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Diagenetic Modification of Kerogens [and Discussion]

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Diagenetic modification of kerogens

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[Plate 1]

Kerogen is the part of sedimentary organic matter that is not petroleum. It can be isolated by using acid destruction of minerals, except in recent sediments where this procedure results in important hydrolysis reactions. Whether the scale of observation is microscopic or molecular, kerogens are heterogeneous mixtures whose compositions vary according to the sedimentation medium. However, they can be globally characterized by their H:C and O:C ratios.

Diagenetic modification is a thermodynamically oriented process that consists of passing from complicated chemical structures inherited from living organisms or created during sedimentation to simple stable molecules. However, it is kinetically controlled by the thermal history of the sediment during burial. Three main steps are distinguished.

(i) Diagenesis, where O:C decreases and CO_2 and H_2O are released.
(ii) Catagenesis, where H:C decreases and petroleum and then gas are produced.
(iii) Metagenesis, which consists of structural reorganization of the carbonaceous residue with little change in the elemental analysis.

Modification can be followed by observing characteristic changes in physical and chemical properties.

Definition of kerogen

The etymological meaning of kerogen is 'generating wax' (the Greek *keros* means wax). The word was coined by A. Crum-Brown (Stewart 1916) to name the organic matter of the oil shale of the Lothians (Scotland), which produces a waxy oil after pyrolysis.

After the work of Forsman & Hunt (1958) and Durand (1980), it is now the usual practice for organic geochemists to give a name to the fraction of sedimentary organic matter that is insoluble in the usual organic solvents (this includes all types of sediments, even coals). The soluble part is called bitumen. This can be treated as a concept of petroleum geochemistry, because bitumen contains mainly extractable hydrocarbons and soluble NSO compounds (i.e. roughly a petroleum composition), while kerogen is roughly the part of sedimentary organic matter that is not petroleum.

A good study of kerogen first requires a good isolation from the mineral matrix. Dancy & Giedroyc (1950) developed a method for this by using acid destruction of minerals; hydrochloric acid for carbonates and hydrofluoric acid for silicates. Some minerals are not destroyed, the most common of these being pyrite.

Extraction of bitumen may be performed either before or after acid attack but is more efficient if performed afterwards. This procedure has little effect on kerogens, except at the recent sediment and early diagenesis stages where a large part of the kerogen is hydrolysed by the acids. Therefore kerogen at these stages cannot be efficiently isolated and its study is particularly difficult.

RELATIONS BETWEEN PETROLEUM AND KEROGEN

Studies of many sedimentary basins have resulted in the proposal of a general scheme of petroleum formation in sediments (figure 1). This formation generally proceeds at depths greater than 1 km and is insignificant at lesser depths (Tissot & Welte 1978). Therefore, at the recent sediment stage, sedimentary organic matter consists primarily of kerogen. Like living organisms, this early kerogen is composed mainly of carbon, hydrogen and oxygen, although in different proportions. Unlike living organisms the kerogen contains little nitrogen and may contain a relatively large proportion of sulphur.

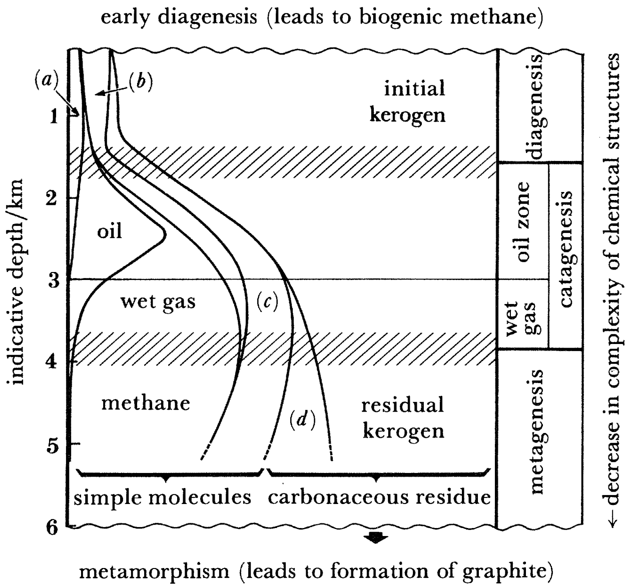

FIGURE 1. General scheme of the diagenetic modification of sedimentary organic matter in a sediment column; (*a*) biomarkers, (*b*) soluble NSO compounds, (*c*) CO_2, H_2O, H_2, N_2, (*d*) neoformed kerogen (pyrobitumen).

Kerogen originates in organic debris that has been reworked by organisms living at the water–sediment interface. The largest part of the initial organic input is destroyed by this biochemical activity. In strictly anaerobic environments, the biochemical activity may result in methane formation by methanogenic bacteria (biogenic methane). In marine environments, when sulphates are dissolved in water, hydrogen sulphide may be produced by sulphate-reducing bacteria. Action of hydrogen sulphide on kerogen results in incorporation of sulphur. This is the explanation given for the high sulphur contents of some kerogens.

At the recent sediment stage bitumen, which is only a small part of the organic matter content of the sediment, contains mainly lipophilic heteroatomic molecules such as esters and fatty acids and very few hydrocarbons. These hydrocarbons are biomarkers, i.e. their chemical structures are obviously derived from biomolecules.

When depth of burial increases, the proportion of kerogen in the organic matter decreases as hydrocarbons and other soluble or volatile molecules are progressively formed. This is mainly a result of the thermal degradation of kerogen as the temperature increases.

Three successive steps, which have some extent of overlap, are distinguished. Tissot & Welte (1978) termed them diagenesis, catagenesis and metagenesis.

