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Molecular Changes in Sediment Lipids as Indicators of Systematic Early Diagenesis [and Discussion]

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Molecular changes in sediment lipids as indicators of systematic early diagenesis

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Studies of the steroidal hydrocarbons in sediment sequences demonstrate that diagenetic changes in their molecular distributions occur systematically with burial and form a coherent continuum linking the lipid constituents of organisms to those of ancient sediments and petroleums. Such changes are initially caused by (i) microbial processes, then (ii) low-temperature reactions, which appear to be catalysed by clay minerals and, finally, (iii) thermal processes. The molecular composition at stage (iii) can depend on the proportions of the different products generated by the divergent diagenetic pathways of stages (i) and (ii).

Organic molecular reactions are sufficiently sensitive that some diagenetic changes are recognizable over small (*ca.* 10 m) depth intervals, which should permit a system of molecular diagenetic zones to be devised. This development should enable the low-temperature thermal history of sediments to be assessed accurately. Specific diagenetic reactions within stages (ii) and (iii) also appear to reflect the sediment heat flow; thus, the reaction rates are higher in rapidly subsiding Neogene sedimentary sequences than they are in Cretaceous sediments from passive continental margins.

Introduction

Most organic constituents derived from living organisms which come to be deposited in sedimentary environments are not geologically stable. During sediment formation, compaction and deep burial they are transformed in various ways which initially modify and eventually break down their chemical structures. The recognition and interpretation of the reactions involved, their pathways and sequence, are an important facet of organic geochemical research (see for example, Mackenzie *et al.* 1982). The organic compounds themselves, commonly referred to as biological marker compounds because of their links to the components of living organisms, include a wide variety of structural types. Experimental procedures for the characterization of such compounds extracted from sediments make extensive use of chromatographic and spectrometric techniques for component fractionation and analysis. Computerized gas chromatography – mass spectrometry (c.g.c.–m.s.) is especially valuable for the identification of individiual components within the complex mixtures obtained from natural systems (such as sediments) and it is this analytical tool that provides the means for the recognition and evaluation of the compounds considered herein. Confirmation of such assignments by direct comparison (for example, g.c. and g.c.–m.s. coinjection) with synthetic standards is desirable and the identifications of all of the compounds considered in this paper, except for 14β*H*-monoaromatic anthrasteroids, have been verified in this manner. The two classes of biological markers that have been studied in the greatest detail are steroids and triterpenoids. Data documenting the diagenetic fate of these polycyclic compounds in uniform sedimentary sequences form the nucleus of this paper.

The principal pathways of steroidal diagenesis–catagenesis can be viewed, in simple terms,

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as a series of transformations that change biological sterols into saturated and aromatic steroidal hydrocarbons (figure 1). Such changes in steroidal structures accompany their transposition from integral lipids of living organisms to components of shallow sediments (possibly via water column particulates) and thence ancient sediments (figure 1). The range of occurrence of individual steroidal compounds in the different biological and geological media (figure 1) typically lie within a burial window related to maturity, a feature analogous to the stratigraphic ranges of individual zonal fossils. Of the compounds shown in figure 1, for example, only sterols have been identified in organisms, but they can survive in immature sediments. Similarly, sterols, sterenes and diasterenes do not occur in petroleums that only contain steroidal components as saturated and aromatic hydrocarbons. In the course of sediment burial the major reaction processes that alter the composition and individual structures of biologically derived lipids are defunctionalization (e.g. dehydration and decarboxylation), isomerization and aromatization (figure 1). They tend to influence individual steroidal components in different ways during the various stages of diagenesis and catagenesis. The defunctionalization reactions typically involve loss of oxygenated groups, giving rise to hydrocarbons and are generally restricted to the diagenesis zone, whereas isomerization and aromatization continue within the catagenesis zone, eventually being superceded by cracking processes.

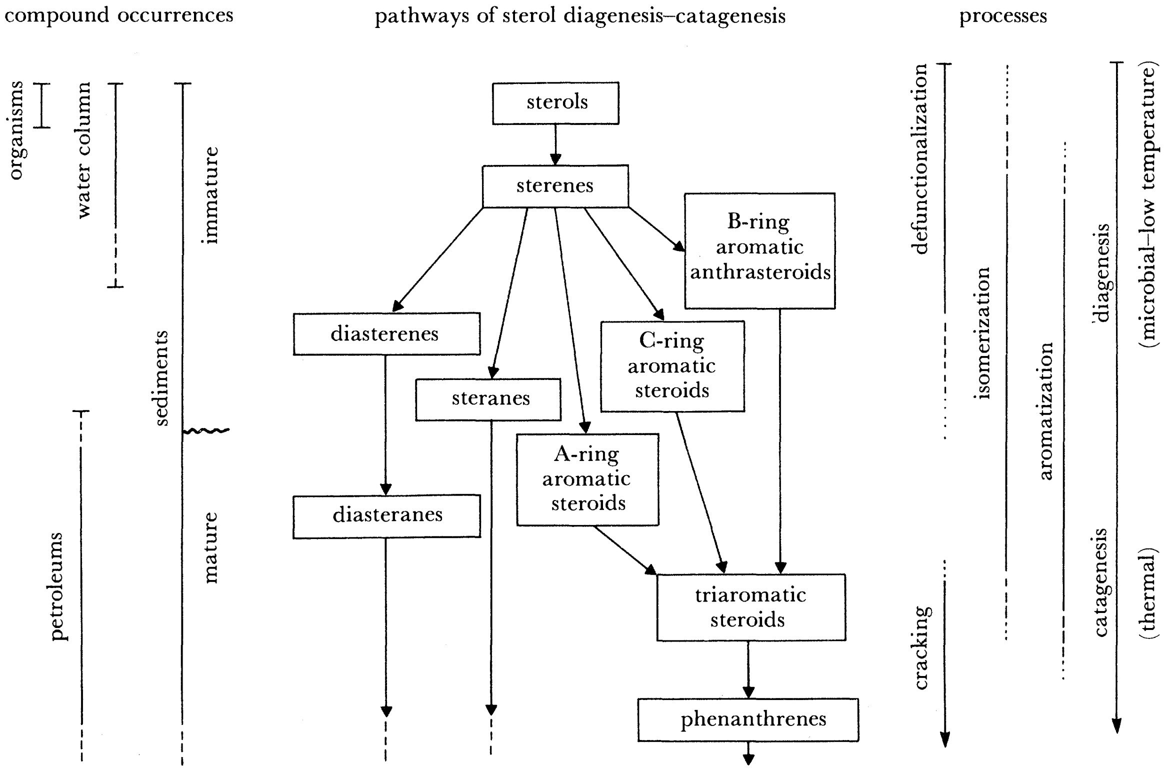

Figure 1. A simplified schematic summary of the presumed geological fate of sterols, showing the biological and geological ranges of occurrence of steroids and the main processes that effect their transformations (modified from Mackenzie *et al.* 1982).

