranwell, 1976). Cranwell suggested that both an odd-even index near unity and an increase in hydrocarbons in the region of n-C<sub>19</sub> to n-C<sub>25</sub> are indicators of microbial alteration. Brooks *et al.* (1976) found that the method of extraction can influence carbon preference index. Hydrocarbons released by a simple solvent extraction at a nearly neutral pH had a large even CPI, reflecting higher plant sources, whereas those bound into microbial cell walls and released only by acid hydrolysis of sediments have much smaller odd-carbon preferences, reflecting bacterial alteration. As catagenesis progresses, thermal degradation of kerogen generates alkanes with no odd-even preference, so the CPI of extractable hydrocarbons approaches unity. Thus, CPI may be used as an indicator of maturation (Fig. 1).

**Light Hydrocarbon Analysis.** The abundance and type of light hydrocarbons, defined as having between one and eight carbon

atoms, have been found to reflect the level of diagenesis. As living organisms produce few light hydrocarbons except for methane (Oremland *et al.*, 1982), most hydrocarbons in the C<sub>2</sub> through C<sub>8</sub> range reflect the diagenetic level of the kerogen in the rocks. Light hydrocarbons are commonly divided into two groups by petroleum chemists: C<sub>1</sub> through C<sub>4</sub> gases from head space gases or drill cuttings, and gasoline range (C<sub>5</sub> through C<sub>8</sub>) compounds from cores and cuttings. At low diagenetic levels (eogenesis), the light gases consist mainly of biogenic methane and gasoline range hydrocarbons are minor or absent (Leythaeuser *et al.*, 1979). At the diagenetic level of oil generation the light gases contain a great many compounds in the C<sub>2</sub> through C<sub>4</sub> range, whereas at the metagenic level methane is again the dominant gas (Fig. 1) and gasoline range hydrocarbons are minor. Bailey *et al.* (1974) used such methods in their evaluation of maturation in western Canada. The ratio of C<sub>2</sub> through C<sub>4</sub> gases to total gases (C<sub>1</sub> through C<sub>4</sub>) has also been found to indicate diagenetic level, and was used in maturation studies in the Canadian Arctic (Snowdon and Roy, 1975; Monnier *et al.*, 1983); a number of other ratio methods for gasoline range hydrocarbons have also been used to assess maturity and migration (Thompson, 1979; Snowdon and Powell, 1982).

Light gases are extracted from cuttings or core samples by heating, treatment with acid or mechanical disaggregation in a blender, followed by collection of the gases from the head space above the sample and analysis by gas chromatography.

As a measure of diagenesis, light hydrocarbon analysis has the advantages that both extraction and analysis are rapid, requiring only simple techniques, and can be applied over a wide diagenetic range. The method lacks precision, however, and is influenced by migration. The best results are obtained when a sequence of strata are examined.

### Geochemistry of Kerogen

**Pyrolysis.** Pyrolysis involves heating a sample at a pre-selected rate in an inert atmosphere and monitoring the type and amount of gases which evolve. A number of methods of determining diagenetic level from pyrolysis products have been proposed. One such method is based on the Rock-Eval instrument (Espitalié *et al.*, 1977a, 1977b), which is essentially a furnace with an on-line gas chromatograph. The analysis simulates maturation (diagenesis) by progressively heating rock samples to temperatures up to 550°C. Three types of gases have been recognized, based on the temperatures at which they are evolved: (S<sub>1</sub>) hydrocarbons already present in the sample, which are evolved below

300°C; ( $S_2$ ) hydrocarbons generated by thermal cracking between 300°C and 550°C; and ( $S_3$ )  $CO_2$  (Fig. 8). The level of diagenesis is obtained from the  $S_1/S_2$  ratio and the temperature at which maximum generation of  $S_2$  occurs. A plot analogous to a "van Krevelen" diagram (atomic H/C versus O/C; Barnes *et al.*, 1984) is obtained by using the "hydrogen index" ( $S_2/TOC$ ) versus the "oxygen index" ( $S_3/TOC$ ), and can be used to estimate both the kerogen type and the degree of maturation. The production index, defined as  $S_1/(S_1 + S_2)$ , increases with depth as the amount of free hydrocarbons ( $S_1$ ) increases. The production index thus increases with the level of diagenesis.

