Biomarkers for Geologists—A Practical Guide to the Application of Steranes and Triterpanes in Petroleum Geology

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FOREWORD

In recent years, analysis of cyclic biomarker molecules has had a great impact on petroleum geochemistry. The development of simple, relatively inexpensive gas chromatography-mass spectrometry (gc-ms) systems has taken biomarker technology out of specialized research laboratories and placed it within the reach of many exploration geologists, who are now frequently asked to use biomarker data as one of their exploration tools. At the present time, however, few documents exist that can serve as guides for exploration geologists seeking to interpret biomarker data. This book attempts to fill that void.

Our scope will be intentionally somewhat narrow, focusing only on the two groups of saturated cyclic compounds (steranes and triterpanes) most frequently applied in exploration. These compounds contain three to six rings and usually from 21 to 35 carbon atoms. Emphasis will be on communicating those ideas about steranes and triterpanes that are generally accepted by biomarker specialists and that are most useful for exploration. The many biomarker problems currently of interest mainly to researchers will not be discussed.

Because we have written this book for exploration geologists rather than as a review for researchers, the references are intentionally not completely comprehensive. No attempt has been made to trace systematically the history of biomarker science, nor to give special credit to the pioneers. Most of the references are included primarily to summarize the most recent thinking on the subject of biomarkers and to guide a reader inexperienced in biomarker interpretation to recently published good sources of further information on a particular topic. Those interested in more detail about the chemistry of biomarkers can consult specialized sources, such as Philp (1985), Johns (1986), and Petrov (1987), or articles cited here and elsewhere.

Finally, we caution that the subject of biomarkers is considerably more complex than this book indicates. In an effort to make biomarker technology accessible to geologists, we have chosen to generalize and oversimplify a bit more than most researchers would prefer. To present all possible variations, ramifications, exceptions, and uncertainties about biomarkers would defeat the purpose of this book, which is to provide a working handbook for nonspecialists. We hope that specialists will not be too offended by some of our generalizations, and that nonspecialists will recognize that some statements herein will have to be modified as knowledge of biomarkers improves in the future.

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About the Authors

Doug Waples received his B.A. in chemistry from DePauw University in 1967 and his Ph.D. in chemistry from Stanford in 1971. He began his career in petroleum geochemistry in 1971 with a post-doctoral fellowship under Prof. Dietrich Welte in Germany, followed by another research and teaching fellowship in Chile. He spent three years in research with Chevron, four years as a faculty member at the Colorado School of Mines, four years in research and exploration with Mobil, and since 1983 has been an independent consultant. He is currently engaged in research on basin modeling with the Japan National Oil Corporation in Chiba, Japan.

Dr. Waples participated as a shipboard scientist on Legs 58 and 80 of the Deep Sea Drilling Project. He received the 1982 Sproule Award from the AAPG. He is the author or coauthor of about 60 publications, including two other books on petroleum geochemistry. His main interests today are basin modeling, exploration applications of petroleum geochemistry, and technology transfer, including teaching of seminars.

Dr. Tsutomu Machihara received his B.S. in chemistry from the University of Saitama in 1975, and M.S. and D.Sc. degrees in organic geochemistry from Tokyo Metropolitan University in 1977 and 1981, respectively. Since 1982 he has worked at the Technology Research Center of the Japan National Oil Corporation. Dr. Machihara also participated as a shipboard scientist on Leg 87A of the Deep Sea Drilling Project. His main research interests include studies of biomarkers in bitumens and oils, studies of hydrocarbon generation by compaction pyrolysis of kerogen, and studies of the chemical structure of kerogen, humic substances, and coal by a variety of chemical and geochemical techniques. Dr. Machihara is the author of about 35 publications in the field of geochemistry.

Chapter 1

Chemical Structures and Nomenclature

The basic structural building block of the biomarkers is the isoprene unit (Figure 1A). The end closer to the methyl branch is called the "head," and the other end is the "tail." Compounds formed biosynthetically from isoprene units are called "isoprenoids." Two isoprene units joined head-to-tail (with minor modifications, such as hydrogenation of double bonds) form a monoterpane (Figure 1B). Two monoterpanes (four isoprene units) linked together form a diterpane, whereas six isoprene units can be joined either to form a sterane or a triterpane, depending upon how the linking is accomplished.

Steranes usually contain four rings, the D-ring of which always contains five carbon atoms (Figure 2A). Triterpanes contain three to six rings (Figure 2B), with five-ring species being most common. The E-ring usually contains five carbon atoms, as in hopane in Figure 2B, but compounds having six carbon atoms in the E-ring are also known (e.g., gammacerane in Figure 2B).

During early diagenesis it appears that one or more of the rings in steranes and triterpanes sometimes can be opened by bacterial (?) activity (Peakman et al., 1986). Figure 2B shows de-A-lupane, a tetracyclic triterpane with the A-ring destroyed.

The precise number of carbon atoms in a given cyclic biomarker varies considerably as a result of differences in source material, effects of diagenesis and thermal maturity, and biodegradation. Thus names like "triterpane" tell us only that there are approximately 30 carbon atoms (3x10) in the compound. Furthermore, the ring structures themselves usually do not account for all the carbon atoms. For example, a four-ring sterane contains only 17 carbon atoms in the ring structure; the remaining 10 to 13 carbon atoms occur in various groups or side chains attached to the ring structure (Figure 2A).

Each carbon atom in a biomarker molecule is numbered for easy reference. The numbering systems for steranes and triterpanes are shown in Figure 3. The numbering system indicates where side chains are attached to the ring system and where small but significant changes in molecular architecture occur. For example, the two triterpanes in Figure 4 differ only by a single methyl group, present in compound A attached to carbon atom number 10, between the A and B rings (designated henceforth in this book as C-10). In compound B, in contrast, the methyl group has been replaced by a hydrogen atom. Compound A is a member of a class of compounds called "hopanes," and itself is called the "C_{30} hopane" or often simply "hopane."

The carbon atom in the methyl group attached to C-10 bears the designation C-25 (see Figure 3B). In one naming system, therefore, compound B can be referred to as the 25-norhopane, where the prefix "nor" means that one methyl group is missing, and "25-" indicates which methyl is absent. The prefix "nor" is only used to refer to methyl groups.

Another more general way to indicate the absence of some group is to use the prefix "des." In this system, however, we must indicate the position where the missing group should be attached to the carbon skeleton, rather than the number of the missing carbon, since the missing group is not always a methyl group. Thus the 25-norhopane in Figure 4 could also be called 10-desmethylhopane. Note that the type of group that is missing must be indicated using this system.

The numbering system also indicates where stereochemical changes occur. "Stereochemistry" refers to the spatial relationship of atoms in a molecule. The ring systems of cyclic biomarkers often are reasonably flat, resembling a piece of corrugated sheet metal. Wherever two rings are joined, each of the atoms at the junction is attached to three other carbon atoms in the ring structure (see Figure 2, 3, or 4). Its fourth bond (usually to a hydrogen atom or to the carbon of a methyl (CH_3–) group) can point either up or down with respect to the plane of the rings. When biomarker structures are drawn on paper, the directions "up" and "down" are often referred to as "out of the page" and "into the page," respectively.

Substituents that point down are called "alpha" (α); those that point up are called "beta" (β). The difference between alpha and beta stereochemistries is important, because the orientation of the substituent at a ring junction can greatly affect the molecular geometry, and hence the stability and properties of the molecule. The two different ways in which alpha and beta orientations can be indicated are shown in Figure 5.

In one system, we indicate an upward direction (toward the viewer) by drawing the bond as a solid wedge; if the group points down, the bond is drawn

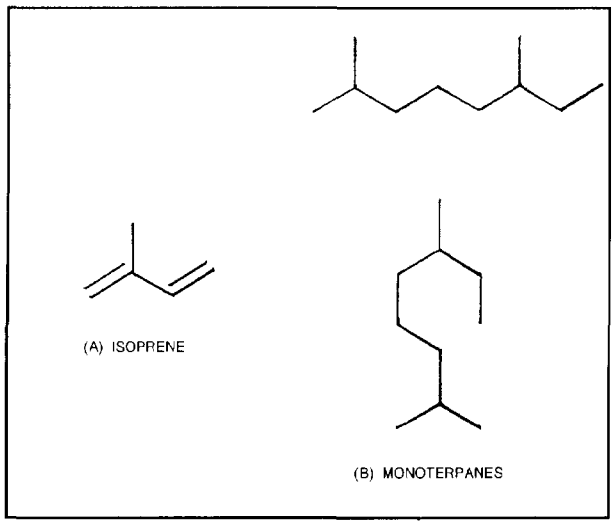


Figure 1—Chemical structure for isoprene (A) and two ways of drawing a monoterpane (B) formed from two isoprene units. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology.*

as a dashed or dotted line (Figure 6, left). (A plain line, as in Figures 2–4, indicates either that one is uncertain about the stereochemistry, or that for the purposes of the illustration it doesn't matter.) This system can be used for any group attached to the ring system.

The other system is only used to indicate the stereochemistry of hydrogen atoms (Figure 5). In this system, a hydrogen atom in the alpha position (pointing down) is shown by an open circle at the point of attachment, whereas a hydrogen in the beta position (pointing up) is shown by a black circle. As Figure 5 shows, the two systems are often mixed.

Stereochemistry can also be important at certain positions in the molecule away from the ring structure. If four different substituents are attached to a particular carbon atom (for example, C-22 in the molecules in Figure 6), that atom is called an "asymmetric" or "chiral" carbon atom. Because carbon atoms at ring junctions are usually asymmetric, biomarkers generally have several chiral carbon atoms.

Chemical compounds that differ only in the configuration of one or more of their chiral centers are called "stereoisomers." Stereoisomers that are mirror images of each other (each chiral center is of opposite configuration in the two molecules) are called "enantiomers," whereas stereoisomers that are not mirror images of each other (one or more of the chiral centers are the same in both molecules) are called "diastereomers." Petroleum geochemists generally do not work with enantiomers, but they do often use pairs or quartets of diastereomers.

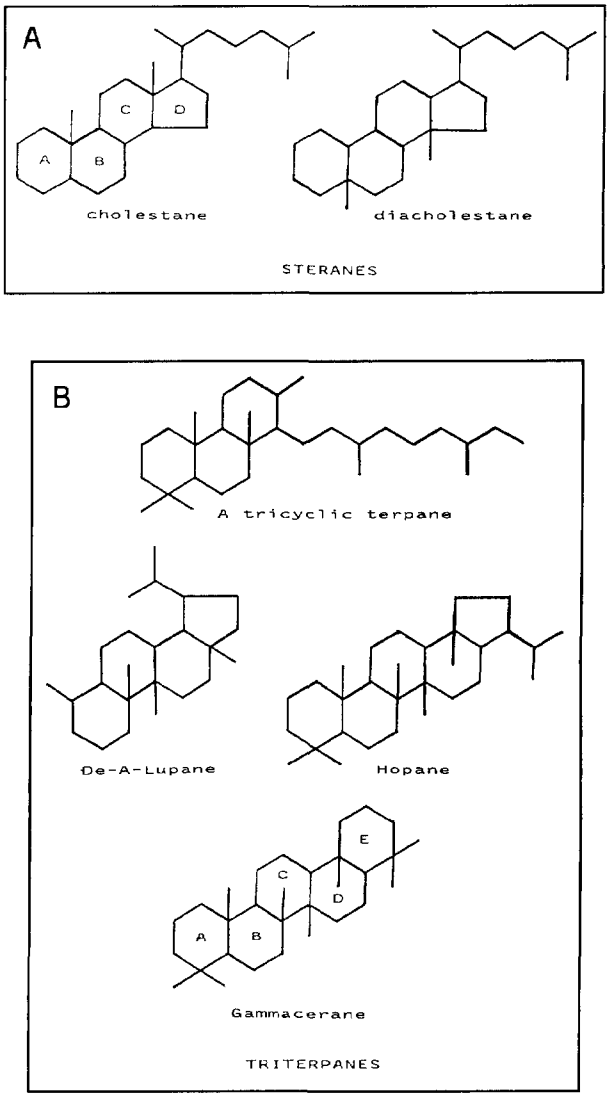


Figure 2—Chemical structures and names for typical steranes (A) and triterpanes (B). Rings are identified by letters. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology.*

Where two diastereomers differ only in the configuration of a single chiral center they are called "epimers" (Figure 6). Many of the pairs of cyclic biomarkers studied by geochemists are epimers. Further discussion of these terms and concepts can be found in any introductory textbook on organic chemistry.