During diagenesis, very few hydrocarbons are formed. This step is also called the immature stage. Oxygenated molecules, mainly water and carbon dioxide but also soluble heavy heteroatomic molecules belonging to the classes of resins and asphaltenes, are produced. This formation is balanced by a loss of oxygen in the kerogen.

Catagenesis is the main stage of hydrocarbon formation. This requires hydrogen, so kerogen loses hydrogen and its aromaticity increases. The mean molecular mass of these hydrocarbons decreases progressively as more and more intense cracking of the hydrocarbons already formed and of the remaining kerogen occurs. As a result, oil (liquid hydrocarbons) and wet gas (gas containing liquid hydrocarbons) are successively observed. Formation of gas needs a large quantity of hydrogen and is balanced by the transformation of part of the hydrocarbons into a hydrogen-poor and therefore highly aromatic residue, analogous to the coke that is formed in pyrolysis of organic molecules, and called pyrobitumen. This pyrobitumen is largely insoluble in organic solvents and therefore belongs to the kerogen category, although it is genetically different.

Metagenesis is a step where few hydrocarbons are formed from the kerogen, which has lost most of its capacity to produce hydrocarbons in the preceding stage. The hydrocarbon formed is mainly methane. Methane is also formed in large quantities from the hydrocarbons formed earlier. Metagenesis is the stage of methane formation that results in acceleration of pyrobitumen formation. Residual kerogen and pyrobitumen evolve towards a very hydrogen-poor carbonaceous residue.

All these modifications take place before mineral metamorphism, where eventually graphite may be formed from the carbonaceous residue.

The general trend of this evolution is to produce highly aromatic residues and simple gaseous molecules that are thermodynamically stable in the subsurface conditions from complex and thermodynamically unstable molecules. The latter are produced at the water–sediment interface by biochemical and physicochemical action on sedimenting organic debris. The role of temperature is to accelerate the evolution towards thermodynamic stability. It is thought at the present time that neither pressure nor the catalytic effect of minerals can modify substantially the evolution pathways and therefore the formation of petroleum and gas from kerogen is mainly a question of temperature, time and initial composition of kerogen and can be described in terms of kinetics. It can be formalized by simple kinetic equations that describe fairly well the observations made in sedimentary basins (Tissot 1969; Tissot & Espitalié 1975).

Kerogen in source rocks and in reservoir rocks

The accumulation of kerogen and subsequent petroleum formation takes place mainly in fine-grained sediments such as clays, marls and some carbonates. This is partly because hydrodynamic conditions are more favourable to sedimentation of organic debris in low-energy than in high-energy media. Also, fine-grained sediments have low permeabilities that restrict the availability of oxygen dissolved in water and therefore activity of aerobic organisms in the vicinity of organic debris. Destruction of organic debris is much less complete in anaerobic conditions than in aerobic ones. In coarse-grained sediments, the availability of dissolved oxygen is not restricted and organic debris, if eventually deposited, will be completely destroyed.

After its formation at depths in source rocks, petroleum may migrate towards coarse-grained sediments that become reservoir rocks. Eventually, further cracking of petroleum in these reservoir rocks will result in the formation of gas and pyrobitumen.

HETEROGENEITY AND VARIETY OF KEROGENS

A variety of initial kerogens is possible depending on the nature of the initial biomass and the conditions of sedimentation. Initial biomasses can be placed in two main categories; (i) the planktonic biomass (mainly phytoplankton) in seas and lakes and (ii) the higher plant biomass on land.

Generally, kerogen derived from higher plant biomass (terrestrial or continental kerogen) is richer in oxygen and poorer in hydrogen than kerogen derived from planktonic biomass (marine or lacustrine kerogen). This is because land plants are rich in ligno-cellulosic parts that contain relatively little hydrogen and also because sedimentation of land-plant debris first needs transportation in a sub-aerial oxidizing medium.

The conditions of sedimentation and especially the redox properties of the sedimentation medium that orientate the biochemical activity towards aerobic or anaerobic conditions are also important for the initial chemistry of kerogen. In particular, whatever the initial biomass, oxidizing conditions will result in impoverishment in hydrogen and enrichment in oxygen. This will be more visible in kerogens of planktonic origin than in kerogens of higher plant origin that are already oxidized. This influence of the sedimentation medium may cause kerogens derived from different biomasses to have the same overall chemical composition. Also, bacterial remains may constitute a significant proportion of the kerogen and modify its composition substantially.

Therefore the overall chemical composition of kerogens at the recent sediment stage is highly variable. Moreover, this composition will be variable at all scales of observation, as follows.

(i) The macroscopic scale, because of variations in local conditions of sedimentation.

(ii) The microscopic scale, because of the variety of organic debris.

(iii) The molecular scale, because of the variety of chemical structures of progenitors.

As shown by Durand & Espitalié (1973) and Tissot *et al.* (1974), the behaviour of kerogens with burial can be fairly well predicted when their overall initial composition in terms of carbon, hydrogen and oxygen is known.

AN EXAMPLE OF MODIFICATION OF KEROGEN WITH BURIAL: THE LOGBABA SERIES, UPPER CRETACEOUS, DOUALA BASIN, CAMEROON

This Series was extensively studied by Dunoyer de Segonzac (1969) (geology) and by Albrecht (1969), Albrecht *et al.* (1976), Durand & Espitalié (1976) and Vandenbroucke *et al.* (1976) (organic geochemistry). It is a fairly homogeneous series in both mineral and organic composition and consists of more than 4000 m of clays, silts and sands deposited in a paralic environment. The clays contain around 1 % (by mass) of organic matter of a continental origin, little reworked by bacteria, i.e. with relatively high oxygen contents and low hydrogen contents.

Figure 2 shows the variations with burial of mean H:C and O:C ratios of kerogens in clays, together with the variation of mean bitumen and C_{15+}-hydrocarbon content related to the unit of mass of organic carbon.