The advantages of the Rock-Eval method are that no sample preparation is required and that level of diagenesis, oil and gas potential and hydrocarbons already present are all determined. Disadvantages include problems associated with mixed kerogen types of varying chemistry and with the presence of carbonates, which evolve  $CO_2$  during pyrolysis.

**Ultimate Analysis.** "Ultimate" analysis involves the determination of the elemental C, H and O content of rocks, commonly by use of a C-H-N analyzer. H/C and O/C ratios are plotted against one another to give a "van Krevelen" diagram which can then be used to determine both kerogen type and level of diagenesis. During eogenesis oxygen is lost as  $CO_2$  and  $H_2O$ ,

which results in a decrease in the O/C ratio with little corresponding change in the H/C ratio; catagenesis results in a rapid loss of hydrogen in the form of hydrocarbons, causing a decrease in the H/C ratio.

The advantage of ultimate analysis is that it provides both a measure of diagenetic level and kerogen type. The disadvantages are that kerogen must be separated before analysis by using HCl and HCl/HF digestion of mineral matter and, less commonly, by specific gravity or hand picking methods. Mixed kerogen types also give results that are difficult to interpret, and the method lacks accuracy.

**Infrared Spectroscopy.** The infrared spectroscopy of kerogen enables the quantification of the main functional groups present. As the level of diagenesis increases there is a progressive loss of carboxyl and carbonyl groups, a loss of saturated hydrocarbons, the formation and removal of aromatic C-H groups, and the evolution of hydroxyl and ether groups (Rouxhet *et al.*, 1980). Quantification of these groups gives a measure of the level of diagenesis attained and of kerogen type, as the initial proportions of these groups is a function of the precursor organisms. The advantage of the method is that sample preparation, apart from isolation of the kerogen, is simple. The kerogen is separated and then pressed into a KBr pellet which is used in the infrared spectrophotometer. Only a few hundred

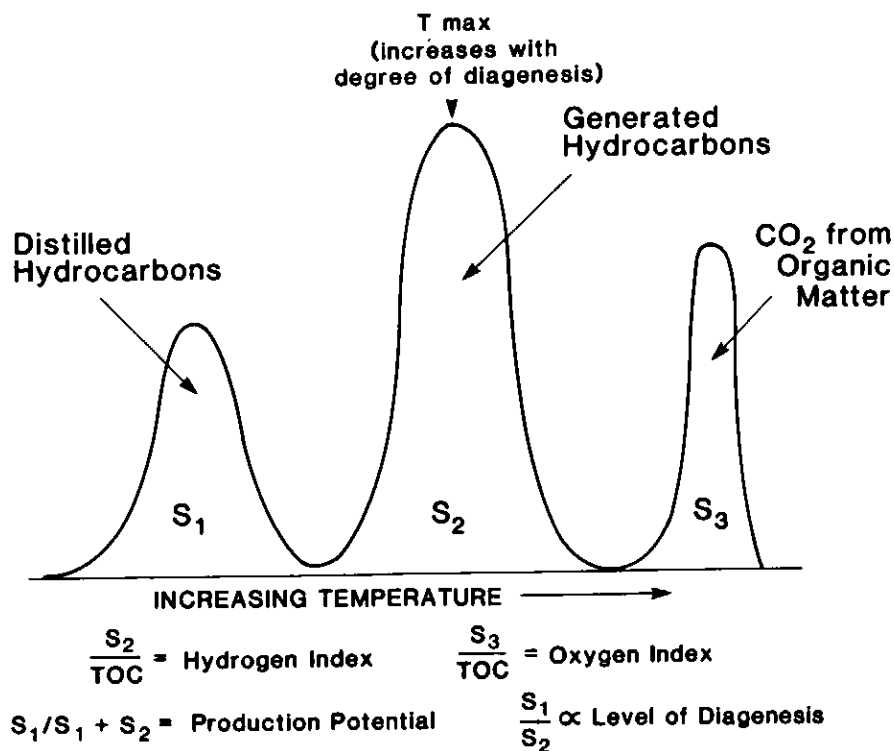
milligrams of kerogen are required for the analysis. The disadvantages of the method are that it is only semi-quantitative and is not widely used.

**Electron Paramagnetic Resonance.** Electron paramagnetic resonance (EPR) studies of kerogen assess the presence of free radicals (polyatomic moieties with unpaired electrons). All kerogens give EPR spectra that depend on the type of kerogen and the level of diagenesis. With increased diagenetic level the number of free radicals first increases to a maximum and then declines because of recombinations that occur as the mean distance between the radical groups decreases. The diagenetic level at which free radicals are at a maximum varies with the type of kerogen.