The configuration at any chiral center outside the ring structure (Figure 6) is referred to as "R" or "S" (from the Latin words "rectus" for right and "sinister" for "left"). The terms R and S are used because the R and S epimers are mirror images, just as your right

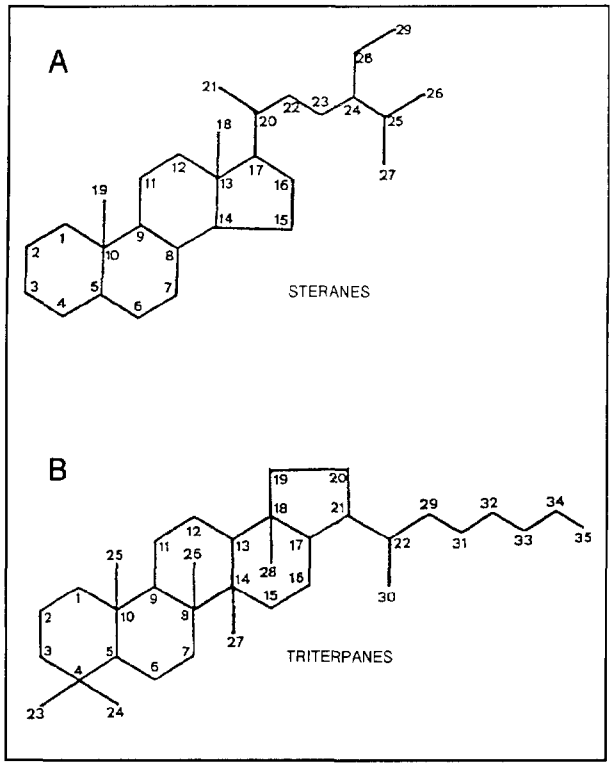


Figure 3—Numbering systems for steranes (A) and triterpanes (B). Adapted from Mackenzie (1984); reprinted with permission of Academic Press.

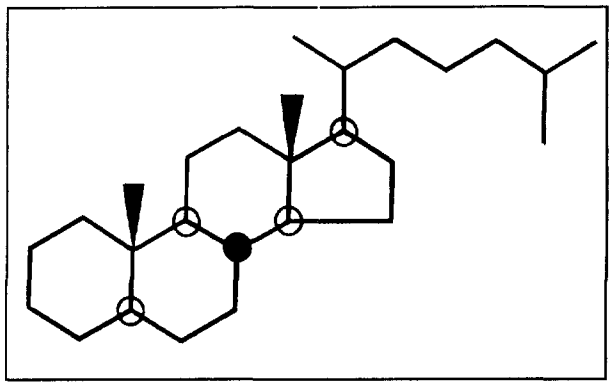


Figure 5—Structure of a typical sterane, the C_{27} species 5α(H),14α(H),17α(H)-cholestane, showing the stereochemistry at each ring junction using the two systems. Open circles indicate alpha configurations (pointing down); wedges and dark circles indicate beta configurations (pointing up). Stereochemistry at C-8 and C-9 is not designated in the name because hydrogens at those positions are always in the beta and alpha positions, respectively. See text for further discussion.

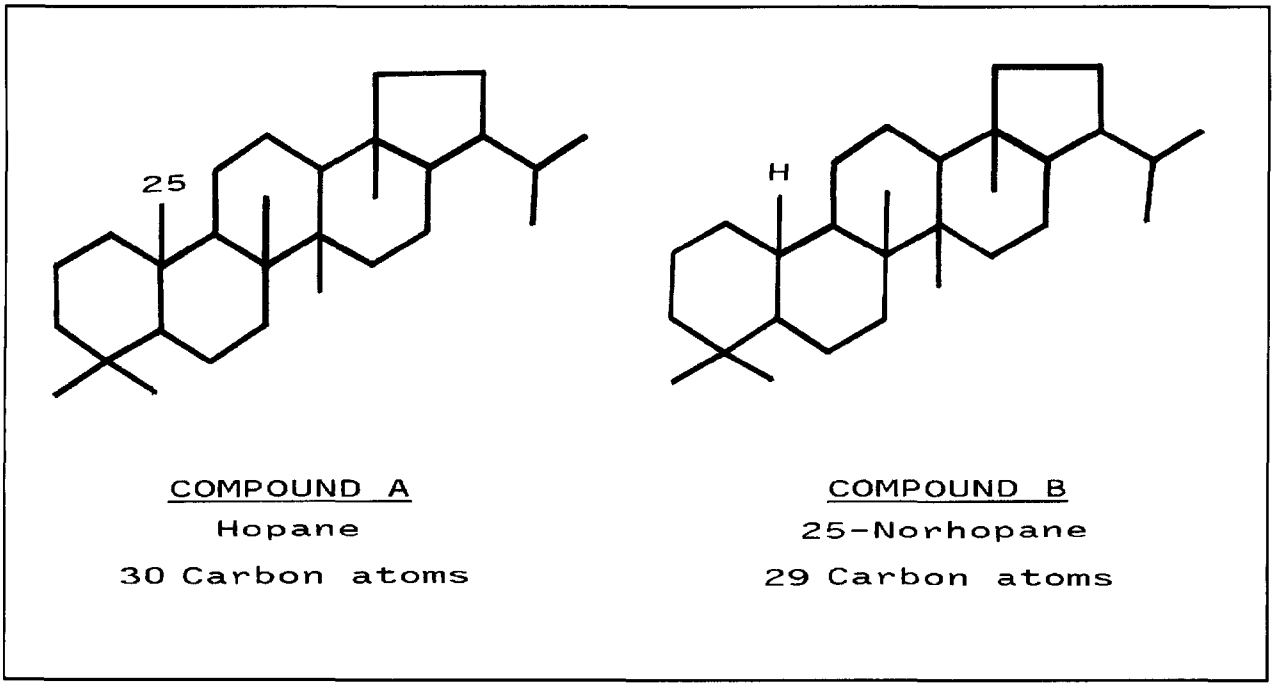


Figure 4—Two hopanes that differ only by the absence of the methyl group (C-25) in compound B. Compound B can result (probably indirectly) from severe biodegradation of compound A. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

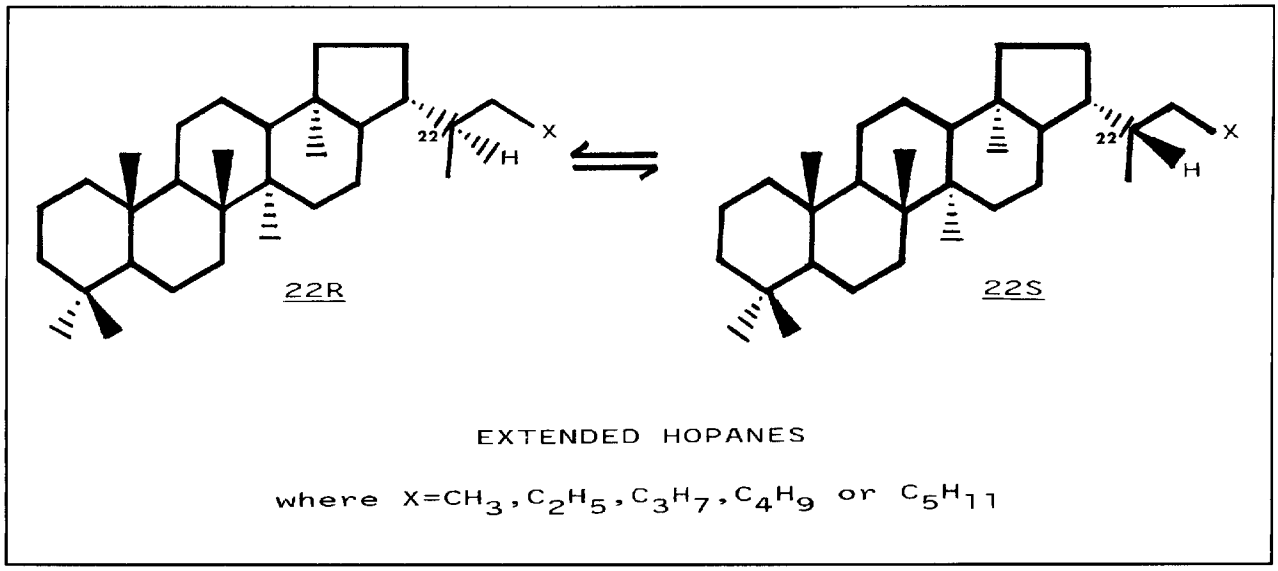


Figure 6—Structures of two diastereomeric 17α(H)-extended hopanes (designated 22R and 22S) which are interconverted in a reversible reaction. These compounds are also called "homohopanes." This illustration shows the stereochemistry at the ring junctions and at the chiral carbon atom C-22. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

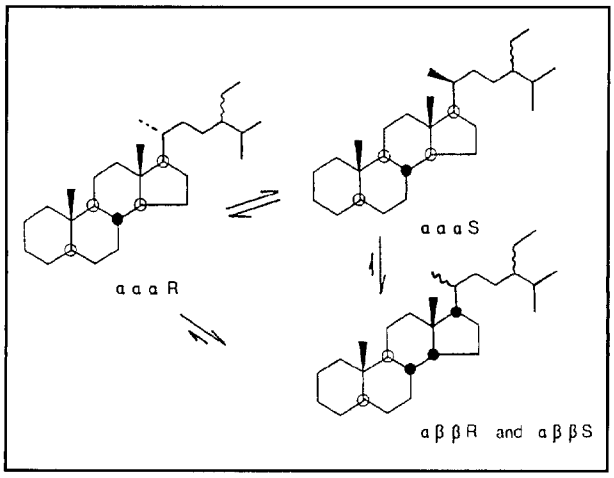


Figure 7—Reversible interconversion of 20R and 20S steranes (epimers) and 5α(H),14α(H),17α(H) and 5α(H),14β(H),17β(H) steranes (diastereomers). In one shorthand notation they are called "ααα" and αββ." The wavy line in the αββ structure at C-20 indicates that the stereochemistry at that site is unspecified. From Mackenzie (1984); reprinted with permission of Academic Press.

and left hands are mirror images. The most important configurational differences in R and S epimers are those at C-20 (20R and 20S) in steranes (Figure 7) and at C-22 (22R and 22S) in triterpanes containing more than thirty carbon atoms (Figure 6). Each of these groups of compounds will be discussed in much more detail in later chapters.

Chapter 2

Origin of Steranes and Triterpanes

INTRODUCTION

Many general facts and some detailed information are known about the origin of steranes and triterpanes. These compounds are saturated hydrocarbons, as indicated by the "-ane" ending in each of the names. Triterpanes and steranes themselves do not exist in living organic matter, but closely related precursor compounds (triterpenoids and steroids, including sterols) are present in varying concentrations in many organisms. During diagenesis some of these precursor molecules are converted, through a complex series of chemical and biochemical changes (e.g., Mackenzie, 1984), into the more stable, saturated-hydrocarbon biomarkers preserved in geological samples.

The precursor steroid and triterpenoid molecules generally contain one or more oxygen atoms and often have double bonds. During diagenesis (the low-temperature processes occurring after the death of an organism but prior to deep burial and thermal maturation), the oxygen atoms are lost and the double bonds are hydrogenated (reduced) to produce the saturated-hydrocarbon biomarkers. Fortunately, in most cases the reactions that occur during diagenesis have little or no effect on the rest of the molecule. (Exceptions that sometimes occur include the opening of one of the rings during diagenesis; the direct formation of aromatic hydrocarbons rather than saturated molecules; the formation of ββ steranes; and the formation of diasteranes.) Thus in most cases the structural peculiarities of each distinct biological molecule are inherited without change by its daughter biomarker molecule. For this reason, biomarker structures can provide much useful information about their precursor molecules. If we know the types of organisms from which specific steroids and triterpenoids come, we can relate biomarkers to particular precursor organisms. Thus an understanding of the origins of biomarkers can lead to an understanding of paleoenvironments, as we shall see in more detail in the following discussion.

STERANES

Steranes are derived from sterols that are found in most higher plants and algae but are rare or absent in procaryotic organisms (Volkman, 1986, 1988). Four principal sterol precursors containing 27, 28, 29, and 30 carbon atoms have been identified in numerous photosynthetic organisms (Figure 8). These sterols give rise to four different "regular" steranes during diagenesis (Figure 9). These four steranes can be called "homologs" or members of a "homologous series" because they only differ by the addition of a sequence of $-CH_2-$ units to a certain place in the molecule. The term "regular" indicates that the carbon skeletons are the same as in the biological precursors.

There are several ways of referring to the C_{27}–C_{29} steranes. In one system they each receive a different name derived from a common sterol with the same number of carbon atoms. From C_{27} to C_{29} these names are cholestane, ergostane, and sitostane, respectively. In other cases they are named as homologs of cholestane: cholestane, 24-methylcholestane, and 24-ethylcholestane, respectively. (Sometimes this system is shortened by dropping the number 24.) These various possible names are shown in Table 1.

In very immature sediments there occur some unstable compounds that are intermediates in the transformation of sterols to steranes. These intermediates are seldom encountered in the samples analyzed in source-rock or correlation studies, however, and are therefore omitted from consideration in this book.