Isomerization reactions, which affect sterenes, diasterenes, B-ring monoaromatic anthrasteroids, C-ring monoaromatic steroids and steranes, involve either the migration of positions of unsaturation to more stable sites in the molecule (geometrical isomerization) or changes of

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configuration at chiral centres (i.e. positions where given carbon atoms possess four different substituents; see Abbott *et al.*, this symposium, on stereochemical isomerization). The latter reactions fall into two categories: they may proceed to completion (i.e. 100% product) or to an equilibrium mixture (e.g. 50:50 or 40:60), depending on the differences in stability of the precursors and products. Examples of both reaction types are considered below. The process of aromatization in the present context involves the formation of a substituted benzene ring within a polycyclic skeleton (see Abbott *et al.*, this symposium). It can be accompanied by ring rearrangement and methyl migration or loss.

A significant feature of organic diagenetic reactions is that they occur non-reversibly in geological environments. Hence the distributions of biological marker compounds reflect their maximum thermal experience and are not altered by subsequent uplift or other cooling influences. Indeed, an understanding of the progression of diagenetic and catagenetic changes in biological markers provides a useful tool for the interpretation and assessment of the depositional history of sediments, notably their thermal experience (see, for example, Mackenzie *et al.* 1980). In this paper the potential of this approach for assessment of the zone of early diagenesis, rather than that of oil generation (see Mackenzie *et al.* 1980, 1981), is investigated.

Specifically, the depth trends of selected diagenetic reactions of steroidal hydrocarbons and other compounds, will be considered. These chosen reactions will demonstrate the systematic nature of sedimentary lipid transformations, illustrating their potential value as indicators of the thermal history of sediment sequences in the zone of early diagenesis.

PRECURSOR–PRODUCT RELATIONS

The overall process of lipid diagenesis and catagenesis involves the transformation of molecules tailored for specific biological requirements into their geologically more stable counterparts. Typically, it encompasses a series of sequential reactions wherein the products initially generated from biologically derived compounds become, in turn, the substrates (or precursors) of subsequent transformations. Each of these transformation steps constitutes a precursor–product relation (figure 2). Hence, the sterols such as 5α*H*-stanols derived directly from organisms may be dehydrated to sterenes, which after double-bond isomerization may undergo hydrogenation to produce steranes (figure 2; see also figure 1). The initial sterane products retain the configuration (14α*H*, 17α*H*) of their sterene precursors; but subsequently isomerize at the C-14, C-17 and C-20 chiral centres during late-stage diagenesis, yielding 20*S*–14β*H*-, 17β*H*-steranes (see, for example, Mackenzie *et al.* 1980). In a similar fashion a C_{35} hopanoid polyol that occurs in many prokaryotes (bacteriohopanetetraol; figure 2 and Ourisson *et al.* 1979) may be oxidized during early diagenesis to its corresponding C_{32} carboxylic acid (17β*H*-, 21β*H*-bishomohopanoic acid). This acid subsequently undergoes decarboxylation to generate a C_{31} hopane (homohopane) product that retains 17β*H*, 21β*H* stereochemistry (Dastillung *et al.* 1977). During late-stage diagenesis this hopane isomerizes to its more stable 17α*H*, 21β*H* counterpart (Ensminger *et al.* 1974). Isomerization at C-22 also occurs, producing a mixture of 22*S* and 22*R* isomers (Ensminger *et al.* 1974). These examples demonstrate that precursor–product reactions occur in a stepwise fashion, with the products of early diagenetic reactions subsequently modified during late-stage diagenesis. Such diagenetic relations are typically inferred from a combination of (i) the sedimentary occurrence and distribution of biological marker compounds, especially in depth sequences and (ii) reactions established by

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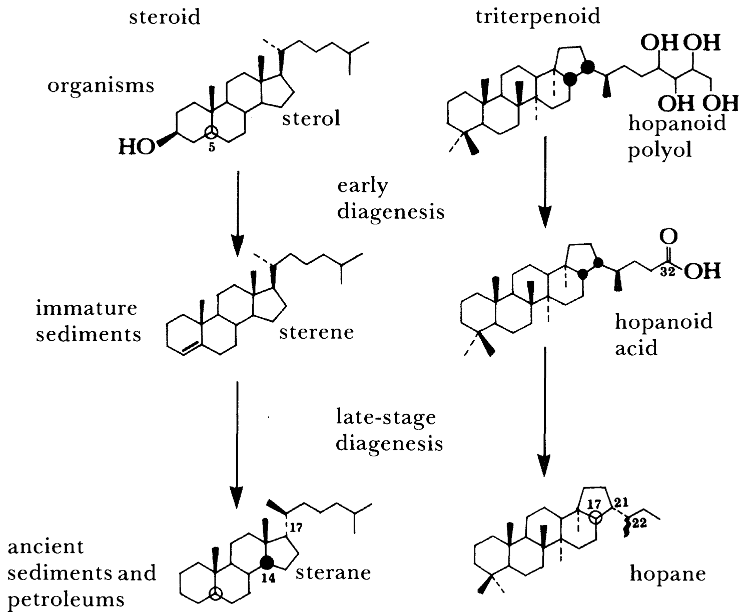

Figure 2. Example of precursor–product transformations occurring during lipid diagenesis.

laboratory simulation experiments. Such simulations may involve the chemical treatment (e.g. acidic rearrangement) of a precursor compound or laboratory heating experiments, typically in evacuated sealed vessels, with chosen matrices (e.g. clay, carbonate, sulphur; see Abbott *et al.*, this symposium).

Early diagenesis of steroids

The main concern of this paper is the diagenetic transformations of steroidal hydrocarbons in a number of sedimentary sequences recovered by the Deep Sea Drilling Project (D.S.D.P.). Such sediments have been selected for the study of early diagenesis because of their excellent coverage of this zone of sediment burial, which falls intermediate between the shallow recovery of piston cores and the deeper drilling characteristic of petroleum exploration (Brassell & Eglinton 1983). Further features of these cores include a wide range of sites of different ages (from Quaternary to Callovian), lithologies and thermal experience (i.e. geothermal gradients from 20 to 100 °C/km). For the sediments considered herein sequences of uniform lithology, with various age ranges and thermal histories have been chosen, which permit a comparative study to be made. Overall emphasis is placed on the transformations of biological markers dependent on the changes in sediment temperature during early diagenesis. So, because there are two agents influencing and effecting early diagenetic processes, i.e. microbial activity and low-temperature physicochemical reactions, the recognition and differentiation of changes attributed to these two separate factors is of direct interest. As a first approximate, microbial processes would be expected to exhibit particular features that might help to distinguish them. For example, any selectivity in precursor–product relations according to compound structure (e.g. carbon number, positions of methylation) or stereochemistry (such as the preferred transformation of specific configurations) that is not readily related to physical or chemical factors might be deemed to be microbially influenced.