An advantage of EPR is that it is non-destructive, but the technique has several disadvantages. The kerogen must be separated carefully from the rest of the rock; impurities such as trace metals affect the spectra. Also, the type of kerogen affects its EPR spectrum, and the EPR signal decreases over long periods of geologic time and in post-mature rocks as free radicals combine (Brooks, 1980).

**Carbon Isotope Studies.** The stable carbon isotope composition reflects both the initial  $\delta^{13}C$  value of the organic source material (DeNiro, 1983) and the isotopic fractionation that takes place during diagenesis (Hayes, 1983). During thermal cracking there is a preferential breaking of  $^{12}C$ - $^{12}C$  bonds with respect to  $^{12}C$ - $^{13}C$  bonds, so that the remaining kerogen is enriched in  $^{13}C$ , whereas the expelled liquids and gases have more  $^{12}C$ . As thermal cracking continues, the reservoir of isotopically light methyl groups is depleted and more of the heavier methyl groups are subject to cracking. As a result the  $\delta^{13}C$  of methane generated at higher levels of diagenesis increases, and the difference in isotopic composition between the gases and the original kerogen decreases. The utility of carbon isotopic analyses in organic maturation studies has not yet been fully evaluated; however, the trend toward lighter (more negative) values for gas relative to oil, which in turn is lighter than source rock kerogen, is widely used for oil-source rock correlation.

**Proximate Analysis.** Proximate analysis determines the fixed carbon, ash, volatile and moisture contents of kerogen-containing rocks. The technique has been used most extensively for the analysis of coals, but can also be used on kerogen separated from other rocks. With an increasing level of diagenesis there is an increase in fixed carbon and a corresponding decrease in volatiles and moisture in the organic matter. Proximate analysis involves heating the



**Figure 8** Rock-eval pyrolysis products. The three gas pulses shown can be used to characterize the kerogen type present, the level of

organic diagenesis and the type of hydrocarbons the kerogen will yield. Modified from Espitalié and others (1977a) and Milner (1982)

sample to a low temperature (about 110°C) to determine moisture, heating to intermediate temperatures in an inert atmosphere to determine volatile content, followed by heating to high temperatures in a stream of oxygen to oxidize all remaining organic matter so that the residual ash may be determined. Fixed carbon is determined by difference. The method has been used for many years for analysis of coal and is widely accepted, well documented and standardized (ASTM D3172-73, 1979). The disadvantages of the method are that the technique is useful only for organic-rich rocks, such as coals, and for kerogen separates. Kerogen type affects the results and, while this is not a significant factor in coals, which are generally composed mainly of type 3 kerogen, other organic rocks commonly contain a mixture of kerogen types, leading to results that are difficult to interpret.

**Caloric Value.** The caloric (heating) value of organic matter increases at higher levels of diagenesis in response to decreased moisture and volatile content and increased relative amounts of fixed carbon. Caloric value is generally determined with a bomb calorimeter; it is commonly used as a technique for determining coal rank, but can be used to determine the diagenetic level of any organic rich rock. The method has the advantage that it is standardized (ASTM D2015-77, 1974) and has been widely applied to coals. Disadvantages of the method include the necessity for correcting for mineral matter in the rocks and that kerogen type influences caloric value, a significant factor for rocks other than coal.

**Other Methods.** A number of other techniques, such as nuclear magnetic resonance, proton magnetic resonance, differential thermal analysis, fluorescence spectra of extractable organics and thermogravimetric analysis, have been used in maturation studies. The applicability of these methods has not been fully evaluated, however, and they are not widely used.

**Correlation Between Diagenetic Indicators.** The correlation between the main diagenetic indicators discussed in this review is shown in Table I and Figure 1. All relationships are based on established or estimated correlations with vitrinite reflectance.

**Predictive Diagenetic Models**

Models to predict the levels of organic diagenesis attained with depth were initially developed to determine the occurrence of the liquid (oil) window in time and space (Landes, 1967) or the degree of coalification (Karweil, 1956). Subsequent studies have shown that the level of organic diage-

nesis, when interpreted in the context of burial history, can be used to interpret the thermal history of strata. Early studies assigned particular temperatures to the liquid window. It is now widely recognized (but see Neruchev in Bostick, 1979) that the thermal history (both temperature and time) must be considered. Numerical models and graphical techniques have been developed to predict organic maturation from an assumed thermal history or to determine the thermal history from measured levels of organic diagenesis.