Except for the loss of oxygen atoms and the hydrogenation of double bonds, the detailed structures of the newly formed steranes and their precursor sterols have generally been assumed to be identical. In particular, all newly formed steranes are believed to exist only as the 20R epimer (Figure 7), because only that form is produced biologically.

Recent evidence, however, suggests that stereochemical changes can occur at C-14 and C-17 during diagenesis. The molecules that occur in sterols have hydrogen atoms in the alpha configurations at both these positions. This form is designated variously as "5α(H),14α(H),17α(H)" or "14α(H),17α(H)," or more simply as "ααα" or "αα." Although most diagenetically produced steranes will also be dominantly or exclusively of the αα form, it has been suggested (e.g., Rullkötter and Marzi, 1988; Peakman et al., 1989) that the 5α(H),14β(H),17β(H) form (αββ or ββ) may also be produced during diagenesis, particularly in hyper-

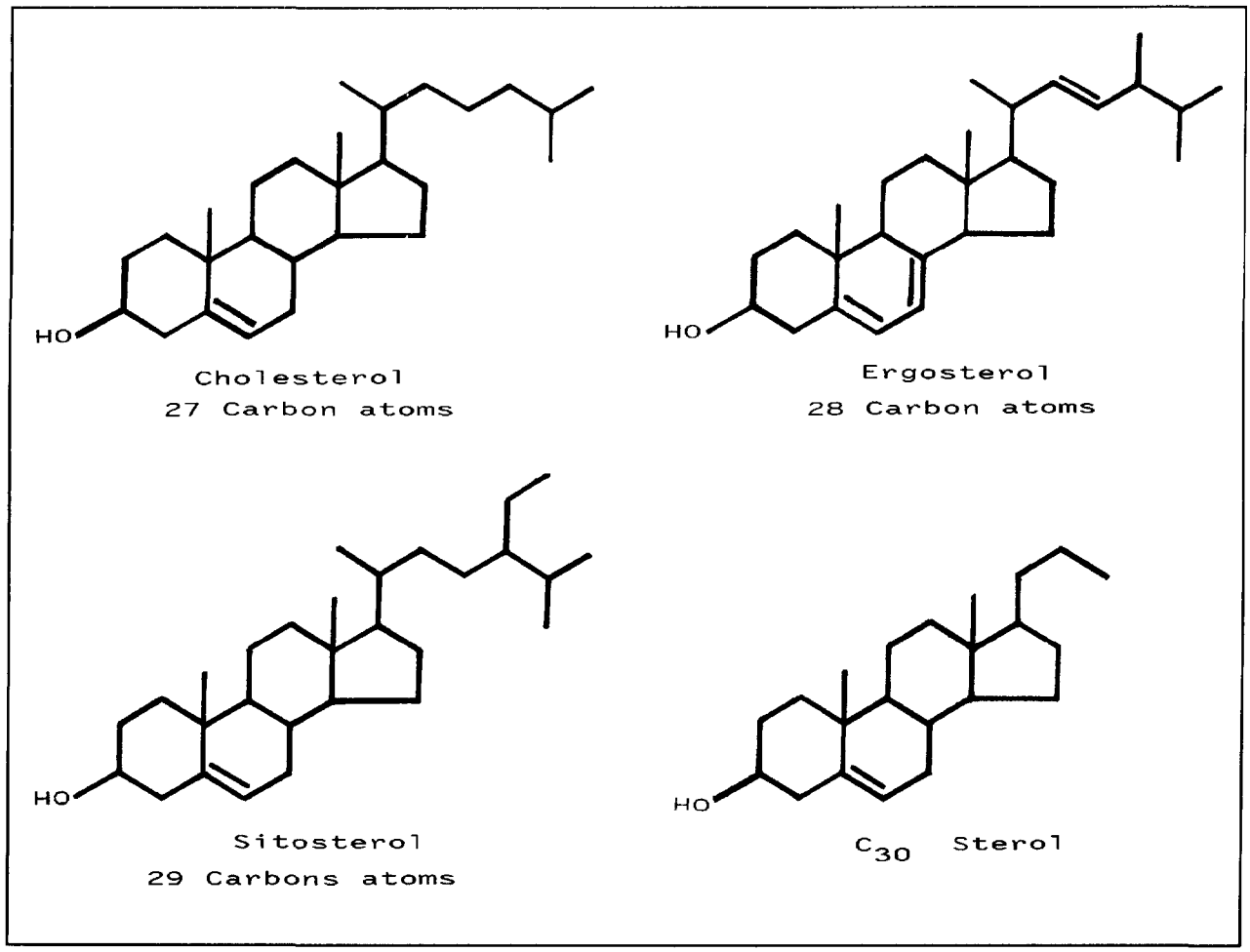


Figure 8—Structures of some important C_{27} to C_{30} sterols in photosynthetic organisms.

saline environments. The ββ structures are shown in Figure 7. Both the αα and ββ steranes are called "regular steranes."

In addition to the regular steranes, a family of "rearranged steranes" or "diasteranes" is commonly encountered (Figure 10). These compounds differ from the regular steranes by having methyl groups attached to C-5 and C-14 instead of hydrogen atoms, and having hydrogens attached to C-10 and C-13 instead of methyl groups. The transformation from regular steranes to diasteranes is believed to occur during diagenesis under certain conditions and during catagenesis (thermal maturation) in other cases. Diasteranes will be discussed in more detail in Chapters 4 and 5.

Besides the regular steranes, 4-methylsteranes (steranes with an additional methyl group attached to C-4 in the A ring) have also been commonly reported. They appear to form two distinct families (Figure 11). One family, called "dinosteranes," is derived from dinoflagellates (de Leeuw et al., 1983; Goodwin et al., 1988). They exist only as the various stereoisomers of the C_{30} homolog. As Figure 11 shows, dinosteranes can be thought of as cholestane (the regular C_{27} sterane) with three additional methyl groups, at positions 4, 23, and 24.

The other family can be considered as the three regular steranes (C_{27}, C_{28}, and C_{29} from Figure 9, also known as cholestane, 24-methylcholestane, and 24-ethylcholestane) containing an additional methyl group at C-4. They therefore form a homologous series with 28, 29, and 30 carbon atoms. In this book we will call them the "4-methylcholestanes." Figure 11 shows the small difference in structure between the C_{30} forms of the two families. The 4-methylcholestanes are of uncertain origin (Goodwin et al., 1988).

TRITERPANES

In contrast to the steranes, which come from steroids in algae and higher plants (and to a lesser

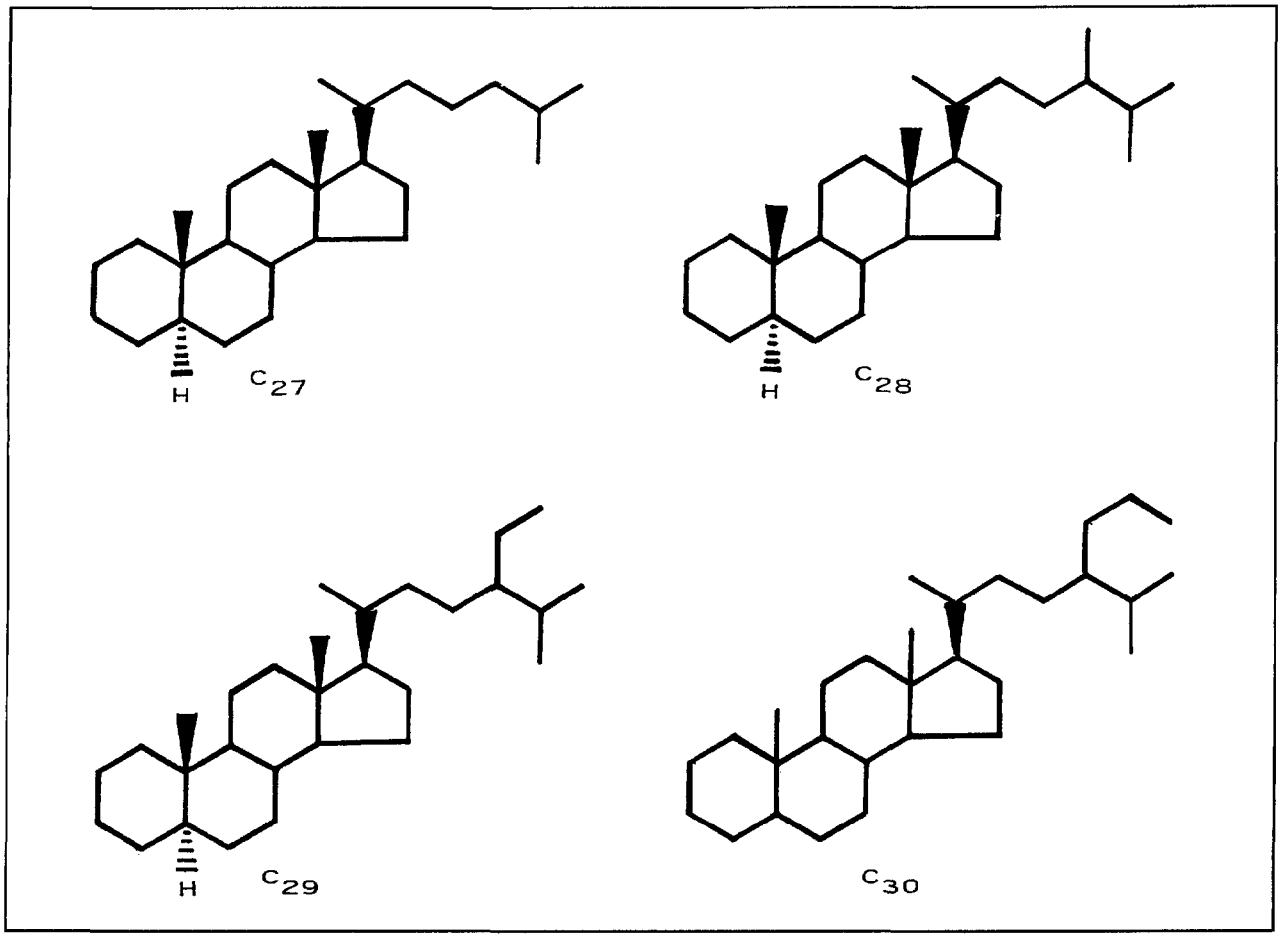


Figure 9—Structures of C_{27}-C_{30} steranes derived from sterols. C_{27} = cholestane; C_{28} = ergostane or 24-methylcholestane; C_{29} = sitostane or 24-ethylcholestane; C_{30} = 24-propylcholestane. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

Table 1. Various ways of referring to the C_{27}, C_{28}, and C_{29} regular steranes. For each name one could also designate the stereochemistry at carbons 5, 14, and 17 as alpha (α) or beta (β).

Number of Carbon Atoms	Common-Name System	Substituted-Cholestane System	Abbreviated System
27	Cholestane	Cholestane	Cholestane
28	Ergostane	24-Methylcholestane	Methylcholestane
29	Sitostane	24-Ethylcholestane	Ethylcholestane

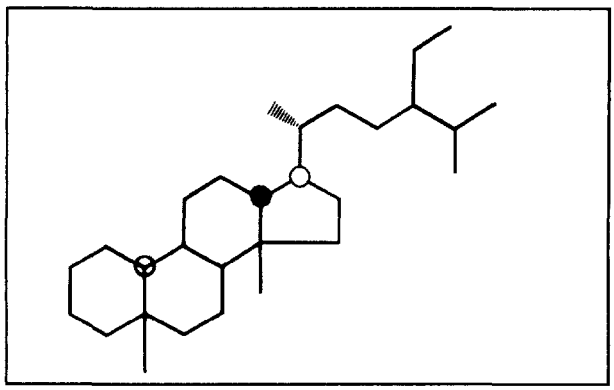


Figure 10—Structure of the 20S epimer of the C_{29} rearranged sterane (a diasterane). Filled circle represents a hydrogen atom in the beta configuration; open circles represent hydrogens in the alpha configuration. By drawing the methyl groups attached to C-5 and C-14 as straight lines we are not specifying whether they are in the alpha or beta position. Both αα and ββ forms exist, but mixed αβ or βα forms are absent or very rare. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