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An example of a diagenetic reaction inferred to be microbially mediated is the dehydration of $5\alpha H$-stanols (figure 3). A close correspondence has been observed in certain shallow-buried sediments between the distributions of $5\alpha H$-stanols and Δ^2-sterenes (see, for example, Mackenzie *et al.* 1982) providing supportive evidence of their precursor–product relation. In addition, the recognition of Δ^2-sterenes in water-column paticulates (Wakeham *et al.* 1984) and shallow marine sediments (see, for example, Dastillung & Albrecht 1977) demonstrates their early formation. In contrast, 4-methylsterenes have yet to be observed in such materials despite the abundance of 4-methyl-$5\alpha H$-stanols in surface sediments (see, for example, Gagosian *et al.* 1980; Smith *et al.* 1982; Brassell & Eglinton 1983; de Leeuw *et al.* 1983). This contrasts directly with the greater stability of their dehydration products, 4-methylster-3-enes over ster-2-enes. Such apparent selective dehydration of $5\alpha H$-stanols relative to 4α-methyl-$5\alpha H$-stanols suggests that this reaction is microbially mediated. It is also significant that the products of this dehydration process, Δ^2-sterenes, are the initial steroidal hydrocarbons considered below in the discussion of physicochemical diagenetic reactions. Hence, microbial processes play a vital role in the generation of the precursors for many biological markers in sediments, as is found to be well demonstrated by the number of diagenetic–catagenetic pathways diverging from sterenes in figure 1.

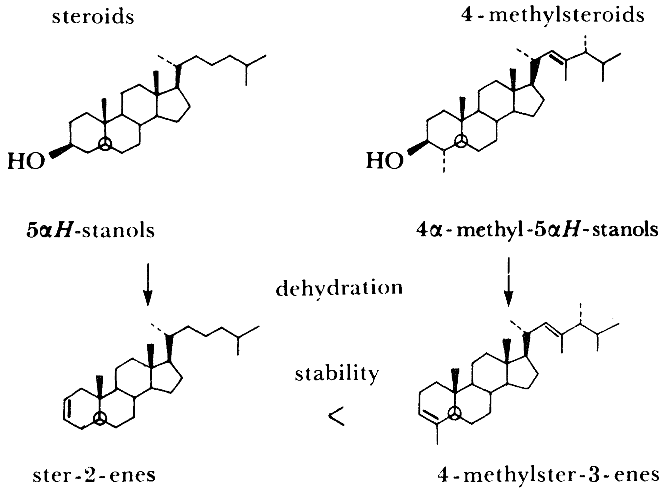

FIGURE 3. Formation of sterenes by dehydration of $5\alpha H$-stanols.

Precursor–product reactions

In the following section, six different transformation of steroidal hydrocarbons in sediments are considered in detail. A fuller account of these diagenetic precursor–product reactions (and others) is given elsewhere (Brassell *et al.* 1984). It is significant that all of these reactions occur in the laboratory under acidic conditions (see, for example, Rubinstein *et al.* 1975; Kirk & Shaw 1975; Hussler & Albrecht 1983; Peakman *et al.* 1984). Because the major source of acidic conditions in environment sediments is generally associated with clays, it is presumed that these diagenetic reactions are clay-catalysed. If clays are actually not the agents responsible for these transformations in sediments then an alternative means of generating acidic conditions must be involved, because the chemical basis of these reactions is firmly established. Further evidence for the influence of clay in diagenetic reactions is provided by the absence of specific products

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in sediments lean in clay. For example, diasterenes are absent in an organic-rich Albian limestone from the Hess Rise (Comet *et al.* 1981), which on a maturity basis would have been expected to contain them.

The diagenetic changes of steroid hydrocarbons in particular sediment sequences are best evaluated from product:(precursor+product) ratios (expressed as a percentage) plotted against depth (figure 4). Clearly, the recognition of a smooth depth trend provides supportive evidence for the diagenetic transformation of proposed precursor into product but does not, by itself, confirm such a relation. All of the precursor:product ratios considered here are plotted against depth for a single carbon number (e.g. C_{27}) rather than for the sum of the range observed (e.g. ΣC_{27}-C_{29}), although the two trends would be expected to be consistent.

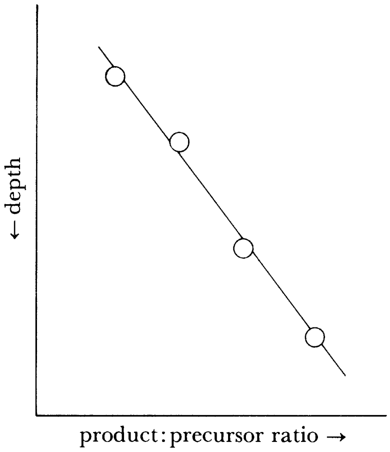

FIGURE 4. Schematic representation of diagenetic trends in product–precursor ratios.

(i) *Sterene isomerization*

Δ^2-sterenes ((**1**) in figure 5) are formed in water-column particulates (Wakeham *et al.* 1980) and in recent sediments (Dastillung & Albrecht 1977; Gagosian & Farrington 1978) by dehydration of stanols, a process that may be microbially mediated (see Gagosian *et al.* 1980 and above). They are found to isomerize to their more stable Δ^4 and Δ^5 counterparts ((**2**) and (**3**) in figure 5, respectively; Mackenzie *et al.* 1982 and references therein) with increasing depth of burial. In sediments from both the San Miguel Gap and the Walvis Ridge (figure 6) this isomerization is relatively rapid, proceeding to completion within a depth interval of *ca.* 50 m in the latter instance. Here and elsewhere (Rullkötter *et al.* 1982), the Δ^4-sterenes ((**2**) in figure 5) and more abundant than their Δ^5 counterparts ((**3**) in figure 5), presumably reflecting their

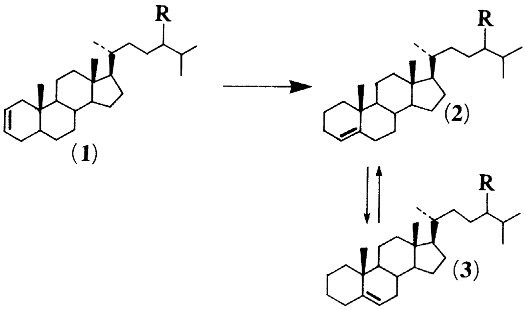

FIGURE 5. Sterene double-bond isomerization; R = H, Me or Et. (After Brassell *et al.* 1984; see also Rubinstein *et al.* 1975; Mackenzie *et al.* 1982.)

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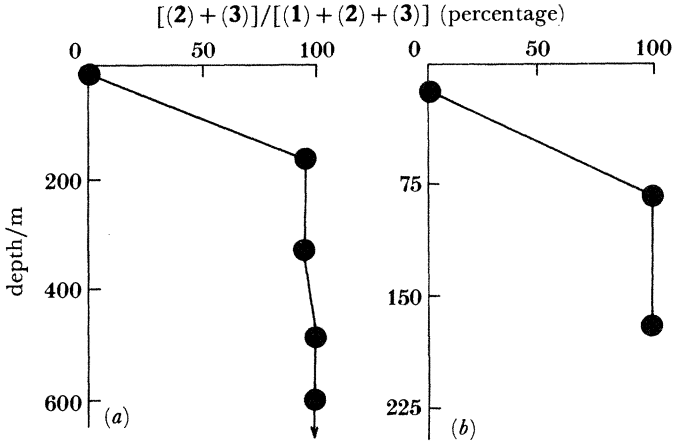

FIGURE 6. Progression of C_{27} sterene double-bond isomerization (see also figure 5; R = H) with depth in two D.S.D.P. sediment sequences; (*a*) San Miguel Gap; (*b*) Walvis Ridge (after Brassell *et al.* 1984).

greater stability (Kirk & Shaw 1975). The observed increase in Δ^4-:Δ^5-sterene ratios ((**2**):(**3**)) with increasing depth for many D.S.D.P. sediment sequences (Brassell *et al.* 1984) supports this hypothesis.