Models of organic diagenesis fall into two broad groups, numerical models and comparative models. Numerical models are based on reaction kinetics, whereas comparative models utilize established relationships between diagenetic level and known thermal history in one set of strata to predict either the thermal history or levels of diagenesis in another set of strata where the diagenetic levels have been measured or which are known to have had a similar thermal history. Comparative models also can be used to extrapolate measured levels of diagenesis to higher or lower strata.

**Numerical Models.**

**Graphical Methods.** Models developed to predict levels of organic diagenesis during a predetermined or assumed thermal history are based on first order reaction kinetics, and thus approximate the Arrhenius equation (Huck and Karweil, 1955):

$$K = A \exp(-ERT)$$

where K = reaction rate  
 A = a frequency factor  
 E = activation energy  
 R = gas constant  
 T = absolute temperature

Huck and Karweil (1955) assumed an activation energy of 35 kJ mol<sup>-1</sup> for the entire range of coalification (for a complete discussion and solution of the Arrhenius equation see Weite and Yukler, 1980). Karweil (1956) combined empirical rank data (diagenetic level) and theoretical calculations to relate the level of coal diagenesis to thermal history (Fig. 9). This relationship between rank and thermal history subsequently has been modified (Bostick, 1973) to better fit established relationships. Bostick (1973) suggested that the activation energy used by Huck and Karweil (1955) predicts too fast a reaction rate for coalification at low levels of diagenesis (R<sub>o</sub> < 0.6) and too slow a rate at higher levels.

Bostick (1973; 1979) adapted Karweil's (1956) method to regions with varied thermal histories. Castano and Sparks (1974) and Hood *et al.* (1975) proposed a graphical relationship between thermal history and an arbitrary scale of diagenesis to define a "Level of Organic Maturation" (LOM). They further suggested the use of an "effective heating time", which they defined as the time during which the rock is within 15C of its maximum temperature, in predicting the level of diagenesis. Shibaoka and Bennett (1977) used a graphical technique similar to that of Hood *et al.* (1975), but related thermal history directly to vitrinite reflectance rather than to LOM.

**Numerical Calculations.** From a consideration of first order reaction kinetics (Arrhenius equation) and from empirical data on activation energies, Lopatin (1971; see also Lopatin and Bostick, 1974; Waples, 1980; Cohen, 1981) showed that the rate of maturation doubles with every 10°C in-

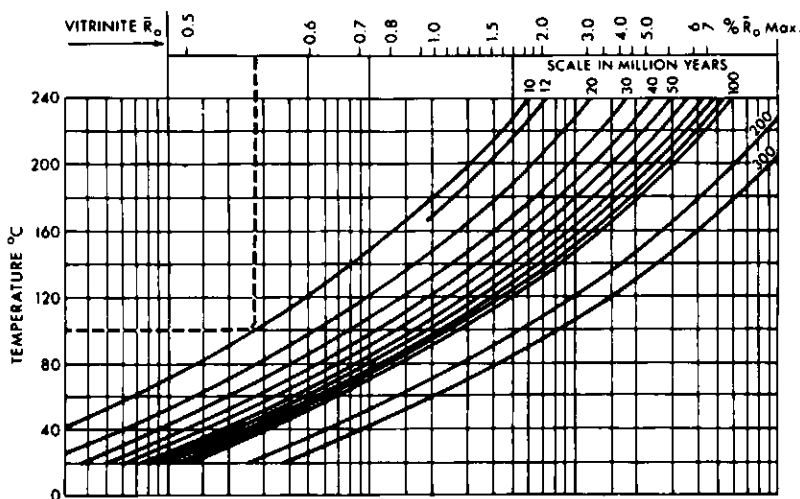


Figure 9 Correlation between temperature, time and level of organic diagenesis (mean maximum vitrinite reflectance, R<sub>o</sub>). The dashed line shows an example in which organic matter exposed to

temperatures of 100°C for 10 Ma would have an expected level of maturation equivalent to an R<sub>o</sub> of 0.56%. Modified from Bustin *et al.* (1977)

crease in temperature (an exponential relationship) but increases only linearly with time. Lopatin's method calculates interval maturation by integrating the length of time spent by the stratum in each 10°C temperature interval. The total maturation (diagenesis) is the sum of the interval maturation:

$$TTI = \sum_{n_{min}}^{n_{max}} (\Delta T_n)(r^n),$$

where TTI = time-temperature index

$n_{max}$  = highest 10°C interval

$n_{min}$  = lowest 10°C interval

$\Delta T$  = time (Ma) spent by strata in each 10°C interval

$r = 2$ ; assuming rank doubles for each 10°C rise in temperature.