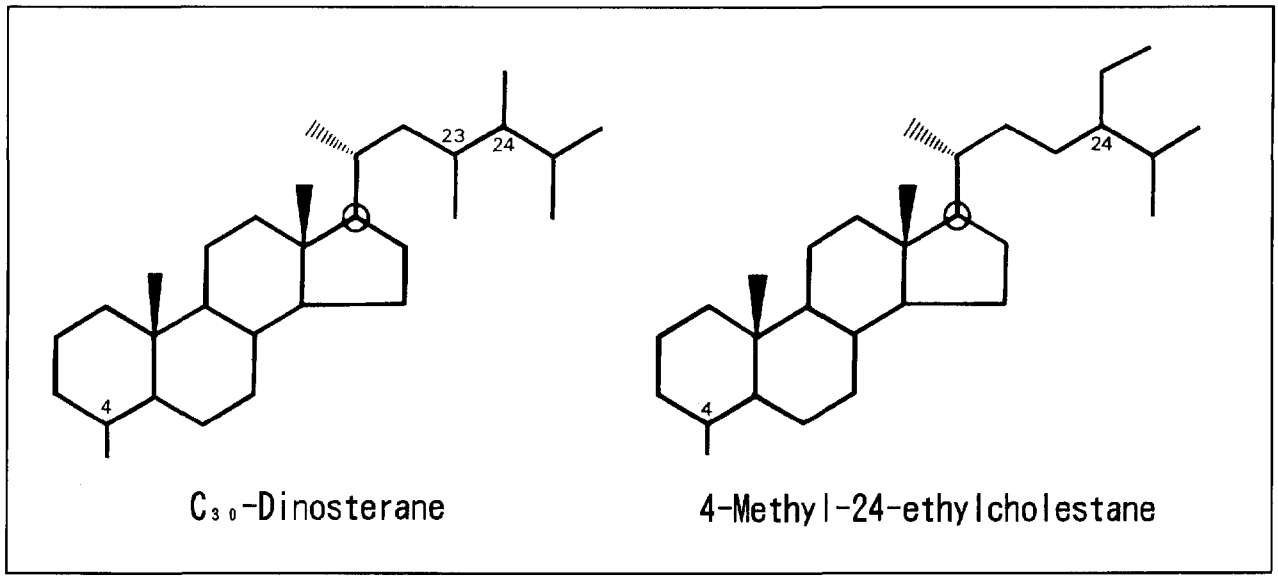


Figure 11—Structures of the ααα C_{30} (20R) members of the two families of 4-methylsteranes. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

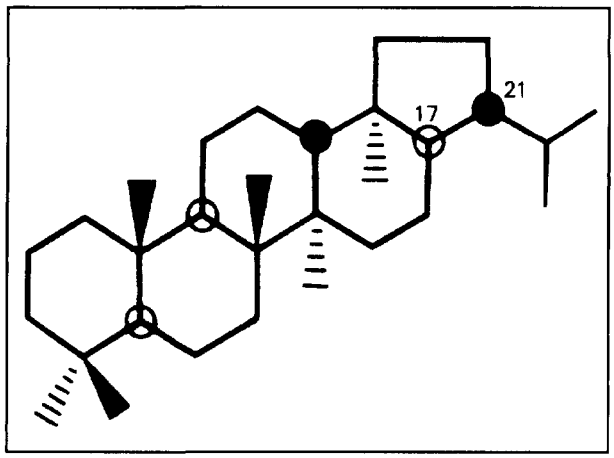


Figure 12—Structure of 17α(H),21β(H) C_{30} hopane.

degree from animals), the source organisms for most triterpane biomarkers are believed to be bacteria. Various triterpenoids containing such features as -OH groups and double bonds have been characterized as important constituents of cell membranes in bacteria. A wide variety of triterpenoids is probably produced among the many types of microorganisms present in different depositional environments, although many details are still missing. In particular, there may be significant differences between aerobic bacteria and anaerobes, especially methanogens. A review by Ourisson et al. (1984) provides a very readable discussion of the bacterial origin and importance of triterpenoids.

Transformation of triterpenoids to triterpanes probably occurs along much the same lines as does transformation of sterols to steranes, although recent evidence from carbon-isotope ratios of individual compounds suggests that transformations in sediments are extremely complex (Freeman et al., 1990). As with steranes, the general molecular architecture of triterpanes is usually little affected by diagenesis. The first important stereochemical transformation that we need be concerned with is the formation during very early diagenesis of 17α(H),21β(H) isomers. This geometry, which is particularly stable, has the hydrogen attached to C-17 in the alpha configuration, and the hydrogen at C-21 in the beta configuration (Figure 12). Hopanes with the 17β(H),21β(H) configuration (ββ hopanes) are present only in very immature samples and, like some very immature steranes, are therefore unimportant in petroleum geochemistry. They are therefore not discussed further in this book.

Triterpanes can be divided into three distinct families based on the number of rings. The most common and most thoroughly studied triterpanes have five rings (e.g., Figure 12), and are therefore called "pentacyclics." Most of these compounds contain from 27 to 35 carbon atoms, although they have been reported up to C_{40} (Rullkötter and Philp, 1981; Farrimond et al., 1990). A less common and more poorly understood group of triterpanes, the tricyclics, has only three rings (e.g., Figure 2B). They range from about 21 to more than 40 carbon atoms, but those with fewer than 25 carbon atoms are dominant. The third family, the tetracyclics, is the least studied and most poorly understood family.

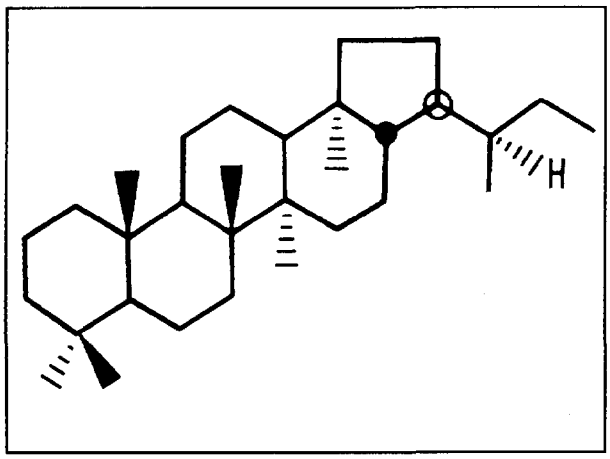


Figure 13—Structure of the C_{31} (20R) moretane.

The pentacyclics often are divided into "hopanoids" and "nonhopanoids." The hopanoids include both the 17α(H),21β(H) hopanes (simply called "hopanes": Figs. 4, 6, and 12) and the 17β(H),21α(H) hopanes (called moretanes: Figure 13).

The most common pentacyclic triterpanes are the hopanes. The hopanes most frequently analyzed contain 27 to 35 carbon atoms and form a homologous series with the 17α(H),21β(H) configuration (Figure 12). They are commonly referred to as both "hopanes" and "17α(H)-hopanes." As noted previously, the 30-carbon member shown in Figures 2B, 4 (left), and 12 is also often called simply "hopane."

Each homolog differs from the next by a single $-CH_2-$ group attached to the side-chain on the E-ring. The C_{29} and C_{30} 17α(H)-hopanes have no chiral carbon atoms in their side chains (Figure 12). The C_{31}–C_{40} 17α(H)-hopanes (often referred to as "homohopanes" or "extended hopanes"), however, all have a single chiral carbon atom (C-22) in the side chain, and thus can exist as both the 22R and 22S epimers (Figure 6). Because all biologically produced hopane precursors exist only in the R form, newly formed extended hopanes in sediments all have the 22R configuration.

A pair of C_{27} hopanes (17α(H)-22,29,30-trisnorhopane and 18α(H)-22,29,30-trisnorneohopane, commonly called Tm and Ts, respectively) are also present in virtually all samples (Figure 14). Tm is believed to represent the biologically produced structure; Ts is generated in sediments and rocks by diagenetic or thermal processes, or both. In the past Ts was believed to be formed from Tm, but that conclusion has not been verified. The source for Ts thus remains unknown.

Recently it has been shown that a homologous series of moretanes containing 29 to at least 35 carbon atoms exists, just like the series of 17α(H)-hopanes (Larcher et al., 1987; Kvenvolden and Simoneit, 1990). The paleoenvironmental significance of moretanes is not yet fully understood. They may have a microbial origin like the hopanes, but at least some are thought to be derived from higher plants (Rullkötter and Marzi, 1988; Ramanampisoa et al., 1990).

It is not unusual to encounter a few other pentacyclic triterpanes in significant concentrations in oils and rock extracts, although the structures of most of these molecules have not been determined. Among those that have been identified are two hopanes (28,30-bisnorhopane and 25,28,30-trisnorhopane), and several

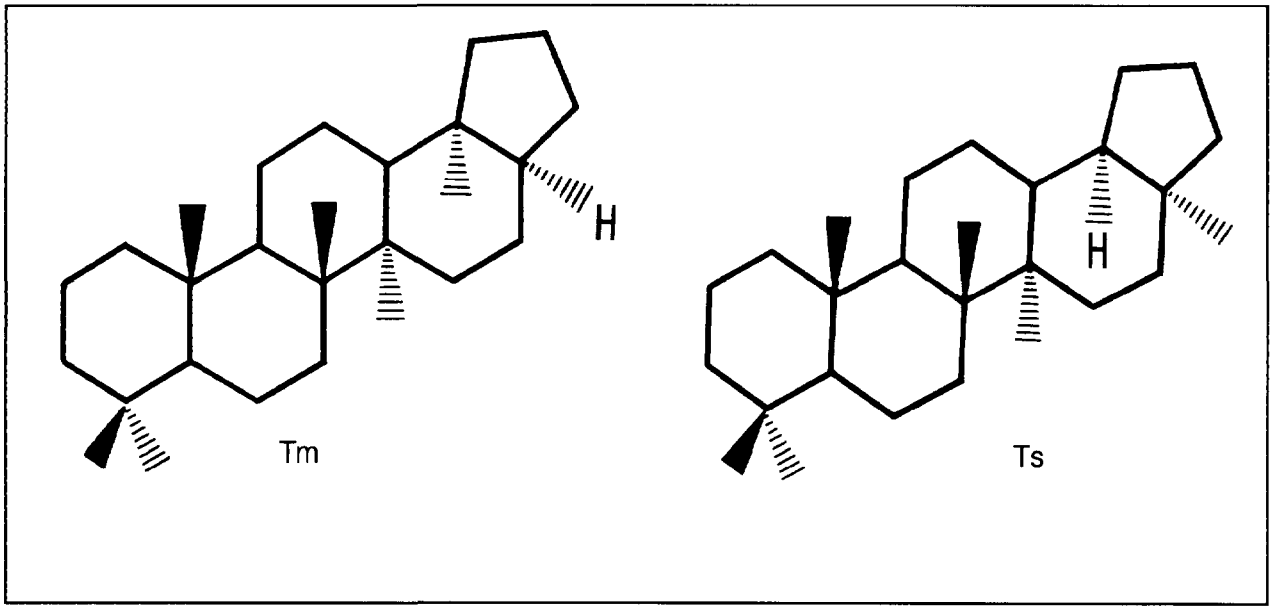


Figure 14—Structures of Tm and Ts.

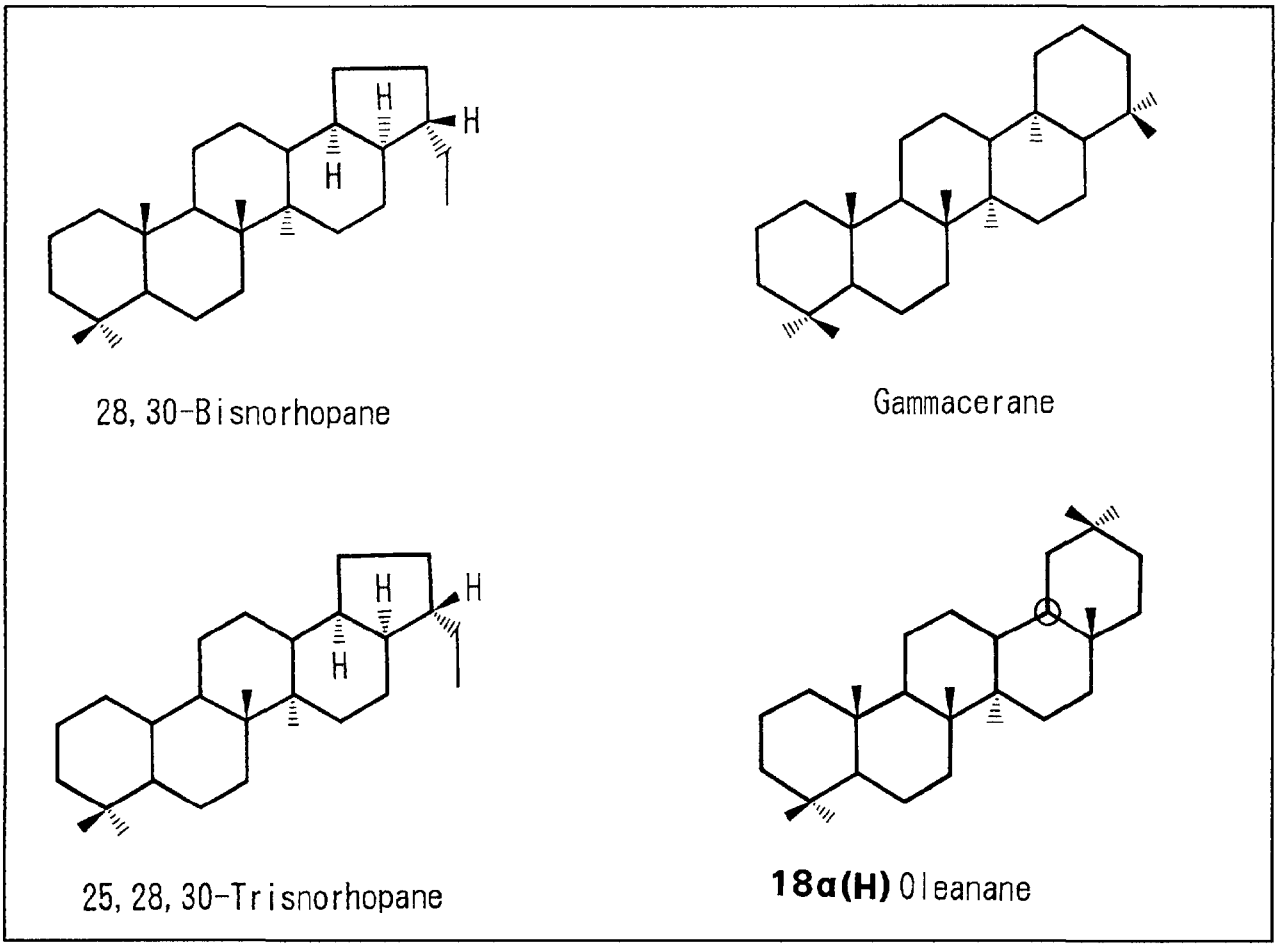


Figure 15—Structures of 28,30-bisnorhopane, 25,28,30-trisnorhopane, gammacerane, and 18α(H)-oleanane. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