The three main steps of the evolution due to burial are clearly visible.

(i) Diagenesis, to a depth of 1500 m, is characterized by a decrease in the content of bitumen, by the small quantity of hydrocarbon, and by a decrease in the O:C ratio in kerogen.

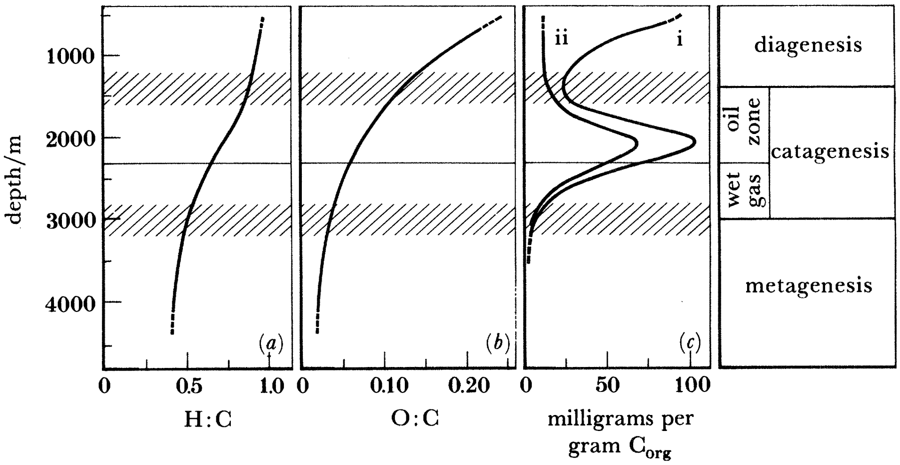

FIGURE 2. (*a*) Changes in H:C atomic ratio of Logbaba kerogens with burial; (*b*) changes in O:C atomic ratio; (*c*) comparison with quantities of (i) extractable bitumen and (ii) C_{15+}-hydrocarbons. (Albrecht *et al.* 1976; Durand & Espitalié 1976.)

(ii) Catagenesis, between 1500 and 3000 m approximately, is characterized by an increase and then a decrease of C_{15+}-hydrocarbons that corresponds to oil and then wet gas formation. This step is also characterized by a strong decrease in the H:C ratio of kerogens.

(iii) During metagenesis (i.e. below 3000 m), there is virtually no extractable bitumen. H:C and O:C ratios in kerogen continue to decrease slowly.

Figure 3 shows the modification of some other properties of kerogen. Figure 3*a* is the variation of the number of spins (measured by electron spin resonance (e.s.r.)) and related to the unit of weight of organic carbon. The number of spins is a measure of the quantity of stable free radicals in the kerogen. To be stable, free radicals have to be localized on polyaromatic nuclei. Their quantity increases during catagenesis, showing that petroleum formation is correlated with the formation of stable polyaromatic free radicals in kerogen. They decrease during

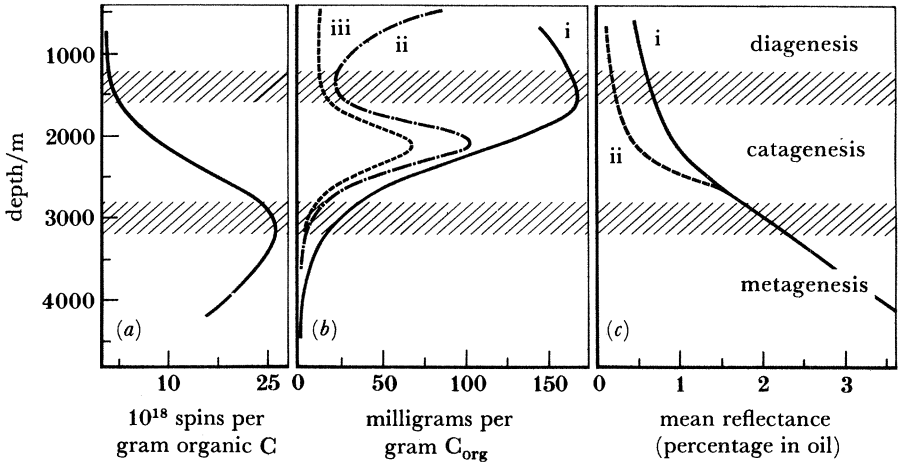

FIGURE 3. Changes in Logbaba kerogens with burial. (*a*) Number of spins (from e.s.r.); (*b*) hydrocarbon yield (i) of kerogens after pyrolysis (Rock Eval system) and comparison with the quantities of (ii) extractable bitumen and (iii) C_{15+}-hydrocarbons; (*c*) reflectance of (i) vitrinite (homocollinite) and (ii) exinite (Albrecht *et al.* 1976; Durand & Espitalié 1976; Marchand & Conard 1980).

metagenesis, indicating that the reorganization of polyaromatic structures occurs once petroleum formation is achieved.

Figure 3*b* records the evolution of the quantity of hydrocarbons produced from kerogens by pyrolysis in the Rock Eval system (Espitalié *et al.* 1977). This quantity is a measure of the capacity of kerogens to produce hydrocarbons in further evolution, and decreases strongly during catagenesis, i.e. when hydrocarbons are formed. It is well correlated with the quantity of aliphatic C—H functions as seen, for example, by infrared spectroscopy (B. Durand & J. Espitalié, unpublished results); this shows that aliphatic C—H functions in kerogen are mainly responsible for hydrocarbon formation during burial.

Finally, figure 3*c* shows the evolution of the reflectance in oil, measured at 546 nm according to petrographic standards, of vitrinite and exinite. Vitrinite, a hydrogen-poor petrographic maceral that derives from ligno-cellulosic cells of higher plants, is abundant in Logbaba kerogens, which are of continental origin. Exinite is a maceral family that derives from spores and leaf cuticles and, more generally, of the hydrogen-rich external parts of higher plants.