Lopatin (1971) set  $n = 1$  for the 100°C to 110°C interval. At lower temperatures  $n$  is zero or negative, and at higher temperatures  $n$  is greater than 1. Lopatin's method enables periods of uplift and subsidence to be considered, so that the entire thermal history is used in calculating the maximum level of diagenesis attained by a stratigraphic horizon that was deposited at time = 0. For calculations by computer the following generalized relationship is more suitable (McKenzie, 1981):

$$TTI = \int_a^b 2^{(T(t) - 105)/10} dt$$

where  $T(t)$  is temperature (°C) as a function of time ( $t$ ) from the time of deposition ( $t_0$ ) to the present ( $t_p$ ).

Using the data presented by Waples (1980), the following relationship between TTI and mean maximum vitrinite reflectance may be defined:

$$R_o = -0.10528 \log TTI + 0.20647(\log TTI)^2 + 0.5011 \quad (r^2 = 0.99)$$

$R$  is not defined by this equation if TTI values are less than 3. An examples of Lopatin's method is shown in Figure 10.

Middleton (1982) proposed a method of calculating levels of organic diagenesis from thermal history based on the graphical procedures of Hood *et al.* (1975) and Shibaoka and Bennett (1977). Middleton (1982) related mean maximum vitrinite reflectance to thermal history by:

$$R_o^a = R_{int}^a + bt \exp(cT)$$

where  $a = 5.5$

$b = 2.8 \times 10^{-6}$

$c = 0.065$

$t$  = age of strata, Ma

$T$  = temperature, °C as a function of time

$R_{int}$  = initial reflectance (0.2 assumed)

This relationship results in an increase in maturation rate of 1.92 for each 10°C increase in temperature, whereas the Lopatin method results in an increase of 2 (a doubling of maturation rate). Middleton's equation can be solved in a manner analogous to the Lopatin method.

Using numerical models of maturation such as those outlined above, it is possible to predict the approximate level of maturation from thermal history of the strata (Fig. 10). Predicting the thermal history from a single maturation level is difficult because many combinations of time and temperature will yield the same maturation level. Where measured maturation levels are available through a stratigraphic succession, however, they can be compared to calculated maturation gradients (rather than a

single point) to infer the thermal history. This method involves calculating maturation gradients using a range of geothermal gradients or depths of burial and matching the calculated curves with the measured curves (Fig. 11). Using this method, it is possible to estimate paleogeothermal gradients (or paleo-heat flow) irrespective of the absolute level of maturation. Such a method has been used by Bustin (1984) to estimate paleo-heat flow in the Bowser Basin of northern British Columbia.

The vitrinite maceral is the product of many chemical reactions, which act at different rates on a complex mixture of organic compounds. Its reflectance is a physical property which develops as the sum of all these temperature-dependent reactions, and thus is affected by differ-