nonhopanoids (gammacerane and a family of compounds called oleananes). Structures are shown in Figure 15. The oleananes are thought to come from angiosperms (terrestrial plants); the other compounds in Figure 15 are all believed to come from microorganisms. Further discussion of the paleoenvironmental significance of these compounds is found in Chapter 5.

The tricyclic and tetracyclic triterpanes (e.g., Figure 2) do not appear to be degraded pentacyclics, but instead appear to be members of separate genetic families. They are probably either generated in smaller quantities by the same bacteria that produce the pentacyclics, or by other species of microorganisms that synthesize them instead of the pentacyclics. However, Philp (1985) has suggested that tricyclics may be formed by partial aerobic oxidation of bacterial membranes. If he is correct, then their abundance in rocks and oils may be related more to diagenetic factors than to direct biosynthetic production by specific organisms.

Chapter 3

Analytical Procedures

SAMPLE PROCESSING

Samples for biomarker analysis can come from many sources: well cuttings, sidewall cores, conventional cores, outcrop material, produced or tested oils, solidified bitumens, tars, or dead-oil stains. Maximum care should always be taken, particularly with rock samples, to avoid contamination by fuels, lubricants, or other petroleum-based products. Because even conventional cores can be stained by mud additives, samples should be taken from the interior of the core to minimize problems.

Because biomarkers normally are not present in lighter distillation fractions such as gasoline or diesel, diesel contamination presents no problem for biomarker analysis. However, if crude oils are used as drilling-mud additives, removal of contamination prior to analysis of rock samples is both crucial and difficult. Coals (indigenous or in the form of lignosulfonate mud additives) or "gilsonite" additives could also cause severe contamination problems if present in even minor quantities in cuttings samples because of their high organic-carbon contents and high concentrations of biomarkers.

The minimum amount of sample required for biomarker analysis is highly variable, because it depends directly on organic richness. Rock-Eval S_1 data (see, for example, Tissot and Welte, 1984) can be used as a rough guide, because the S_1 yield is approximately equivalent to the quantity of hydrocarbons in the solvent-extractable material. Because a minimum of 50 mg of hydrocarbons is normally required to permit gas chromatography-mass spectrometry (gc-ms) analysis, the quantity of sample required is that which would give 50 mg of S_1. For example, if the S_1 value for a given rock sample is 2.0 mg/g rock, a minimum of about 25 g would have to be extracted to perform biomarker analyses.

Rock samples are air dried, crushed, and extracted with an organic solvent such as dichloromethane. The soluble material (extract) is then recovered by evaporation of the solvent. From this point onward extracts and oils (including tars and other solidified organic substances) are handled in the same manner. The asphaltenes are removed from the extract or petroleum by precipitation with a light solvent such as pentane. The asphaltene-free material is then separated, using liquid chromatography, into fractions consisting of saturated hydrocarbons, aromatic hydrocarbons, and polar (NSO) compounds. Although some light compounds (up to about C_{15}) are lost during evaporation of the solvent in this step and the previous one, steranes and triterpanes are unaffected by evaporative loss.

The saturated-hydrocarbon fraction commonly is treated further with molecular sieves to remove the n-alkanes, which might interfere with subsequent analysis of the steranes and triterpanes. The remaining fraction contains the branched and cyclic alkanes, including the steranes and triterpanes.

GC-MS ANALYSIS

A typical gc-ms system used for analysis of biomarkers consists of a capillary gas chromatograph connected to a mass spectrometer and a computer work station (Figure 16). The mixture to be analyzed is injected into the gas chromatograph, where the various compounds are separated according to the speed at which they move through the gas-chromatographic column. Separation of the saturated hydrocarbons is achieved primarily according to molecular weight and volatility, although molecular shape may also play a role. The separated compounds leave the gas chromatograph in sequence and enter the mass spectrometer's ion chamber, where they are analyzed in the same sequence.

Each compound entering the mass spectrometer is bombarded with a high-energy electron beam that ionizes the molecules by knocking off one electron. The molecular ions formed in this manner are unstable, however; most break apart to give a variety of smaller fragment ions. The molecular and fragment ions produced in this manner differ in mass, but most bear a +1 charge. Because of the differences in their mass/charge ratios (m/z; also sometimes called m/e) caused by the differences in mass, they can be separated by a magnetic field or a quadrupole. The separated ions move sequentially to the detector where the relative abundances of each mass are recorded. The complete record of the quantities and masses of all ions produced from a compound is called its mass spectrum.

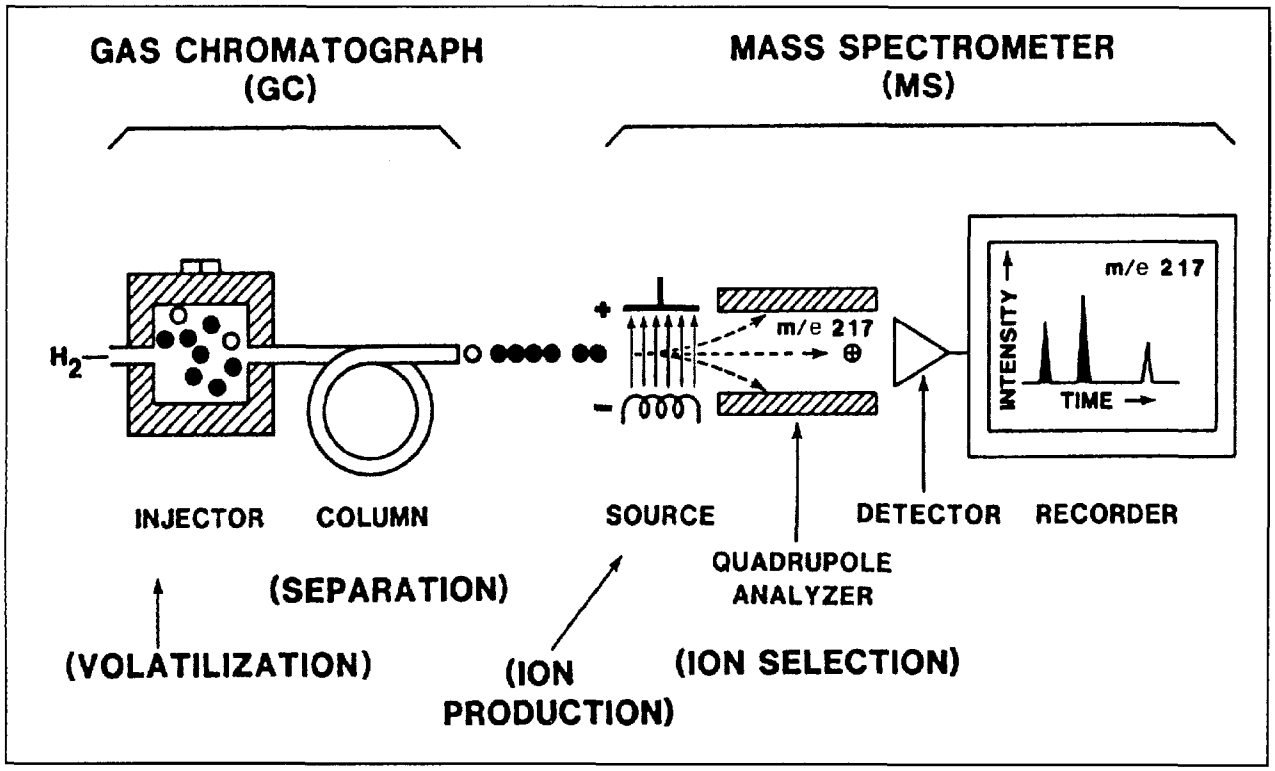


Figure 16—Schematic diagram of a gas chromatography-mass spectrometry system. From Waples (1985), p. 78; reprinted with permission of Prentice Hall, Inc., Englewood Cliffs, New Jersey.

The various classes of biomarkers all fragment in characteristic ways in the mass spectrometer, depending upon their molecular structures. For example, the dominant fragmentation patterns for steranes and triterpanes are shown in Figure 17. Nearly all sterane molecules (except 4-methylsteranes, discussed later) will yield a large amount of the fragment ion with a mass of 217 daltons (m/z 217). Similarly, triterpanes (except bisnorlupanes and 25-norhopanes, also discussed later) will generally yield large quantities of the m/z 191 fragment ion. Both types of compounds yield many other fragments in lesser quantities as well.

In practice, however, we normally do not record the entire mass spectrum for individual compounds. Instead, we monitor each compound coming out of the gas chromatograph to see if it gives the ions characteristic of the most common types of biomarkers: e.g., m/z 217 for steranes or m/z 191 for triterpanes. Normally we scan each compound emerging from the gas chromatograph for the presence of several preselected fragment ions. This process is called "selected ion monitoring," "single ion monitoring," or "SIM." SIM is the key to using gc-ms effectively in petroleum geochemistry, because it allows us to classify quickly a large number of different molecules in each sample.

The output from an SIM analysis is called a "mass chromatogram" or "mass fragmentogram." Several different ions can be monitored for each sample. The following generalizations serve as the basis for most of our interpretations of SIM data: m/z 217 mass chromatograms show steranes (Figure 17B), whereas m/z 191 mass chromatograms show triterpanes (Figure 17C). Of course, other types of compounds can also give small amounts of m/z 217 or m/z 191, and thus will appear as minor peaks in these mass fragmentograms. In most cases, therefore, we only interpret the data for the major peaks in each mass fragmentogram.

Other fragment ions besides m/z 217 and 191 can also be valuable. The m/z 177 mass chromatogram is useful for looking for an important class of triterpanes that have lost the methyl group attached to the A/B ring junction. Examples include 25-norhopane, shown in Figure 4, and the bisnorlupanes. The m/z 231 mass chromatogram can be used to search for 4-methylsteranes, since the dominant fragment ion is now 14 daltons larger than the typical sterane fragment. These compounds are covered in more detail in Chapter 6. As discussed next, the m/z 218 mass chromatogram can be a useful alternative to the m/z 217 in looking at the regular steranes.