(ii) *Diasterene formation*

Under acidic conditions in the laboratory sterenes undergo a skeletal backbone rearrangement, generating diasterenes (Kirk & Shaw 1975). In sediment sequences the precursors of diasterenes (**4**) and (**5**) (20*R*- and 20*S*-diasterenes) appear to be Δ^4- and Δ^5-sterenes ((**2**) and (**3**)) and there is the additional possibility that series of tentatively assigned Δ^8 (or $\Delta^{8(14)}$) sterenes with partly rearranged skeletons may be intermediates in the backbone rearrangement (see figure 7 and Brassell 1984, Brassell *et al.* 1984). In a sequence of Mesozoic black shales from the Falkland Plateau the gradual conversion of sterenes to diasterenes is well illustrated (figure 8).

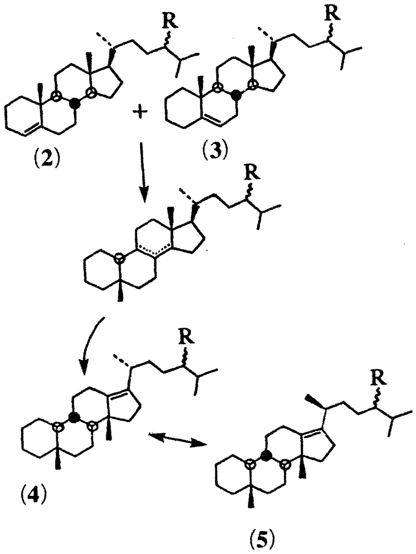

FIGURE 7. Sterene backbone rearrangement leading to diasterenes, and C-20 isomerization; R = H, Me or Et (after Brassell *et al.* 1984).

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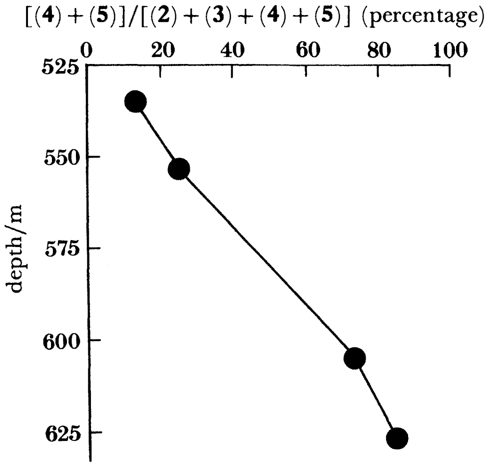

FIGURE 8. Progression of C_{27} diasterene formation from sterenes with depth (see also figure 7; R = H) in Falkland Plateau samples (after Brassell *et al.* 1984).

(iii) *Diasterene isomerization*

The diasterene initially formed by the backbone rearrangement of sterenes under acidic conditions retains the inherited 'biological' 20*R* configuration (Kirk & Shaw 1970; figure 7). Continued acid treatment leads subsequently to isomerization at C-20, producing a 1:1 mixture of 20*R*- and 20*S*-isomers ((**4**) and (**5**) respectively in figure 7). Such progressive isomerization at C-20 in diasterenes occurs with increasing depth in many D.S.D.P. sediment sequences (Brassell *et al.* 1984), including that of black shales from the Falkland Plateau (figure 9).

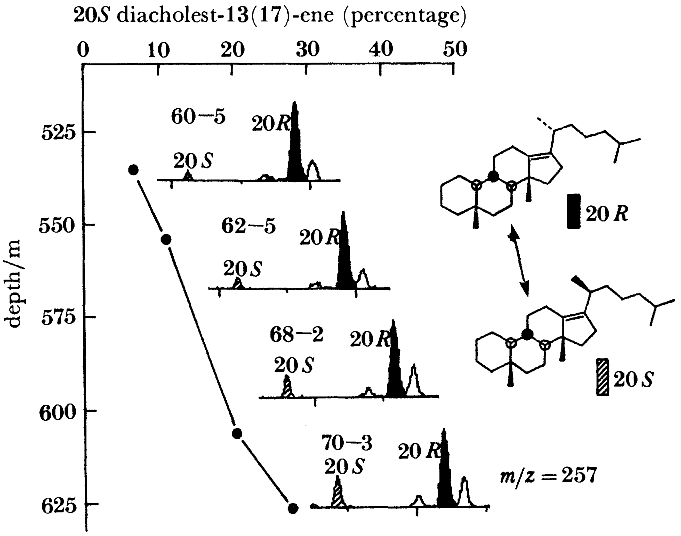

FIGURE 9. Progression of C_{27} diasterene isomerization at C-20 with depth in Falkland Plateau samples. (After Brassell *et al.* 1984. Insets show partial m/z = 257 mass fragmentograms.)

(iv), (v) *Spirosterene isomerization and formation*

Among the minor products of the laboratory backbone rearrangement of sterenes under acidic conditions are 20*R*- and 20*S*-spirosterenes (12, 14α-cyclo-12,13-seco-5α*H*-ster-13(17)-

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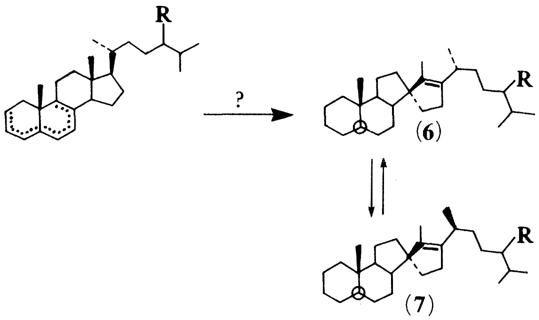

FIGURE 10. Proposed pathways of spirosterene generation and isomerization at C-20; R = H, Me or Et (after Brassell *et al.* 1984).

enes; (**6**) and (**7**) in figure 10 and Peakman *et al.* 1984). The formation and isomerization at C-20 of these compounds is analogous to that of the diasterenes (Brassell *et al.* 1984), and they show similar downhole trends in the same sediment sequences. The identification of such minor components among the steroidal hydrocarbons in sediments provides further evidence for the parallel nature of acidic rearrangement reactions performed in the laboratory and those observed in sediments.

(vi) B-*ring monoaromatic anthrasteroid formation*

The generation of 14α*H*-B-ring monoaromatic anthrasteroids (1(10→6)-abeo-stera-5,7,9-trienes; see Hussler & Albrecht 1983) occurs at an early stage of diagenesis (Brassell *et al.* 1984) and their precursors appear to be stera-3,5-dienes ((**8**) in figure 11). In the sediment sequence from the San Miguel Gap this proposed precursor : product relation shows a smooth depth trend (figure 12), which proceeds to completion (i.e. 100% of product) at *ca.* 500 m depth.