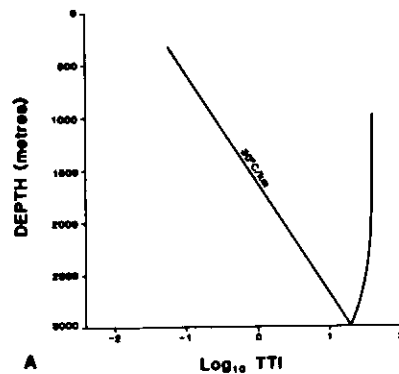
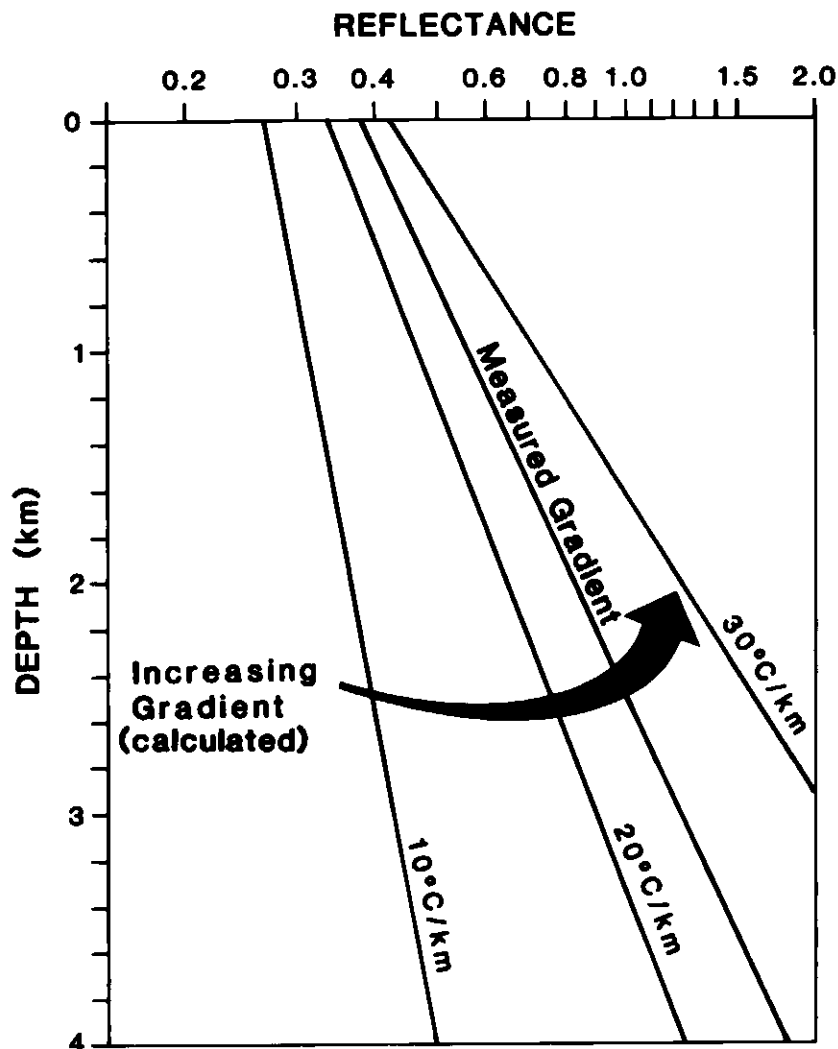


Figure 10 Lopatin's method of predicting organic maturation. (A) shows the burial history of a hypothetical rock that was deposited at 140 Ma, buried to 3000 m by 60 Ma, followed by uplift to 1000 m by time = 0. (B) shows the method of incrementally calculating maturation using Lopatin's formula (see text) for the burial history shown in (A). With a constant geothermal gradient of 30°C/km and a surface temperature of 20°C, the present maturation of the rock would be 39.6 TTI or 0.86%  $R_o$ . If the oil window is assumed to occur between 0.50% and 1.35%  $R_o$  (Dow, 1977), then the rock entered the oil window at a depth of about 2600 m at 72 Ma and still lies within the oil window.

Interval °C	$r^n$	Interval TTI	Cumulative TTI	Time in Ma B.P.	Hydrocarbon Generation
20.0-30.0	2 <sup>-8</sup>	0.04	0.0	140.00	Immature
30.0-40.0	2 <sup>-7</sup>	0.08	0.1	130.00	
40.0-50.0	2 <sup>-6</sup>	0.16	0.3	120.00	
50.0-60.0	2 <sup>-5</sup>	0.31	0.6	110.00	
60.0-70.0	2 <sup>-4</sup>	0.63	1.2	100.00	
70.0-80.0	2 <sup>-3</sup>	1.25	2.5	90.00	
80.0-90.0	2 <sup>-2</sup>	2.50	5.0	80.00	
90.0-100.0	2 <sup>-1</sup>	5.00	10.0	70.00	Oil Window
100.0-110.0	2 <sup>0</sup>	10.00	20.0	60.00	
110.0-100.0	2 <sup>0</sup>	10.00	30.0	50.00	
100.0-90.0	2 <sup>-1</sup>	5.00	35.0	40.00	
90.0-80.0	2 <sup>-2</sup>	2.50	37.5	30.00	
80.0-70.0	2 <sup>-3</sup>	1.25	38.7	20.00	
70.0-60.0	2 <sup>-4</sup>	0.63	39.3	10.00	
60.0-50.0	2 <sup>-5</sup>	0.31	39.6	0.0	