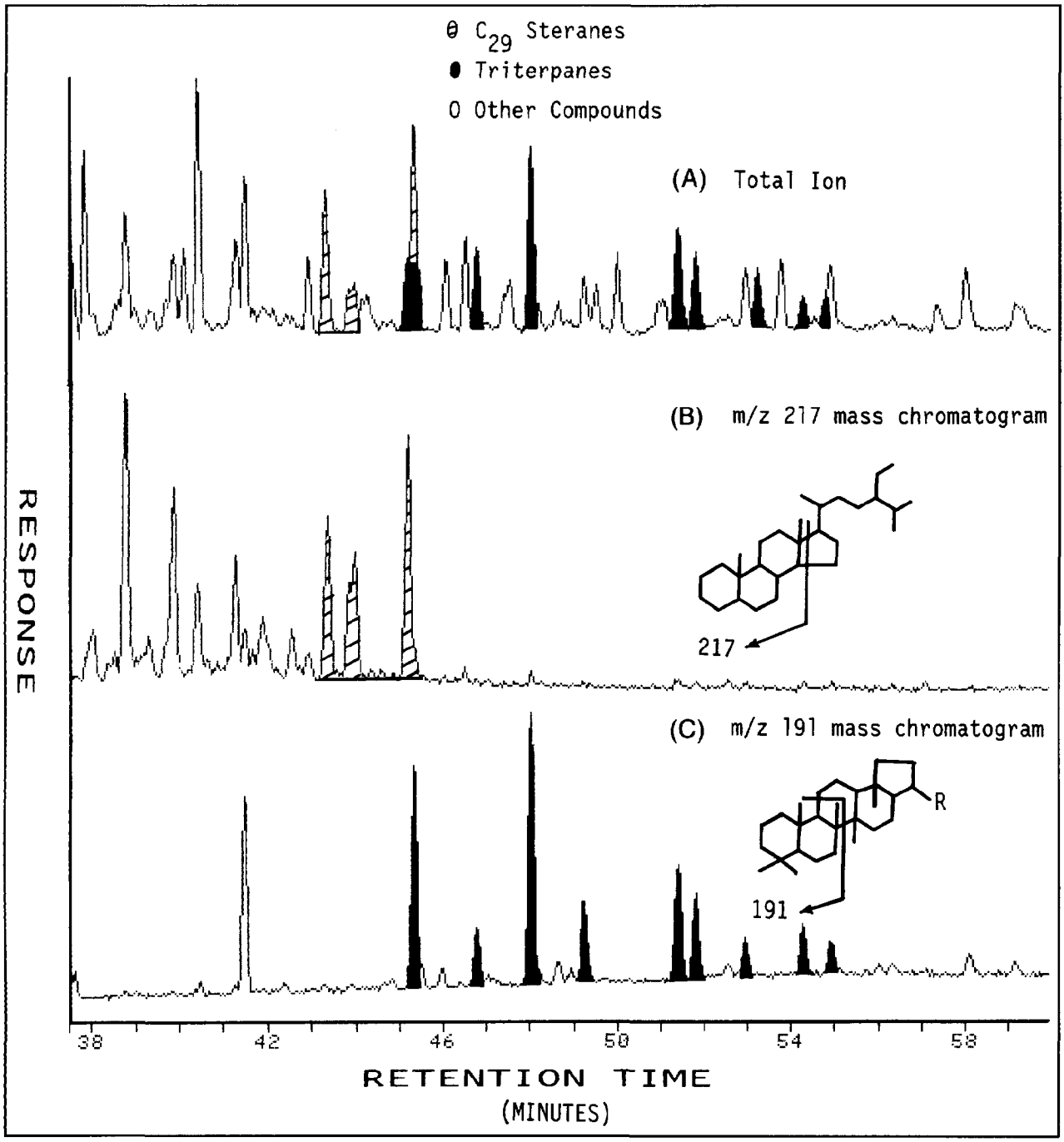


Figure 17—Examples of a total-ion-current trace (A) and mass chromatograms for steranes (B) and triterpanes (C). Dominant fragmentation patterns for steranes and triterpanes are also shown. The lower-left portion of the molecule yields the charged fragment ion in both cases. The m/z 217 and m/z 191 mass chromatograms used for analyzing steranes and triterpanes, respectively, are chosen because they represent the most abundant ion from each type of molecule. From Waples and Machihara (1990); reprinted with permission from *Bulletin of Canadian Petroleum Geology*.

Although compounds within a single class (such as steranes) all have similar mass-spectral characteristics, the actual probability (or ease) of forming any particular fragment ion (for example, m/z 217) will be different for every individual compound in the class. Consequently, the distribution of peaks observed in any mass chromatogram is not an absolute indication of the true relative concentrations of the compounds.

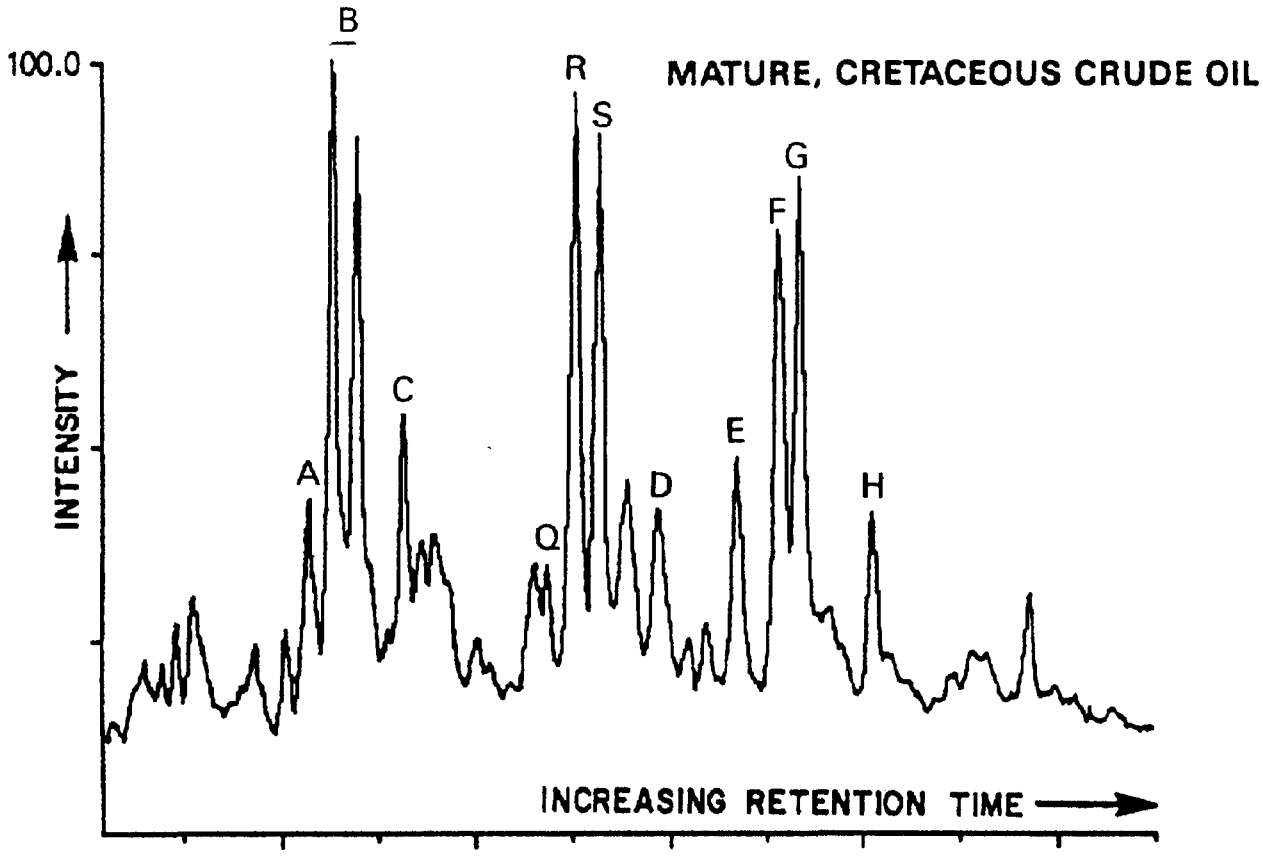


Figure 18—Mass chromatogram of a mature oil showing the combined signals from the m/z 217, 218, and 259 fragment ions, representative of steranes. See Table 2 for identifications of peaks indicated with letters. This type of data handling is claimed to give a more realistic picture of the actual abundances of the various types of steranes. The relative peak heights are not directly comparable to those from chromatograms for single fragment ions, and can only be compared with other chromatograms of the same type. This particular sample lacks diasteranes. From Grantham (1986b); reprinted with permission of Pergamon Press PLC.

Furthermore, the distribution of, for example, regular steranes obtained from the m/z 217 fragmentogram will be slightly different from the distribution obtained from the m/z 218 fragmentogram.

Therefore, if one wishes to obtain quantitative information about the relative concentrations of individual compounds, one must (a) always use the same mass fragmentogram (i.e., do not mix data from m/z 217 and m/z 218), and (b) establish response factors for each compound for that particular fragment ion and use them to correct the observed ion intensities. Furthermore, if one wishes to compare absolute concentrations from sample to sample one must include an internal standard.

For most applications, however, we simply take ratios of observed peak intensities from a single fragmentogram. These ratios may not represent the true relative concentrations, but they will be comparable from sample to sample. True quantitative treatments are rather unusual in most applications today.

The contributions from all fragment ions can be summed to show all the material emerging from the gas chromatograph. This "total-ion-current trace" (TIC) looks very much like a normal gas chromatogram (Figure 17A).

Grantham (1986a,b) has used a technique for displaying sterane data that combines SIM and TIC. He sums three fragment ions (m/z 217, 218, and 259) that are characteristic of the three types of steranes ($\alpha\alpha$ regular steranes, $\beta\beta$ regular steranes, and diasteranes, respectively) to give a single chromatogram, called m/z (217 + 218 + 259). An example is shown in Figure 18. Grantham feels that this display is the most objective way of describing the true distribution of steranes in a sample. However, quantitative data obtained from such a mass chromatogram cannot be compared directly against the standard forms of data using individual fragment ions, such as m/z 217.

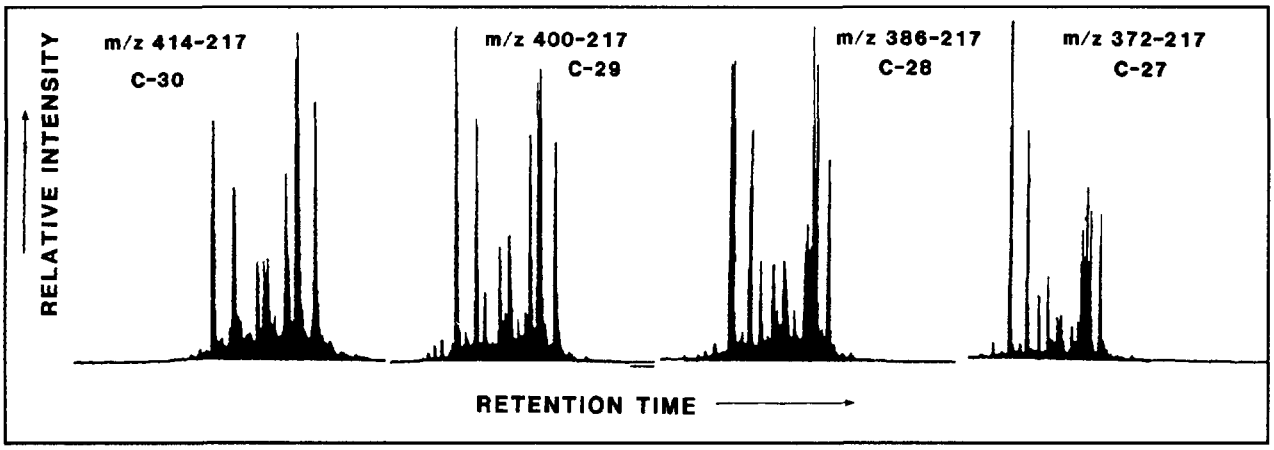


Figure 19—Selected metastable ion monitoring (SMIM) traces for the formation of the m/z 217 fragment ion from each of four parent ions: m/z 414 (C_{30} steranes, left); m/z 400 (C_{29} steranes, center left); m/z 386 (C_{28} steranes, center right); and m/z 372 (C_{27} steranes, right). The two largest peaks on the left side of each trace are the βα diasteranes; the four large ones on the right are the four regular steranes. From Telnaes and Dahl (1986); reprinted with permission of Pergamon Press PLC.

Another technique that has become increasingly popular recently is called "selected metastable ion monitoring" (SMIM). (Other names for this technique are also used, but all include the key word "metastable.") In SMIM the material in a single peak coming out of the gas chromatograph is ionized gently to produce as many molecular ions and as few fragment ions as possible (Gallegos, 1976; Warburton and Zumberge, 1983). The molecular ions represent the metastable ions. Next, the metastable ion mixture is subjected to a magnetic field that accelerates the ions in inverse proportion to their mass. The desired ions are then selected according to their acceleration (and hence according to their mass), as in a normal mass spectrometer. However, they do not pass immediately to a detector, but rather to another mass spectrometer, where they are allowed to produce fragment ions. The fragment ions are then analyzed as in a normal mass spectrometer. Then the process is repeated for each gas-chromatographic peak in turn to produce the entire series of metastable-ion mass chromatograms.

One advantage of SMIM is that by selecting only a certain metastable molecular ion (for example, m/z 400, corresponding to the C_{29} steranes) in the first step, we can look only at the fragments produced from this parent molecule. Ions from other sources, such as those derived C_{27} and C_{28} steranes, simply do not appear. Thus we can remove much of the complexity in a normal mass chromatogram and look at a much simpler set of data. For example, in one study where the 4-methylsteranes were so abundant that the regular steranes could not be analyzed by traditional gc-ms techniques, SMIM was used to remove the 4-methylsteranes electronically (Fowler and Brooks, 1990). The signal-to-noise ratio is also improved using SMIM (Steen, 1986).