Reflectance in carbonaceous material is a result of delocalized electrons in aromatic systems. Therefore it will be higher in hydrogen-poor components than in hydrogen-rich components, because of a higher aromaticity. This is demonstrated here by a lower reflectance in exinite, at least during diagenesis and catagenesis. The general increase of reflectance for both exinite and vitrinite indicates an increase of aromaticity, and the merging of the two curves indicates a convergence of properties of the two maceral families, although they are derived from very different chemical structures. The increase of reflectance is particularly strong after mid-catagenesis (wet gas zone) and goes on during metagenesis. At the end of catagenesis the reflectance becomes anisotropic and this anisotropy develops further during metagenesis.

Figure 4, plate 1 shows the images obtained from Logbaba kerogens at the beginning of catagenesis and at the beginning of metagenesis by high-resolution electron microscopy, with the use of the so-called dark-field imaging method. In this method the diffracting properties of the electron beams are used. It consists of isolating by a diaphragm in the image focal plane of the electronic lens the location corresponding to the passage of beams making the Bragg angle with the optical axis corresponding to a selected spacing (0.02 spacing of graphite in figure 4). The image of the kerogen particle will, therefore, be dark, with the exception of regions diffracting at this Bragg angle that will appear as bright spots (Oberlin *et al.* 1980). This method shows the existence in kerogen of small aromatic sheets less than 10 Å† in diameter (i.e. less than 12 aromatic rings). These small sheets are arranged in little stacks of two or three parallel sheets with a spacing close to 0.02 spacing of graphite. These are responsible for the diffractive phenomenon.

Because molecules in living organisms are never polyaromatic and so are never present at the beginning of catagenesis, polyaromatic structures in kerogens have to be created during sedimentation and diagenesis. Figure 4 shows that at the beginning of catagenesis such

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† 1 Å = 10^{-10} m = 10^{-1} nm.

DESCRIPTION OF PLATE 1

FIGURE 4. Dark-field imaging of Logbaba kerogens for a spacing of 0.02 times that of graphite. The bright spots are the images of stacks of polyaromatic nuclei less than 10 Å in diameter. Note their random distribution for a low degree of evolution (*a*) and their reorganization into clusters for an advanced degree of evolution (*b*). (Oberlin *et al.* 1980.)

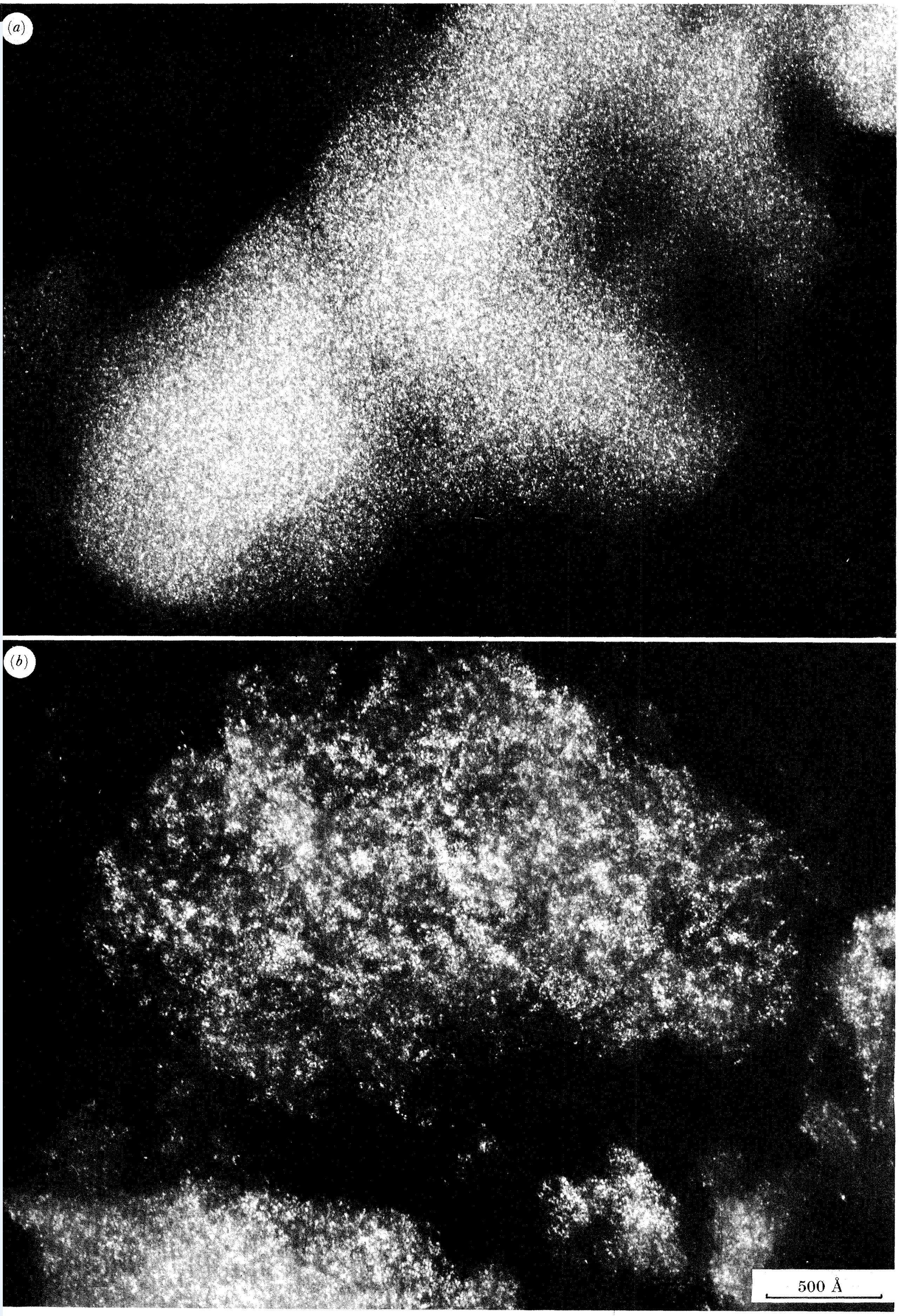

FIGURE 4*a*, *b*. For legend see opposite.