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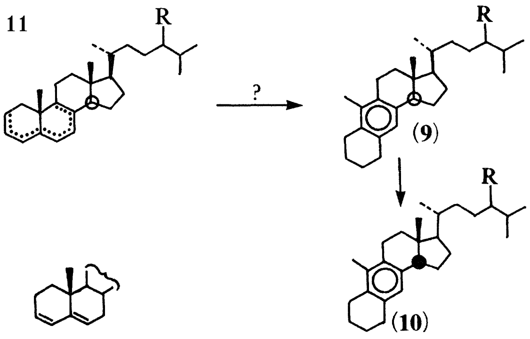

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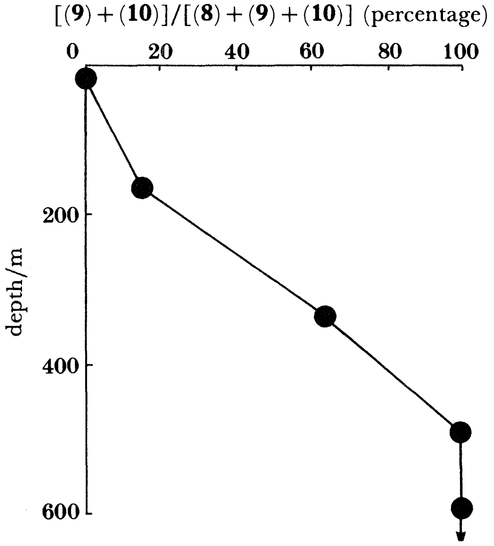

FIGURE 11. Proposed generation and subsequent isomerization at C-14 of B-ring monoaromatic anthrasteroids; R = H, Me or Et (after Brassell *et al.* 1984).

FIGURE 12. Progression of C_{29} B-ring monoaromatic anthrasteroid formation from 24-ethylcholesta-3,5-diene (see also figure 11; R = Et) with depth in San Miguel Gap sediments (after Brassell *et al.* 1984).

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(vii) B-*ring monoaromatic anthrasteroid isomerization*

14α*H*-B-ring monoaromatic anthrasteroids possess a *trans* C–D ring junction that is less stable than the *cis* isomer (figure 11 and Hussler & Albrecht 1983). Hence, an isomerization at C-14 yielding 14β*H*-B-ring monoaromatic anthrasteroids ((**10**) in figure 11) is likely. This proposed diagenetic transformation can be seen in the San Miguel Gap sediment sequence (figure 13), although the 14β*H*-isomers occur even in the shallowest sample containing B-ring monoaromatic anthrasteroids. By contrast, the Walvis Ridge sediments (not shown) only contain 14α*H*-isomers, suggesting that the generation of the 14β*H*-compounds is a subsequent isomerization process, perhaps influenced by clay catalysis. In addition, both 14α*H*- and 14β*H*-B-ring monoaromatic anthrasteroids are present as doublets in capillary g.c.–m.s. analyses, suggesting a further isomeric position in their structures (Brassell *et al.* 1984), which has yet to be determined.

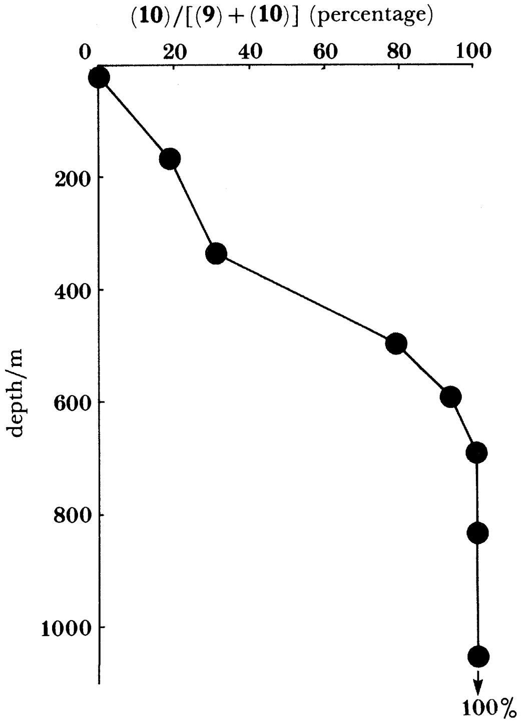

FIGURE 13. Progressive C_{27} B-ring monoaromatic anthrasteroid isomerization at C-14 (see also figure 11; R = H) with depth in San Miguel Gap sediments (after Brassell *et al.* 1984).

(viii) A-*ring monoaromatic steroid formation*

The aromatization of ring A in steroids giving rise to A-ring monoaromatic compounds is thought to be catalysed by clays (Hussler *et al.* 1981). These compounds appear in immature sediments and their origin from $\Delta^{3,5}$-steradiene precursors has been proposed (figure 14 and Brassell *et al.* 1984). This precursor–product relation proceeds to completion in sediments from the San Miguel Gap (figure 15), whereas in the shallower sequence from the Walvis Ridge the onset of their formation is seen between *ca.* 90 and 170 m depth. In deeper sediments towards the threshold of oil generation the A-ring monoaromatic steroids are thought to be aromatized

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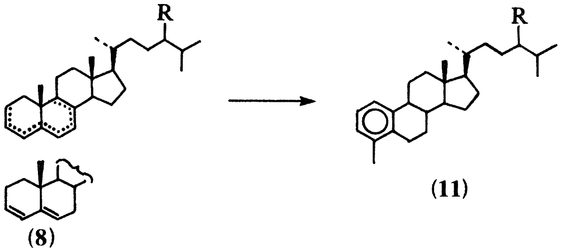

Figure 14. Proposed generation of 4-methyl A-ring monoaromatic steroids; R = H, Me or Et (after Brassell *et al.* 1984).

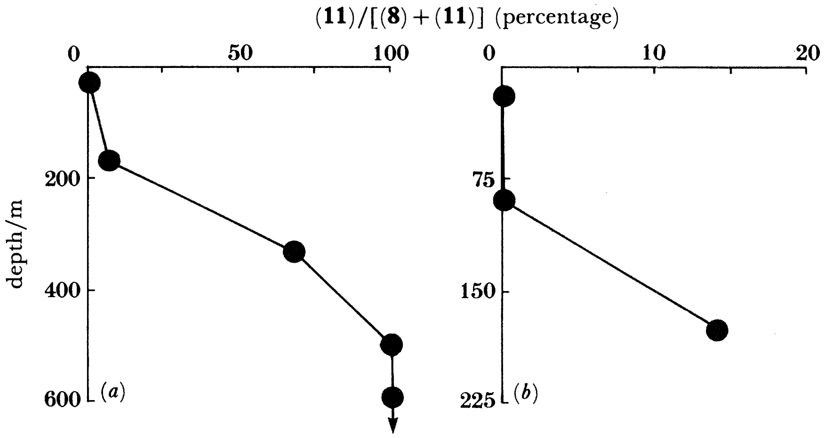

Figure 15. Progression of C_{27} 4-methyl A-ring monoaromatic steroid formation (see also figure 14; R = H) with depth for two D.S.D.P. sediment sequences; (*a*) San Miguel Gap; (*b*) Walvis Ridge (after Brassell *et al.* 1984).

further to triaromatic steroids (Hussler *et al.* 1981; Mackenzie *et al.* 1982). The lower limit of stability of A-ring monoaromatic steroids and their proposed transformation to triaromatics are not observed in D.S.D.P. sediment sequences (Brassell *et al.* 1984) and lie outside the scope of this paper.