Figure 19 shows a series of four SMIM mass chromatograms (C_{30}, C_{29}, C_{28}, and C_{27} steranes) for an oil from the Norwegian North Sea. In each chromatogram only the fragments from the designated parent ion are shown. The two large peaks to the left in each chromatogram represent the βα diasteranes, and the four peaks to the right are the αα-20S, ββ-20R, ββ-20S, and αα-20R forms of the regular steranes, respectively (Telnaes and Dahl, 1986).

SMIM analysis is becoming increasingly popular, particularly in research laboratories and in internal technical service within large oil companies. Its application by service companies has not yet become routine, however, and examples in the literature of its application are still rare (see Snowdon et al., 1987, for an example). Because of the limited use of SMIM at present by many companies, it is not discussed in detail in this book.

The final step in most analyses is to compare the mass chromatograms against known examples in order to identify the various components. Many biomarkers occur in virtually all samples, and are thus rapidly and easily identified by comparison of mass chromatograms. However, simultaneous elution of two or more compounds (coelution) will hinder identification and quantitation.

If coelution of two or more compounds occurs or is suspected, compound identification and quantitation are both called into question. This problem is often particularly severe for steranes, especially where C_{29} diasteranes overlap with C_{27} regular steranes. Because diasteranes produce many fewer m/z 218 fragments than do regular steranes, in order to analyze the regu-

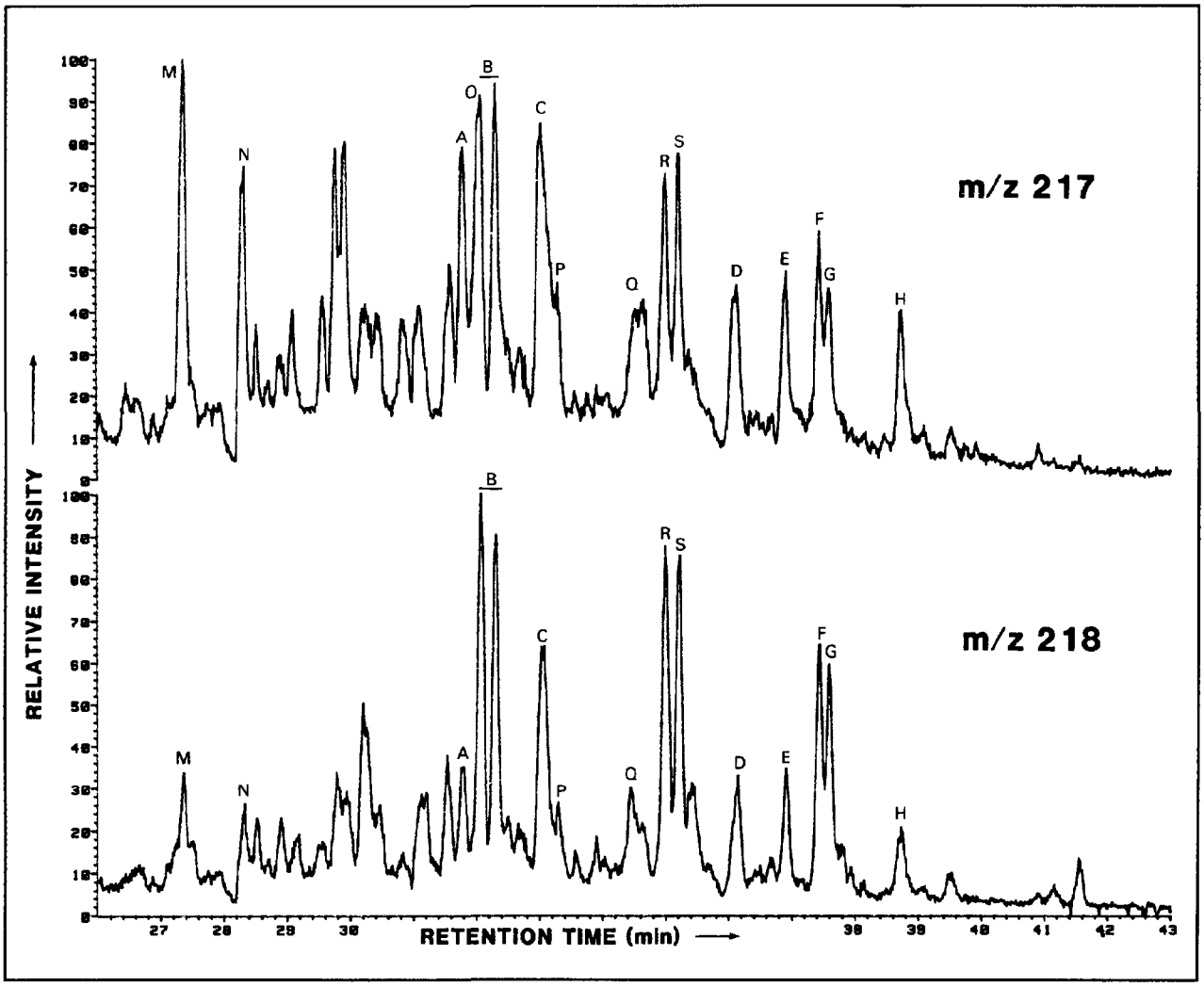


Figure 20—Comparison of m/z 217 and m/z 218 (sterane) mass chromatograms for a single sample, showing how the diasterane interference in the m/z 217 chromatogram (top) is reduced in the m/z 218. Note also that the ββ steranes are exaggerated in importance in the m/z 218 mass chromatogram. Identities of peaks are given in Table 2.

lar steranes alone it is common to look at the m/z 218 mass chromatogram in addition to the m/z 217 (Figure 20). Thus the m/z 218 mass chromatogram is often used in comparing the relative amounts of C_{27}, C_{28}, and C_{29} regular steranes (Figure 21).

However, the ββ forms of the regular steranes give m/z 218 fragments more easily than the αα forms, as shown by the abnormally high ββ peaks in Figures 20 and 21. Therefore, the m/z 218 mass chromatogram should not be used for determining the ββ/αα ratio (see Chapter 4).

In other cases of overlapping peaks a gc-ms specialist should be asked to check on the identities of the compounds by consulting a number of other mass chromatograms diagnostic of the compound in question. Philp (1985) has compiled a catalog of data useful to specialists for identifying unknown compounds.

The well-characterized compounds in mass chromatograms usually are more valuable than rare, minor, or unidentified compounds, because their histories are better understood. The rare compounds potentially are more useful for correlations, but if we do not know their identities or their sensitivities to maturation processes, we must use them with caution until more information about their structures, origin, and transformations becomes available.

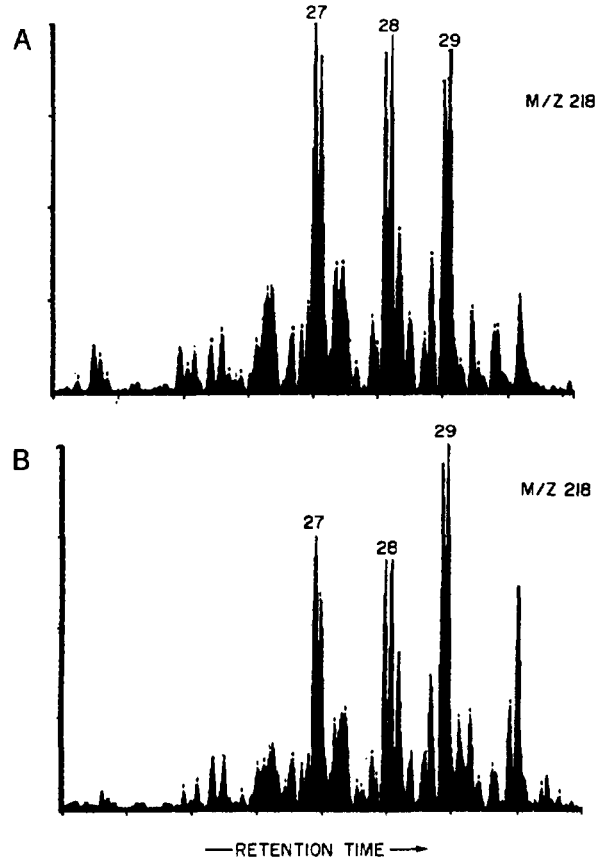


Figure 21—M/z 218 (sterane) mass chromatograms for (A) La Luna type marine oil and (B) terrestrial oil from the Maracaibo basin, Venezuela, showing the exaggeration of the ββ C_{27}–C_{29} regular steranes (tall peaks labelled as C_{27}, C_{28}, and C_{29}) compared with the αα steranes. Comparisons of C_{27}–C_{29} sterane distributions can be done using the ββ isomers. From Talukdar et al. (1986); reprinted with permission of Pergamon Press PLC.

Chapter 4

Biomarkers as Maturity Indicators

INTRODUCTION

Some transformations of biomarkers occur as the result of thermal reactions, whose rates are controlled both by subsurface temperatures and by the length of exposure of the biomarkers to those temperatures. Biomarkers can thus be used as indicators of the total thermal history of the organic matter, and hence as indicators of maturity. Maturities derived from biomarkers have been applied to source rocks, oils (including tars, biodegraded oils, etc.), and even to fluids produced from very young sediments by hydrothermal activity (e.g., Simoneit, 1990; Simoneit et al., 1990; Kvenvolden et al., 1990; Michaelis et al., 1990; Clifton et al., 1990).

One important difference between source-rock maturities determined from biomarkers and maturities obtained from kerogen analysis (vitrinite reflectance, Thermal Alteration Index, pyrolysis T_{max}, etc.) is that kerogen is immobile. Its maturity is therefore always the same as the maturity of the rock or sediment in which it is found. Biomarkers in the mobile bitumen fraction of rocks and sediments, on the other hand, can be used as maturity indicators for a rock or sediment only if we are confident that the bitumen is indigenous. Fortunately, various geochemical tests (Extract/TOC ratio, Production Index from pyrolysis, extract composition, etc.) are available to help determine if a given rock is stained or contaminated (e.g., Peters, 1986).

Biomarkers in oils are valuable for estimating the level of maturity at which the oils were generated, provided that the oils have been reservoired at temperatures low enough to minimize maturation in the reservoir. (In cases where the reservoir temperatures are high, biomarkers may indicate the thermal history of the reservoir instead of that of the source rock.) If oils are known to have suffered little or no in-reservoir maturation, comparison of their maturities with those of suspected source rocks can help pinpoint the geographic areas and depths at which the oils were actually generated. The applications and weaknesses of the most commonly used maturity parameters for steranes and triterpanes are discussed below.

STERANES

20S/(20R+20S) epimer ratios

The most important measure of maturity using biomarkers is the proportion of two epimeric forms (20R and 20S) of the αα steranes. This proportion has been expressed in a number of ways in the literature, including 20S/(20S+20R), %20S, and 20S/20R, with 20S/(20R+20S) being most popular. The biologically produced form is exclusively the ααα form in the 20R configuration, but with increasing maturity the proportion of 20S increases as some of the 20R molecules change configuration (Figure 7). Eventually an equilibrium between the two forms is reached, comprising approximately 55% 20S and 45% 20R. Once equilibrium is reached no further change in the proportions occurs, and no further changes in maturity can be recorded.

The series of m/z 217 mass chromatograms in Figures 22 and 23 show qualitatively the changes in the proportions of the 20R and 20S forms of the C_{27}, C_{28}, and C_{29} steranes (peak pairs C-A, D-Q, and E-H, respectively) that occur with increasing maturity. (Identities of the steranes in this and other figures are given in Table 2.) Many of the other differences among the three examples in Figure 22 are due to facies differences rather than to maturity (e.g., variable contents of the αα-20R epimer of the C_{30} sterane, peak L).

Note that peaks bearing the same identification do not have the same retention time (the time required for a compound to come out of the gas-chromatograph column) in each of the three runs in Figure 22. Differences in retention time, which are often seen when comparing samples that were run at different times or by different laboratories, can cause some inconvenience in interpreting mass chromatograms. Samples run at different times or by different laboratories may look at least somewhat different even if they are identical. Pattern recognition is much more important than absolute retention time in identifying the most-common compounds.