structures are randomly distributed; at the beginning of metagenesis, they are organized in clusters whose C-axes are more or less parallel and whose dimensions are of around 50 Å in Logbaba kerogens (dimensions of up to 100 nm have been observed in other types of kerogens).

A MODEL OF KEROGEN STRUCTURE AND OF ITS DIAGENETIC MODIFICATION

When studying other series of kerogens of the same origin and initial elemental composition, the sequence of diagenetic modifications that is observed with burial is qualitatively the same as that reported above for Logbaba kerogens. However, differences in the intensity of phenomena may exist.

A convenient tool to follow the diagenetic evolution pathway of a kerogen series is the van Krevelen diagram, where O:C and H:C atomic ratios of kerogens are recorded. This is done in figure 5 for three reference series; (*a*) kerogens of Logbaba clays, (*b*) kerogens of the Lower Toarcian Shales from the Paris basin and Western Germany and (*c*) kerogens of the Green River Shales, U.S.A. The initial H:C and O:C compositions are very different for the three series. This corresponds to very different original biomasses and sedimentation media. The origin of Logbaba kerogens has been described above, Lower Toarcian Shales kerogens are derived from a planktonic marine biomass and Green River Shales kerogens are derived from a lacustrine planktonic biomass deeply reworked by bacteria in an evaporitic sedimentation medium (Tissot & Welte 1978).

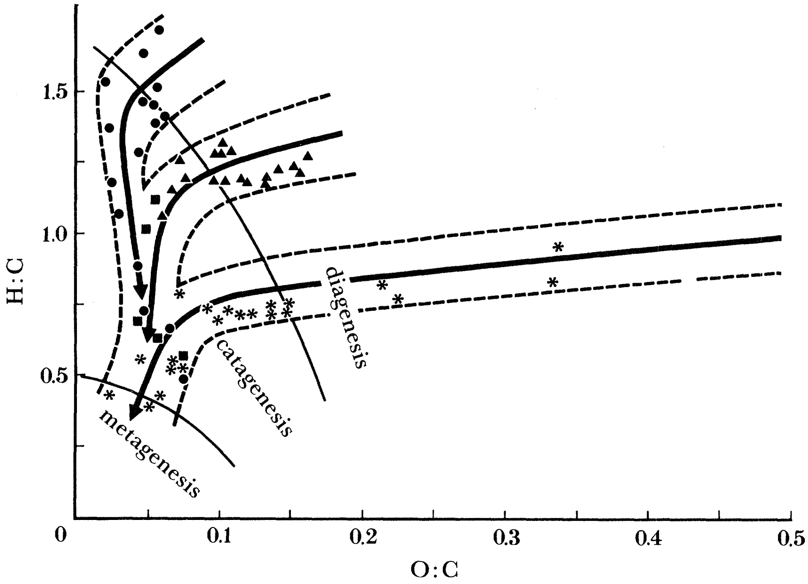

FIGURE 5. Diagenetic pathways in a van Krevelen diagram of three reference series of kerogens. All kerogens in each series derive from a single origin and chemical composition. *, Logbaba Clays; ▲, ■, Lower Toarcian Shales; ●, Green River Shales. Increasing burial shown by arrows. (After Durand & Espitalié 1973.)

For all three series the same modifications are observed, but with different intensities. During diagenesis, there is a strong decrease of O:C ratios and a small decrease of the H:C ratio. The decrease in the O:C ratio is strongest for the kerogens that initially had the highest O:C ratio. This is the immature stage, where few hydrocarbons are formed. Oxygenated molecules, mainly