It is significant that both A-ring monoaromatic steroids ((**11**) in figures 14 and 16) and B-ring monoaromatic anthrasteroids ((**9**) and (**10**) in figures 11 and 16) are thought to be diagenetic products derived from $\Delta^{3,5}$-steradiene precursors ((**8**) in figures 11, 14 and 16). Clearly, these two reaction pathways may be competitive, although the first appearance of A-ring monoaromatic steroids can be observed in sediments from greater depth than those containing B-ring monoaromatic anthrasteroids (see figure 19). Thus, the two reactions may not be in direct competition throughout early diagenesis. The possible formation of two different types of aromatic steroidal product from a single precursor (i.e. stera-3,5-dienes) demonstrates the divergence of specific diagenetic pathways (figure 16). Clearly, the generation of such components during early diagenesis will have an influence on the steroidal composition of more mature sediments, affecting the relative amounts of the products arising from subsequent late diagenetic and catagenetic transformations.

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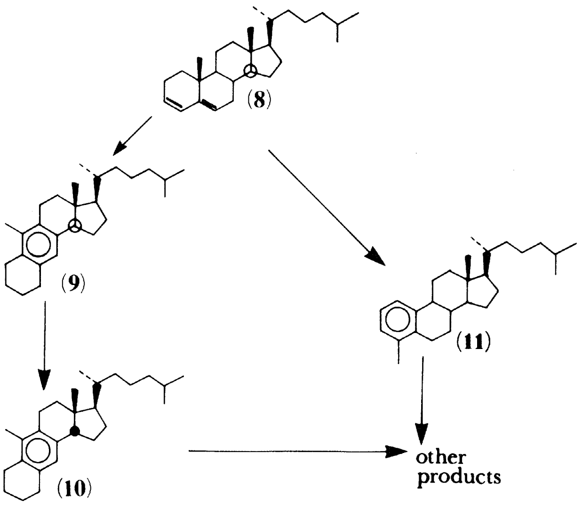

Figure 16. Example of the divergence of steroid diagenetic pathways generating different products from a single precursor.

(ix) C-*ring monoaromatic steroid formation*

The generation of these major compounds of immature sediments from sterene precursors (see figure 1) is poorly understood (Brassell *et al.* 1984) and will not be considered in detail here.

Diasterene isomerization

Depth ranges

A comparison of the extent of diasterene isomerization for several sediment sequences shows that it occurs at different depths at the various localities (figure 17), as expected, given their different thermal régimes. In addition, it is evident that the extent of isomerization shows differences between sediments *ca.* 20 m or less apart. This represents a clear indication of the sensitivity of such diagenetic transformations.

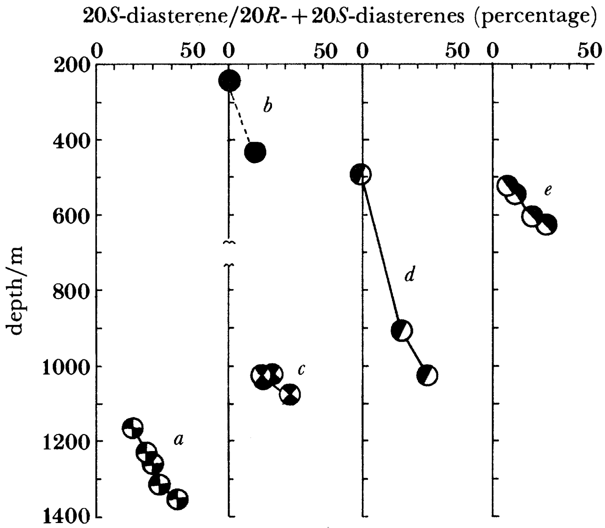

Figure 17. Progression of C_{27} diasterene isomerization at C-20 (see also figure 9) with depth for various D.S.D.P. sediment sequences; (*a*) Moroccan Basin; (*b*) Guaymas Basin; (*c*) Angola Basin; (*d*) San Miguel Gap; (*e*) Falkland Plateau. Modified from Brassell *et al.* (1984).

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Temperature relations

From the *in situ* temperature readings at the various D.S.D.P. sites or from regional geothermal gradients (Brassell *et al.* 1984) the extent of diasterene isomerization can be plotted against present sediment temperature rather than depth (figure 18). The accuracy of the trends observed is limited by the quality of the temperature data, which is poor in some instances (Brassell *et al.* 1984). A difference is apparent, however, between the Neogene samples (Guaymas Basin and San Miguel Gap) and those of Mesozoic age (Angola Basin, Moroccan Basin and Falkland Plateau). The former possess rather steeper slopes than the latter indicating an increase in reaction rate for the younger, hotter, more rapidly subsiding sedimentary sequences. This observation requires further assessment with a larger range of downhole profiles for diasterene isomerization. In addition, similar evaluation of other reactions should aid the assessment of the thermal history of these sediments.

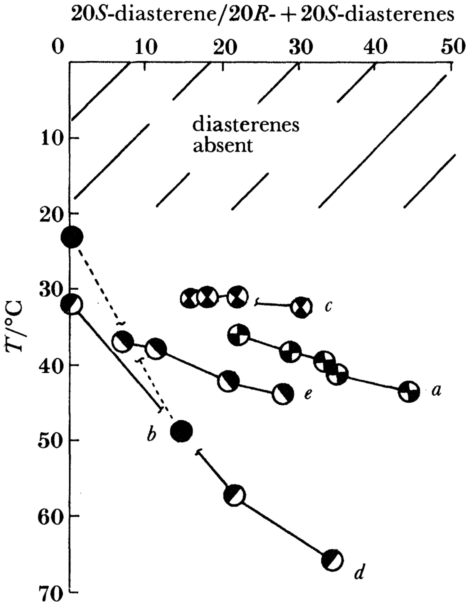

FIGURE 18. Progression of C_{27} diasterene isomerization at C-20 (see also figure 9) with temperature (estimated from *in situ* sediment measurements or regional geothermal gradients) for various D.S.D.P. sediment sequences (as figure 17). Modified from Brassell *et al.* 1984.