Total Maturation = 39.6 TTI  
Equivalent Reflectance = 0.86  $R_o$



**Figure 11** Method of predicting paleogeothermal gradients or paleo-heat flow based on organic maturation. Maturation gradients are calculated iteratively using a Lopatin-type method with varying temperatures, subsidence rates, etc. until the slope (in metres/log cycle) of the calculated

gradient is the same as the measured gradient. In the example shown, the paleo-geothermal gradient would be between 20°C and 30°C. The method requires knowledge of the burial history of the strata

ences in source materials and their reaction rates, as well as by temperature history (Jones *et al.*, 1984). As a result, calibration of vitrinite reflectance scales is empirical, and differs from basin to basin. By selecting specific chemical reactions as a basis for modelling, Mackenzie and McKenzie (1983) developed a model which reflects kinetic effects of thermal diagenesis in stretched basins but is independent of variations in depositional history or in organic precursors. An intramolecular chemical change which is temperature dependent but independent of the source or of other chemical reactions is measured for single chemical compounds.

Side chain isomerization in steranes and hopanes and the shift from monoaromatic

[M] to triaromatic steranes [T] are used to monitor the subsidence and thermal history of stretched basins in the North Sea and the Pannonian Basin (Hungary), and to model subsidence and subsequent uplift in the Lower Saxony Basin (West Germany) and the Paris Basin (France). Three reactions which occur prior to and during the early stages of oil formation were selected:

(1) the shift from *R* to *S* at C-20 in the C<sub>29</sub> sterane (Fig. 4: 2f goes to 2l); (2) the shift from *R* to *S* at C-22 in the αβ-C<sub>22</sub> hopane (Fig. 4: 12q goes to 12r); and (3) the shift from the 5α or 5β C<sub>29</sub> monoaromatic (Fig. 4: 4f) to the C<sub>29</sub> triaromatic steranes (Fig. 4: 5f). These three reactions fit the following assumptions reasonably well: (1) initial concentrations of thermal products

are small or negligible in immature sediments; (2) thermal alteration spans the oil window; (3) a single reactant gives rise to a single product in a unimolecular first order reaction which follows Arrhenius' Law; (4) the reactions are free of matrix effects; if mineral catalysis occurs, the number of active sites is assumed to be large relative to the concentration of reactant and the reaction is pseudo first order. While the side chain isomerizations are reversible, the aromatization is irreversible. Activation energies (*E*), and frequency factors (*A*), are derived from Arrhenius' plots of the logarithm of the rate constants versus the reciprocal of the borehole temperatures. Rate constants (*k*) and gamma, the ratio of the forward to reverse reaction for side chain isomerizations, are derived from the ratio of products to reactants measured by GC-MS for samples from the North Sea and the Pannonian Basin. Kinetic parameters are estimated as:

$$A = 1.8 \cdot 10^{14} \text{ s}^{-1} \quad E = 200 \text{ kJ mol}^{-1} \text{ for the aromatization;}$$

$$A = 0.006 \text{ s}^{-1} \quad E = 91 \text{ kJ mol}^{-1}$$

$$\gamma = 1.174 \text{ for side chain isomerization in steranes;}$$

$$A = 0.016 \text{ s}^{-1} \quad E = 91 \text{ kJ mol}^{-1}$$

$$\gamma = 1.564 \text{ for side chain isomerization in hopanes.}$$

Temperature was calculated from equations for the variation in temperature in a subsiding basin (McKenzie, 1978; Mackenzie and McKenzie, 1983) with heat flux, time, depth, the quartz-clay content and estimates of the extension factor ( $\beta$ ) from sediment thickness (Sclater and Christie, 1980; Wood, 1981; McKenzie, 1981). Kinetic parameters for the chemical reactions are independent of basin history, while calculated temperatures are dependent on basin age and extension. These values are used to generate theoretical curves for isomerization relative to aromatization from equations for the change in rates with temperature and time in a subsiding basin. The fit of observed values for the extent of reaction and borehole temperatures or depth are shown for the North Sea (Fig. 3D) and the Pannonian Basin of Hungary (Fig. 3C). Plots of hopane relative to sterane isomerization are independent of the basin thermal history.