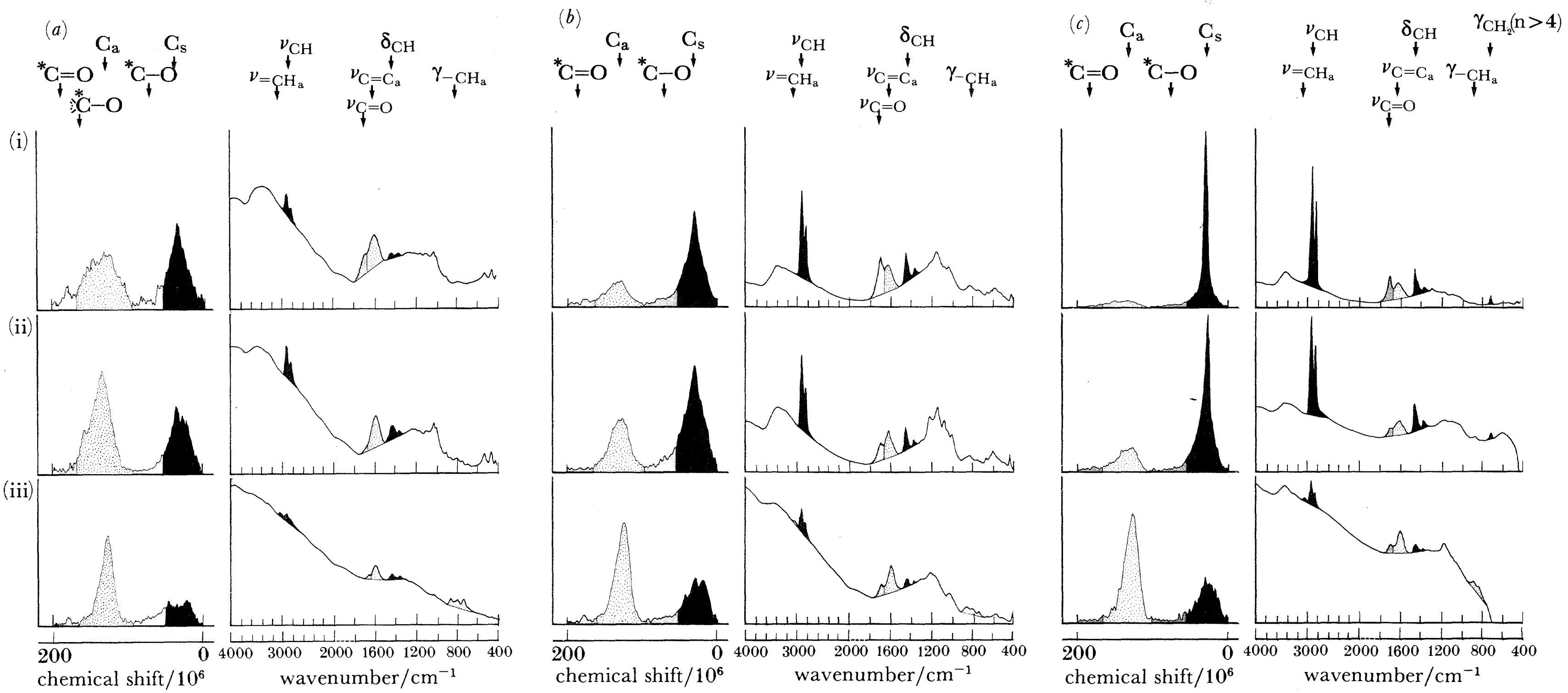

FIGURE 6. Changes in ^{13}C m.a.s. n.m.r. (left-hand side) and F.t.i.r. (right-hand side) spectra for the three reference series of kerogens of figure 5 at three stages of evolution after burial (advancing from (i) to (iii)). (*a*) Logbaba Clays, (*b*) Lower Toarcian Shales (France and western Germany), (*c*) Green River Shales. Note the disappearance of aliphatic C—H groups (C_s in n.m.r. spectra γ_{CH} and δ_{CH} in i.r. spectra) during catagenesis, which results in petroleum formation.

CO_2 and H_2O, are produced in proportion to the initial oxygen contents. During catagenesis there is a strong decrease of the H:C ratio, which corresponds to hydrocarbon formation in proportion to the initial hydrogen content. So, the Green River Shales produce more hydrocarbons per unit weight of kerogen than do the Lower Toarcian Shales, which in turn produce more hydrocarbons than the Logbaba kerogens.

The decrease of O:C during diagenesis is accompanied by the disappearance of thermolabile oxygenated functions (figure 6*a*, *b*, *c*) where Fourier transform infrared (F.t.i.r.) and ^{13}C magic angle spinning nuclear magnetic resonance spectra (^{13}C m.a.s. n.m.r.) are recorded for the three series. The decrease of H:C is accompanied by the disappearance of aliphatic C—H groups, indicated as C_s in the n.m.r. spectra and C—H in i.r. spectra. The importance of these groups at the beginning of catagenesis can be correlated with H:C values, so decreases in the order Green River Shales, Lower Toarcian Shales, Logbaba clays. The disappearance of aliphatic groups can be correlated with hydrocarbon formation during catagenesis.

At the same time, aromaticity increases in the remaining kerogen, as shown in n.m.r. spectra by the development of the C_a absorption band and in i.r. spectra of C═C and aromatic C—H absorption bands. This will result in an increase of reflectance. Generation of free radicals is also evident from e.s.r. examination as has been shown above for the Logbaba series, but different values were obtained (Marchand & Conard 1980). This reveals that the formation of hydrocarbons is accompanied by the creation of stable free radicals (therefore deriving from polyaromatic structures) as a result of breakage and pruning of kerogen structure.

During metagenesis a slow decrease is observed in H:C ratios and O:C ratios change very little. But strong modifications in the remaining polyaromatic structures occur. The main ones are the appearance of clusters where stacks of polyaromatic nuclei (as seen by electron microscopy) have a similar C-axis orientation, the size of these clusters being larger for the initially H-rich than for the initially H-poor kerogens; the disappearance of free radicals in relation to the appearance of the above clusters; a strong increase of reflectance and the development of anisotropy.

The generality of these observations, whatever the kerogen series, leads to the proposition of a model of kerogen structure and of its diagenetic modifications as represented on figure 7*a*, *b* for the Lower Toarcian Shales kerogen. At the beginning of catagenesis (figure 7*a*), the kerogen consists of an overall structure made by the association of a variety of chemical structures in a polycondensed network, insoluble in organic solvents. Some molecules of small size are not chemically bound but cannot be extracted because they are trapped in the network. A significant part of the structure is made up of polyaromatic nuclei less than 10 Å in diameter. Some of these nuclei are associated (stacks of two or three), having a spacing close to that of graphite. They will appear as bright spots under examination by dark-field electron microscopy with selection of the Bragg angle corresponding to 0.02 of that of graphite. These stacks are randomly distributed in the kerogen. During catagenesis, the polycondensed network is broken down into smaller units. The weakest points, by order of increasing stability, are oxygenated bonds such as ester linkages (where the largest part was destroyed during diagenesis but some still remain), C—C bonds between aromatic nuclei and aliphatic groups and finally, C—C and C—H bonds in aliphatic groups. This will result in the release of trapped molecules but more importantly in the formation of hydrocarbon molecules and creation of new polyaromatic structures and stable free radicals. This corresponds to the formation of petroleum and wet gas.