Depth ranges of diagenetic reactions

The sequence of the diagenetic transformation reactions considered above in four sediment sequences shows little variation (figure 19), although the depth ranges vary markedly. For example, sterene isomerization (reaction *a* in figure 19) occurs before diasterene formation and isomerization (reactions *b* and *c* in figure 19, respectively) in both the San Miguel Gap and Gulf of California (Guaymas Basin) sediments. In addition, isomerization of B-ring monoaromatic anthrasteroids (reaction *g* in figure 19) continues to depths below that at which the formation of A-ring monoaromatics (reaction *h* in figure 19) is complete for both these sequences. By contrast, the first appearance of A-ring monoaromatic steroids (reaction *h* in figure 19) succeeds sterene isomerization (reaction *a* in figure 19) in Walvis Ridge sediments, but not in the San Miguel Gap, where the two reactions apparently cease at the same depth

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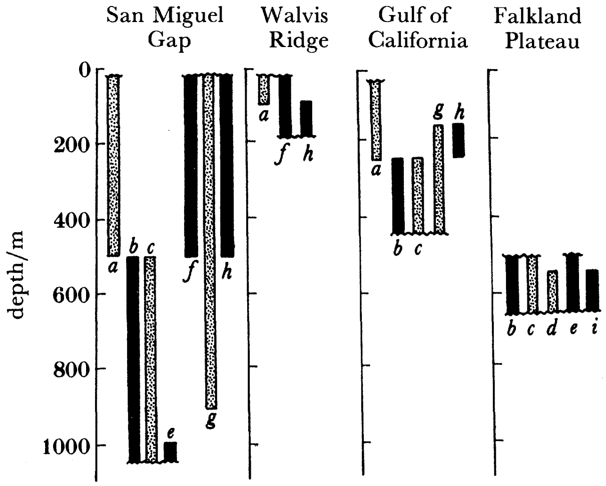

FIGURE 19. Depth ranges for the progression of the reactions discussed in this paper in four D.S.D.P. sediment sequences (after Brassell *et al.* 1984). Shadowed areas show formations and dotted areas show isomerization. (*a*) Sterenes, (*b*, *c*) diasterenes, (*d*, *e*) spirosterenes, (*f*, *g*) anthrasteroids, (*h*) A-ring monoaromatics, (*i*) C-ring monoaromatics.

level. Such anomalies may be attributed to the different temperature histories of these sediments (Brassell *et al.* 1984). There is, however, considerable scope for further study and refinement of the details of the diagenetic fate of steroidal hydrocarbons.

Summary

The study of the steroidal hydrocarbons of sediment sequences recovered by the D.S.D.P. can aid the recognition and confirmation of precursor–product relations during early diagenesis. Laboratory simulations of these reactions indicate that they require acidic conditions that may be met in sediments by the action of clays. It is also apparent that single precursor compounds can give rise to more than one product as some of the diagenetic pathways are divergent. Hence, the components present in mature sediments may depend, in part, on the relative amounts of different products generated during early diagenesis.

The evaluation of precursor–product relations in a series of sediment sequences demonstrates the sensitivity of molecular transormations, because differences in the extent of reactions are apparent over tens of metres and a few kelvins. A comparison of the progression of diagenetic reactions for D.S.D.P. sediments from several sites shows that a given reaction can occur (i) in sediments of different ages, (ii) at different depths and (iii) at different temperatures. Sediment sequences with similar temperature histories, however, appear to show parallel diagenetic trends. Also, precursor–product ratios may reflect the rates of heating of sediments, differentiating Neogene and Mesozoic sequences from active and passive margins, respectively. Overall, the sequence of diagenetic transformations shows a generally consistent pattern between sediments from different locations and thermal régimes.

A major objective for the future is the study of the kinetics and rate constants of diagenetic reactions. In addition there is every opportunity of extending this approach to investigate the effects of diagenesis on other compound types; examples of changes in triterpenoids are examined below. A further requirement for a better appreciation of diagenetic molecular

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changes is the recognition of the precise relation between the biological marker compounds and clays, especially the nature of their interaction and whether adsorption or surface phenomena are involved. Such associations between organic and inorganic media are poorly understood.

Early diagenesis of triterpenoids

The early-stage diagenesis of triterpenoids is generally less well understood than that of steroids. In particular the precise route encompassing the generation of extended hopanoids from bacteriohopanetetrol is unclear.

Hopane isomerization

The isomerization of hopanes, namely their sequential conversion from 17β*H*-, 21β*H*- to 17β*H*-, 21α*H*- and subsequently 17α*H*-, 21β*H*-isomers (Ensminger *et al.* 1974) is well known. The latter transition is accompanied by the further isomerization at C-22 for components greater than C_{31} yielding 22*S* and 22*R* isomers.

Hopene isomerization

Hopenes of direct biological origin found in shallow, subsurface sediments undergo double-bond isomerization and eventual methyl migration to form their most chemically stable isomers. Thus, hop-22(29)-ene appears to be isomerized to hop-21-ene, hop-17(21)-ene and eventually neohop-13(18)-ene (Brassell *et al.* 1980).

Fernene isomerization

Three fernene isomers have been recognized in many marine sediments (e.g. Brassell *et al.* 1980, 1981). The most chemically stable of these is fern-8-ene, which can be formed by isomerization of fern-7-ene and fern-9(11)-ene under acidic conditions (Berti & Bottari 1968 and figure 20). This isomerization is observed in various D.S.D.P. sediment sequences (figure 21). In the San Miguel Gap and Guaymas Basin sediments the isomerization occurs more rapidly (i.e. fern-8-ene is the dominant isomer at depths of 170 and 250 m respectively) than in those from the Walvis Ridge and the Japan Trench. This difference is probably a reflection of the higher heat flow in the former sequences.

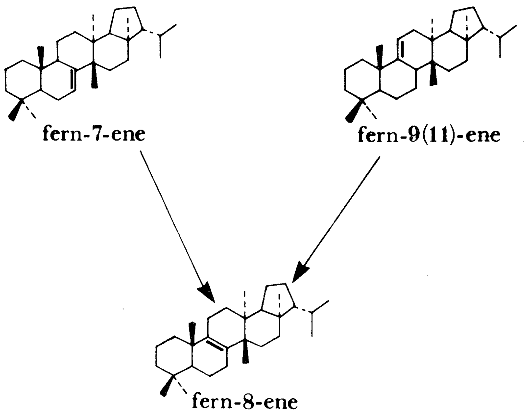

Figure 20. Proposed isomerization of fernenes (after Berti & Bottari 1968).

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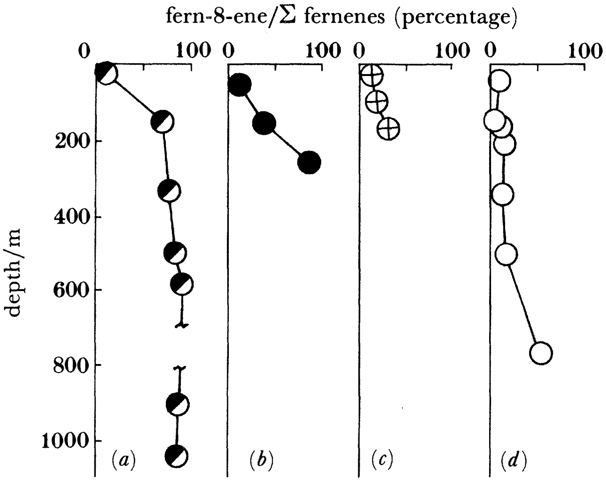

FIGURE 21. Progression of fernene isomerization with depth in four D.S.D.P. sediment sequences; (*a*) San Miguel Gap; (*b*) Guaymas Basin; (*c*) Walvis Ridge; (*d*) Japan Trench.