Mackenzie and McKenzie's model has the advantage that it is based on kinetics that measure rates for known single reactions, rather than on the unknown multiple reactions that cause changes in vitrinite reflectance. By using pairs of reactions, it is possible to determine uniquely the entire time-temperature history of a basin, including not only its development but also subsequent uplift after extension. As a result, the time of hydrocarbon generation

may be determined and compared with the time of formation of suitable traps, creating a powerful tool for petroleum exploration.

**Comparative Methods.** Comparative methods have been used to establish either levels of organic diagenesis if thermal history is known or assumed, or thermal history if the level of organic diagenesis is known. These methods are based on the premise that a given thermal history will result in particular levels of diagenesis, and have been used mainly to compare geothermal gradients in different areas. Hacquebard and Donaldson (1974), for example, compared the coalification (diagenetic) gradients of strata from the Canadian Rocky Mountains and Foothills with the gradients established in the Peel area of the Netherlands. Bustin *et al.* (1977) noted the similarity of coalification gradients of Tertiary strata from the Canadian Arctic with those of the T jon area of California reported by Castano and Sparks (1974). Because of the similar burial histories of strata in both areas, Bustin *et al.* (1977) assumed that the paleogeothermal gradient in the Arctic was similar to the known geothermal gradient of the T jon area.

Similar methods were used by Buntebarth (1978) in the upper Rhine graben and by Barker and Elders (1979) in the Cerro Prieto geothermal field. In both studies known temperatures and coalification levels from boreholes were used to develop general relationships between thermal history and coalification levels, so that the thermal histories of adjacent areas can be interpreted.

On the assumption that changes in level of diagenesis with depth are predictable, a number of studies have extrapolated measured diagenetic gradients to higher or lower stratigraphic levels. This method was applied by Hacquebard (1977) to calculate the amount of overburden that had been removed by erosion from the Mannville coals in southern Alberta. Hacquebard extrapolated the moisture content of the coals at the surface to that prior to burial, based on assumed changes in moisture content with depth.

### Summary

Quantification and modelling of organic diagenesis have proven to be useful in assessing petroleum source rocks, coal rank and thermal history of strata. A large number of methods have been utilized to quantify organic diagenesis. Almost all involve detailed and generally expensive analytical procedures and require isolation, or at least concentration, of either the kerogen or bitumen prior to analysis. At present, the most widely accepted and precise methods are petrographic: vitrinite reflectance, fluorescence and kerogen colour. Of these,

fluorescence microscopy and kerogen colour are useful only for a limited range of diagenesis (less than 1.2%  $R_o$ ), and vitrinite reflectance, although useful for the entire range of diagenesis, has its greatest utility only in Carboniferous and younger strata.

A large number of geochemical methods have been proposed. Of these, ultimate analysis, proximate analysis and calorific value are best suited to coal, where the relative abundance of kerogen is high. One of the most useful methods of evaluating finely dispersed organic matter is by the pyrolysis method proposed by Espatali  *et al.* (1977a, 1977b), which provides an indication of diagenetic level and kerogen type without requiring concentration of the organics. A number of geochemical techniques, such as carbon preference index (CPI), total extractable organics and light hydrocarbon analysis, are influenced by the type of organic matter present and by migration, and thus are most useful for resolving the relative degree of diagenesis in a stratigraphic succession. While isolation and identification of individual organic compounds are more expensive and time consuming than measurement of vitrinite reflectance, biological markers can be used for a more sensitive assessment of diagenesis, especially at low and intermediate levels of maturity. In addition, they are now commonly used in oil-source rock correlation and as measures of thermal maturation, migration and biodegradation. Geochemical techniques which have not been totally assessed as to their utility as diagenetic indicators include infrared spectroscopy, electron paramagnetic resonance, nuclear magnetic resonance and carbon isotopes. Such methods require highly specialized equipment that is not readily available outside major research centres.

Models of organic diagenesis have been developed to predict levels of organic diagenesis and have also been used to interpret thermal history of strata where the level of diagenesis is known. Although the accuracy of the models has not been fully tested, it is now possible to predict diagenetic levels and thermal history which compare favourably with measured values. One of the most useful methods is that initially proposed by Lopatin (1971), which predicts that the level of diagenesis increases exponentially with temperature and linearly with time.

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