At the end of catagenesis, the remaining kerogen consists mainly of a network of polyaromatic

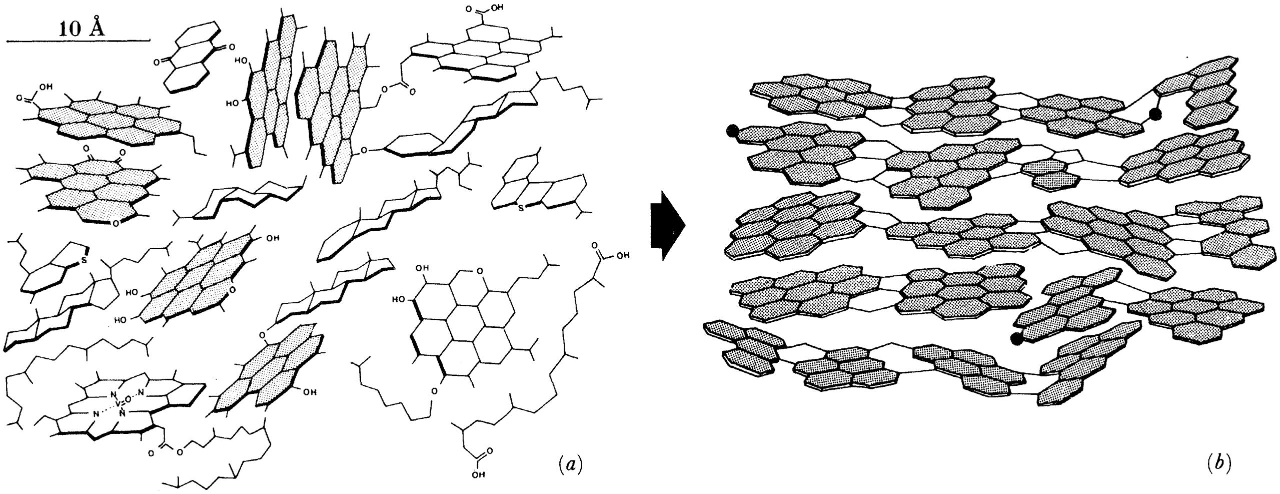

Figure 7. Model of kerogen structure and of its evolution with burial (example of the western European Lower Toarcian Shales); (*a*) low degree of evolution (beginning catagenesis); (*b*) advanced degree of evolution (beginning metagenesis). (After Oberlin *et al.* 1980.)

nuclei whose sizes are not changed. Some of the nuclei produce stable free radicals. The main steric hindrances to the reorganization of this network, i.e. O and H atoms, have been largely eliminated. This reorganization begins with the creation of small clusters of aromatic nuclei with similar orientation of their C-axes, as represented on figure 7*b*.

Metagenesis will consist of a progressive amelioration of this 'precrystalline' organization by 'cleaning' of the remaining heteroatoms and defaults and disappearance of free radicals. The result of this reorganization should be the formation of graphite crystals. However, this formation is not straightforward and it is believed that elevated temperature is not enough and that existence of shearing stresses is necessary (Bonijoly Roussel 1980).

In this analysis, kerogens of different initial composition will differ mainly in the relative proportions of the main constitutive elements. For example, Logbaba kerogens will be initially much richer in polyaromatic nuclei and oxygen linkages and much poorer in aliphatic groups than Green River Shale kerogens. This will result in large differences in the quantities of generated hydrocarbons and some differences in the kinetics of the above described modifications.

Conclusion:

SOME PRESENT AND POSSIBLE FUTURE APPLICATIONS OF THE RESEARCH ON DIAGENETIC MODIFICATIONS OF KEROGENS

At the present time, this knowledge is mainly used for petroleum exploration purposes. Basically, this use consists of determining the stages of formation of petroleum (stages of maturity) reached by source rocks in sedimentary basins, assessed by measuring the values of parameters such as H:C and O:C ratios, yields and characteristics of hydrocarbons produced by pyrolysis and reflectances of the kerogens contained in these source rocks. The trend of evolution of these parameters, when the formation of petroleum is under way, is now well known. However, their precise values depend not only on maturation but also on the origin of the kerogen.

Therefore, establishment of the calibration curves required for precise work cannot be done without knowledge of the origin of the kerogen, particularly in terms of the initial H:C and O:C values. Furthermore, knowledge of the initial composition of kerogens (particularly the initial H:C ratio) is also very important because it determines the quantities of hydrocarbons to be generated (the petroleum potential). This initial composition may be very difficult to assess, because there is a large possible variation of initial compositions even in sedimentologically homogeneous series. This is exemplified by the width of the evolution tracks of the three reference series on figure 5. The more advanced the evolution, the more difficult it is to know the initial composition, because as evolution proceeds there is a progressive merging of the properties of the kerogens of different origins in the properties of a single carbonaceous residue. This is illustrated by the progressive merging of the three evolution tracks on figure 5.

Another way to use this information, which is of increasing importance in petroleum exploration, is to use models of hydrocarbon formation to reconstruct the history of the formation in sedimentary basins and to calculate the quantities that are formed as a function of time. This idea is based on the observation that hydrocarbon formation from kerogen depends mainly on temperature and time and little on other factors. In the model developed at the Institut Français du Pétrole (Tissot 1969; Tissot & Espitalié 1975), this formation is represented by a set of first-order kinetic equations with different activation energies, which correspond to the breaking of different chemical bonds in the kerogen. Input data comprise the thermal history of the source rocks and the initial composition of their kerogens, which determines the proportions of the different chemical bonds to be broken.