Summary

These few data for triterpenoid hydrocarbons suggest that, like the steroids, they should prove valuable measures of early diagenetic processes.

CONCLUSIONS

Among lipid diagenetic reactions a continuous sequence of appearance, transformation and disappearance of compounds is observed. These transformations form part of the continuum that links the components of living organisms to those found in mature sediments and petroleums. Such changes appear to be sensitive, systematic and non-reversible. These features make them valuable assets in the assessment of the thermal maturity of sediments.

For the future a major aim is the development of a system of diagenetic zonation by using the molecular descriptions of the sediments. Such a system should prove a precise measure of sediment maturity becase of the sensitivity of organic compounds to diagenetic transformations. In addition, the enormous range of organic components in sediments (see, for example, Brassell *et al.* 1983) provides an almost limitless number of possible precursor–product relations amenable to study.

I am grateful to my collaborators at Bristol, particularly Drs James Maxwell, Jim McEvoy, Neil Lamb and Chris Hoffman; also Torren Peakman and Mrs A. P. Gowar for valuable discussions during the preparation of this paper.

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Discussion

D. G. MURCHISON (*Organic Geochemistry Unit, The University, Newcastle-upon-Tyne*). Is the depth range over which the reactions that Dr Brassell has discussed occur governed by the geothermal gradient alone?

S. C. BRASSELL. I believe that the reaction rates are principally controlled by temperature, but this is not easy to demonstrate because the temperature within the D.S.D.P. holes is not generally measured accurately.

D. G. MURCHISON. Have the reactions also been done under laboratory conditions, and if so, how well do the rates compare with those estimated from deep-sea sediments?

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S. C. Brassell. Colleagues at Bristol and elsewhere have done a number of laboratory experiments, examples of which are described by Dr Maxwell in his paper. The problem with such laboratory experiments is that they have to be performed at a higher temperature than that at which they occur in the sediments, and there is therefore the concern that the reaction mechanism may be different.

R. Mason (*Department of Geology, University College London*). Can Dr Brassell give any indication of the mechanism by which clay minerals act as catalysts for organic reactions? Are all types of clay mineral equally effective, or does the effect depend on the structure of the clays?

S. C. Brassell. The clays appear to act by providing a suitable acidic medium on which the reactions can occur. In the laboratory all these reactions require an acidic environment. To what extent the clays provide surfaces on which the compounds can be adsorbed and desorbed and to what extent the clay mineral structure and its change with depth is involved, is not yet clear. There is, however, good evidence that the clay minerals provide the acidic media required for the reactions.

B. Durand (*Institut Français du Pétrole, Rueil Malmaison, France*). The reactions which Dr Brassell has described occur at low temperatures and appear to me to depend more on the environmental conditions than they do on temperature. Has he estimated the activation energies corresponding to the modifications observed and how do these compare with other observations of the activation energy for isomerization? Furthermore, his reaction scheme branches and it is not then straightforward to determine the kinetics of each step, in such a complicated scheme.

Dr Brassell has also suggested that clays act as acid catalysts, yet the usual reactions catalysed by clays occur in a water-free environment. The sediments in which the reactions occur contain large amounts of water, and I am not clear what happens under these conditions.

S. C. Brassell. The question of how the clays act as catalysts and the effect of water on this are unclear. A temperature difference of only a few degrees can have a significant effect on the extent of a reaction in sediments which are 100 Ma old. Such behaviour is compatible with a reaction whose rate is controlled by a thermal activation process.

G. Eglinton (*Organic Geochemistry Unit, School of Chemistry, University of Bristol*). Many of the reactions Dr Brassell has described involve a particular precursor whose characteristic structure can be followed throughout the reaction chain. This is true of the reactions involving the steroids, for instance. In other cases a single reactant may produce a variety of products, or a single product may be produced from a number of reactants. Under these circumstances it is obviously more difficult to disentangle the reaction pathways. However, similar complications occur in inorganic reactions in sediments.

P. A. Comet (*Organic Geochemistry Unit, The University, Newcastle-upon-Tyne*). To what extent does Dr Brassell believe that the reactions described reflect differences in lithology rather than rate of heat flow? Surely drastic differences in reaction rate might be expected on different substrates such as sulphur-rich against sulphur-poor sediments, smectite-rich against illite-rich sediments? Would this not have considerable implications for any calculations of reaction rates?

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S. C. Brassell. All the reactions I have discussed occurred in clay-rich sediments and not carbonates. In certain carbonates some of the diasterenes that are formed from sterenes by a clay-catalysed reaction are not found. It is therefore clear that the lithology does affect the final products of diagenesis. I am uncertain of the extent to which the concentration or type of the clay would affect its proposed catalytic role.

C. D. Curtis (*Beaumont Building*, *The University*, *Sheffield*). One way to investigate the importance of natural clay catalysis would be to study the progress of the organic reactions in sediments in which the clay minerals have been properly characterized. Have any such studies been made?

S. C. Brassell. I am not aware of such studies. One difficulty is that suitably organic-rich sediment sequences are not commonly found in D.S.D.P. holes and therefore there are few opportunities for such comparative studies. I would be interested to know about any suitable sequences.

J. Bada (*Scripss Institute of Oceanography*, *La Jolla*, *California*, *U.S.A.*). One straightforward test of the proposed reactions would be to plot the extent of the reaction against the total organic carbon content. Do such plots provide any useful information?

S. C. Brassell. The sequences we have studied all have a relatively constant organic carbon content and were selected for this reason.

J. W. de Leeuw (*Technical University Delft*, *Delft*, *The Netherlands*). Before we can investigate the influence of clays and other minerals on the reaction mechanisms we must understand better the chemistry of dehydration and isomerization reactions. Although these reactions look simple, there are indications that the mechanisms involved are quite complex. For instance, molecular-mechanical calculations suggest that Δ^2-5α*H*-sterenes are as stable as the Δ^4- and Δ^5-sterenes. Yet measurements on sediments like those Dr Berner discussed show that the Δ^2-sterenes disappear with increasing depth before the Δ^4- and Δ^5-sterenes. These obervations suggest that there is no thermodynamic equilibrium between the Δ^2- and Δ^4-, Δ^5-sterenes. Such studies may well help to understand the mechanisms involved.

S. C. Brassell. When the Δ^4- and Δ^5-sterenes first appear their abundances are approximately equal, but with increasing depth the Δ^4-sterenes become steadily more dominant. Is this reflected in the molecular calculations or is this also a result of factors other than thermodynamic stability?

J. W. de Leeuw. The equilibrium concentration should be about 40 % Δ^4- and 60 % Δ^5-sterene and this proportion is observed in some of the measurements. This difference in stability therefore does not account for the preferential disappearance of Δ^5-sterenes with increasing depth.