An application that is developing under the impulse of structural geologists is the reconstruction of the thermal régimes of sedimentary basins. The idea stems from the fact that diagenetic modifications of kerogens in sediments are sensitive markers of their thermal histories. The work consists of logging and mapping kerogen properties, as in the identification of maturity stages for petroleum exploration purposes. The comparison of the gradients observed for each of these properties between different sedimentary basins allows the establishment of a crude classification of sedimentary basins with respect to their thermal régimes. It should be emphasized, as it is still not clearly realized by geologists, that the legitimate comparison of gradients should be made on appropriate properties, i.e. for the same property recorded on kerogens having the same initial composition, exactly as for the identification of maturity stages. Indeed, as explained earlier, the values of the parameters that can be used depend on both thermal history and the origin of kerogens.

To go beyond a crude comparison of thermal régimes and to reach the thermal history of sedimentary basins requires knowledge of the kinetics of the evolution of the parameters that are used and, more precisely, the establishment of kinetic models. Except for the transformation of kerogen into hydrocarbons, a phenomenon that can be used only in the range of catagenesis, no such models have yet been established. This is an interesting but difficult challenge for organic geochemists.

Finally, an application that should develop, but has as yet received little realization, is the understanding of mineral diagenetic modifications under the action of the mobile molecules that are released by kerogen during burial. Although kerogen is a minor constituent of sedimentary rocks, it is not evenly distributed and the products of its decomposition might modify mineral diagenesis in the places where it is abundant. Also, at the recent sediment stage, abundance of kerogen creates reducing conditions that should orientate the precipitation of some mineral species. However, little is known of these organo–mineral interactions.

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Discussion

S. C. BRASSELL (*School of Chemistry, University of Bristol*). What information exists about the structure of pyrobitumen and the way in which this material can be distinguished from residual kerogen?

B. DURAND. One surprising observation is that pyrobitumen is probably less stable to pyrolysis than is the residual kerogen. Also the size of the sheets of aromatic nuclei is probably smaller in pyrobitumen than in kerogen.

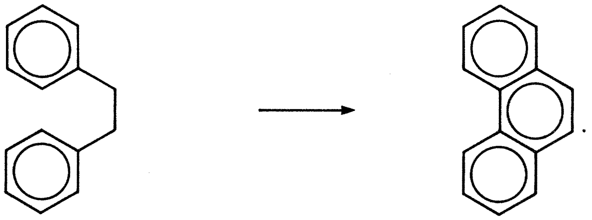
S. C. BRASSELL. Is the distinction between pyrobitumen and kerogen made on a theoretical basis or are there differences in their physical and chemical properties that allow them to be separated?

B. Durand. It is not possible to separate these materials physically in source rocks. When the oil has migrated to a reservoir, further heating produces pyrobitumen in the form of aliphatic material in the reservoir rock. Because the reservoir rock initially contains no kerogen, pyrobitumen can be isolated and characterized.

G. Eglinton (*Organic Geochemistry Unit, School of Chemistry, University of Bristol*). In Dr Durand's diagram, showing the changes that occur in catagenesis, he proposed that the reaction involves a change from a kerogen, which contains a considerable number of fused rings, to a more graphitic structure. Is this model of kerogen valid even for the highly aliphatic kerogens like that of the Green River Shale?

B. Durand. I believe that the main difference between different types of kerogen at the beginning of catagenesis is in the number and length of the side chains attached to the polyaromatic nuclei. The ratio of carbon in the side chains to carbon in the polyaromatic nuclei will be much greater in Green River Shale kerogen than, for instance, in a coal. In all cases, most of the polyaromatic nuclei have to be created during sedimentation or diagenesis or both, because they are not present in living organisms. How this creation proceeds is not clear.

G. Eglinton. The fused rings in kerogen may well have come from lignin, or they may have had a humic origin. The formation of kerogen would then require the loss of oxygen and of the $—CH_2—CH_2—$ bridges. But the reactions leading to the formation of a number of fused rings might be helped by the rings already being attached to each other and so fused structures could be produced by intramolecular reactions, followed by aromatization. For example,



B. Durand. This scheme could well produce the large flat structures visible in the electron microscope.

A. S. Mackenzie (*BP Geochemistry Branch, Sunbury-on-Thames*). Possible sources of the aromatic stacks observed at low maturity could be perylene and other related compounds derived from similar precursors to that of perylene. Perylene is present in substantial amounts in immature sediments.

B. Durand. But does Dr Mackenzie believe that perylene is present in sufficient abundance to produce the structures we see?

M. L. Coleman (*BP Research Centre, Sunbury-on-Thames*). Does Dr Durand believe that there is any relation between pyrite and kerogen? Diagenetic pyrite is often found in the absence of kerogen, but it is rare to find kerogen without pyrite.

B. Durand. The relation Dr Coleman proposes is often found to be true, though there are exceptions when the sediments contain no sulphur.

M. L. Coleman. In a sense I am asking the reverse of the question Dr Durand asked me about the immobile organic matter. I am worried about the immobility of the iron. Sulphur is clearly mobile in sediments.

D. G. Murchison (*Organic Geochemistry Unit, The University, Newcastle-upon-Tyne*). I believe that there are a number of different types of kerogen, only some of which are involved in pyrite production.

B. Durand. It is commonly the case that pyrite is protected from oxidation by an organic film.

FIGURE 4. Dark-field imaging of Logbaba kerogens for a spacing of 0.02 times that of graphite. The bright spots are the images of stacks of polyaromatic nuclei less than 10 Å in diameter. Note their random distribution for a low degree of evolution (*a*) and their reorganization into clusters for an advanced degree of evolution (*b*). (Oberlin *et al.* 1980.)