In principle, we could determine maturity by following the change in 20S/(20S+20R) in any of the C_{27},

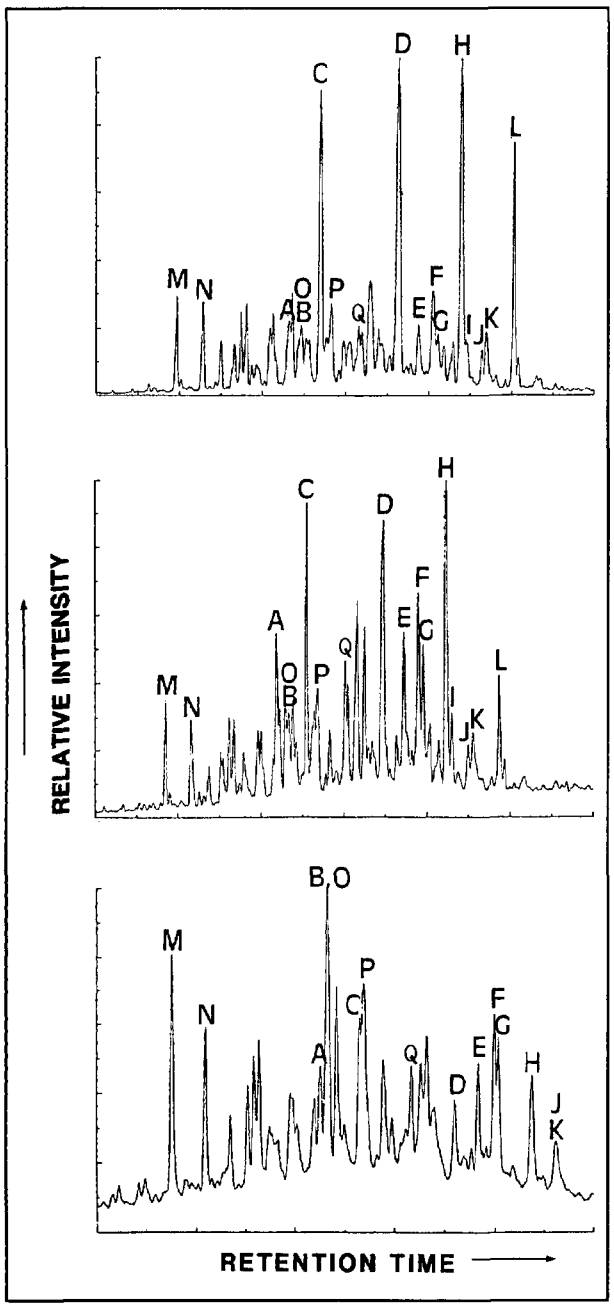


Figure 22—Series of m/z 217 (sterane) mass chromatograms showing the gradual conversion of 20R steranes to 20S and αα steranes to ββ from least mature (top) to most mature (bottom). Identities of peaks are given in Table 2.

C_{28}, or C_{29} steranes. In practice, however, we derive our most-accurate data from the C_{29} species (peaks E and H), which are least susceptible to overlapping peaks in the mass chromatograms. The main problems with 20S/(20R+20S) measurements occur in samples in which all sterane concentrations are low or in which the C_{29} steranes are scarce. In such cases, baseline noise or the presence of coeluting components can introduce unacceptable error.

Although most workers assume that the initial 20S/(20R+20S) ratio at the start of thermal maturation is 0.0, there may be minor variations in the initial 20S/(20R+20S) ratio caused by early-diagenetic processes (Moldowan et al., 1986; Peakman and Maxwell, 1988), or by lithologic differences such as those between coals and shales (Strachan et al., 1989). This phenomenon could in some cases introduce error into maturity determinations made using the 20S/(20R+20S) ratio, particularly at low degrees of transformation of 20R to 20S.

Figure 24 shows a plot of 20S/(20S+20R) versus depth for the same well represented by the five samples in Figure 23. There is considerably more scatter in the data from the shallower, less-mature samples than in the deeper ones, perhaps as the result of diagenetic variations or analytical error.

There are a number of other possible causes for errors in biomarker parameters, including the 20S/(20R+20S) sterane ratios. Natural contamination sometimes can occur, although often it is easy to recognize. Figure 25 shows steranes from five samples in the Higashi Niigata NS-6 well in the Niigata basin, in which the shallowest sample shows an anomalously high sterane maturity compared with the other samples. The most common explanation for such an anomalous maturity would be either oil staining or contamination by some kind of drilling additive containing mature steranes. In this case, however, lack of evidence for staining or contamination suggested that the shallowest sample contained mainly reworked organic matter eroded from deeper, older, more-mature rocks. Figure 26 shows the depth trend of the 20S/(20S+20R) sterane ratios for this well.

In samples containing large amounts of the triterpane 28,30-bisnorhopane, quantification of the αα-20S form of the C_{29} sterane may be difficult by SIM, because the two compounds coelute, and because bisnorhopane gives a minor m/z 217 peak in addition to

Figure 23—M/z 217 (sterane) mass chromatograms of five rock extracts from the Noshiro GS-1 well in the Akita basin of Japan. Sample depths are given in meters. Formation names and ages are: SB = Shibikawa (late Pleistocene); SA = Sasaoka (late Pleistocene); U.T. = upper Tentokuji (early Pleistocene); L.T. = lower Tentokuji (Pliocene); and FU = Funakawa (middle Miocene-Pliocene). See Table 2 for peak identifications. The poorer resolution here compared with the mass chromatograms in Figure 22 is due to poor separation on the gas-chromatograph column.

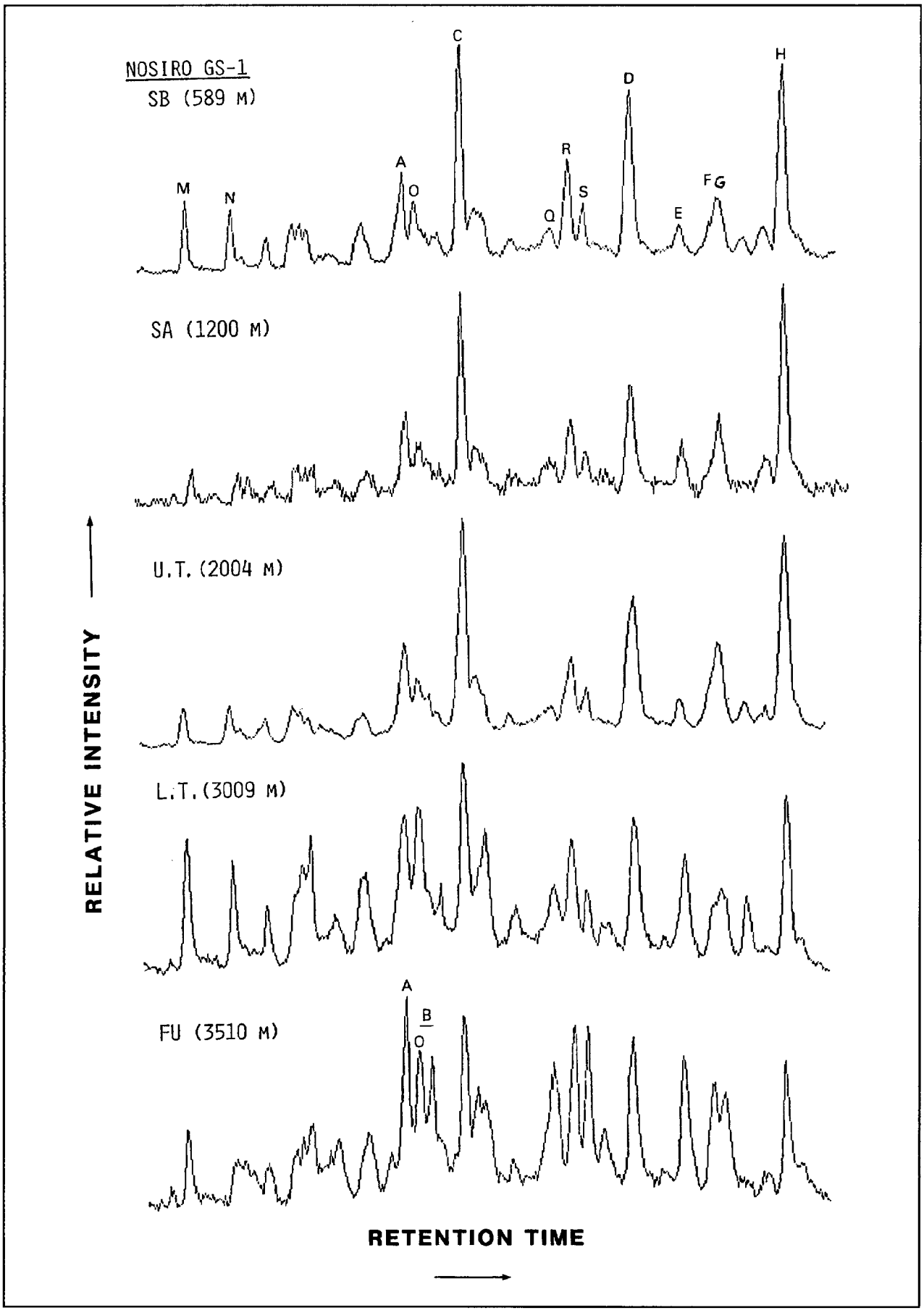

NOSIRO GS-1
SB (589 M)
SA (1200 M)
U.T. (2004 M)
L.T. (3009 M)
FU (3510 M)
M
N
A
O
C
Q
R
S
D
E
F
G
H
A
B
O
RELATIVE INTENSITY
RETENTION TIME

Table 2. Identities of common steranes in the m/z 217 mass chromatograms in most of the illustrations in this book.

Designation	Number of Carbon Atoms	Ring Stereochemistry*	Side-chain Stereochemistry
		Regular Steranes	
A	27	αα	20S
B	27	ββ	20R + 20S
C	27	αα	20R
Q	28	αα	20S
R	28	ββ	20R
S	28	ββ	20S
D	28	αα	20R
E	29	αα	20S
F	29	ββ	20R
G	29	ββ	20S
H	29	αα	20R
I	30	αα	20S
J	30	ββ	20R
K	30	ββ	20S
L	30	αα	20R
		Diasteranes	
M	27	βα	20S
N	27	βα	20R
O	29	βα	20S
P	29	βα	20R

*Stereochemistry of hydrogen atoms at positions 14 and 17 for regular steranes and 13 and 17 for diasteranes.

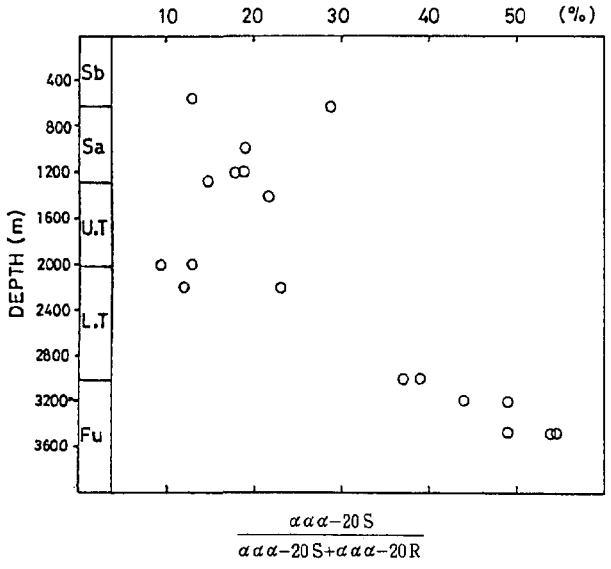


Figure 24—Plot of 20S/(20S+20R) for C_{29} regular steranes in rock extracts in the Noshiro GS-1 well, Akita basin, Japan. See Figure 23 for mass chromatograms of selected samples. Data scatter is worse for low-maturity samples, where diagenetic effects and analytical errors may be more important. Formation abbreviations are explained in the caption for Figure 23.

its dominant m/z 191 fragment ion (Dahl, 1987). Using SMIM one could easily distinguish between the two different sources for the m/z 217 peak.

The work of a number of authors (e.g., Mackenzie and McKenzie, 1983; Mackenzie, 1984; Rullkötter and Marzi, 1988) indicates that sterane epimerization does not occur at the same rate as does kerogen maturation (e.g., vitrinite reflectance), nor does it precisely parallel oil generation. Grantham (1986b) concurs, presenting evidence that the role of time is significant in sterane isomerization. Thus the application of 20S/(20R+20S) ratios to estimate either kerogen maturation or oil generation is only approximate. Nevertheless, it has been popular to attempt such a correlation.

Figure 27 shows trends of the 20S/(20R+20S) ratio for the regular C_{29} steranes versus vitrinite reflectance (%Ro) for samples from three different studies. The data on which the line of Zumberge (cited in Bein and Sofer, 1987) is based were not specified. Bein and Sofer (1987) used Zumberge's line for samples with 20S/(20R+20S) ratios up to 0.52, but their preference for the equilibrium ratio was not given. We therefore have not extended their line beyond 20S/(20R+20S) = 0.52.

The other two lines, interpreted by us from limited data sets, generally agree rather well with Zumberge's

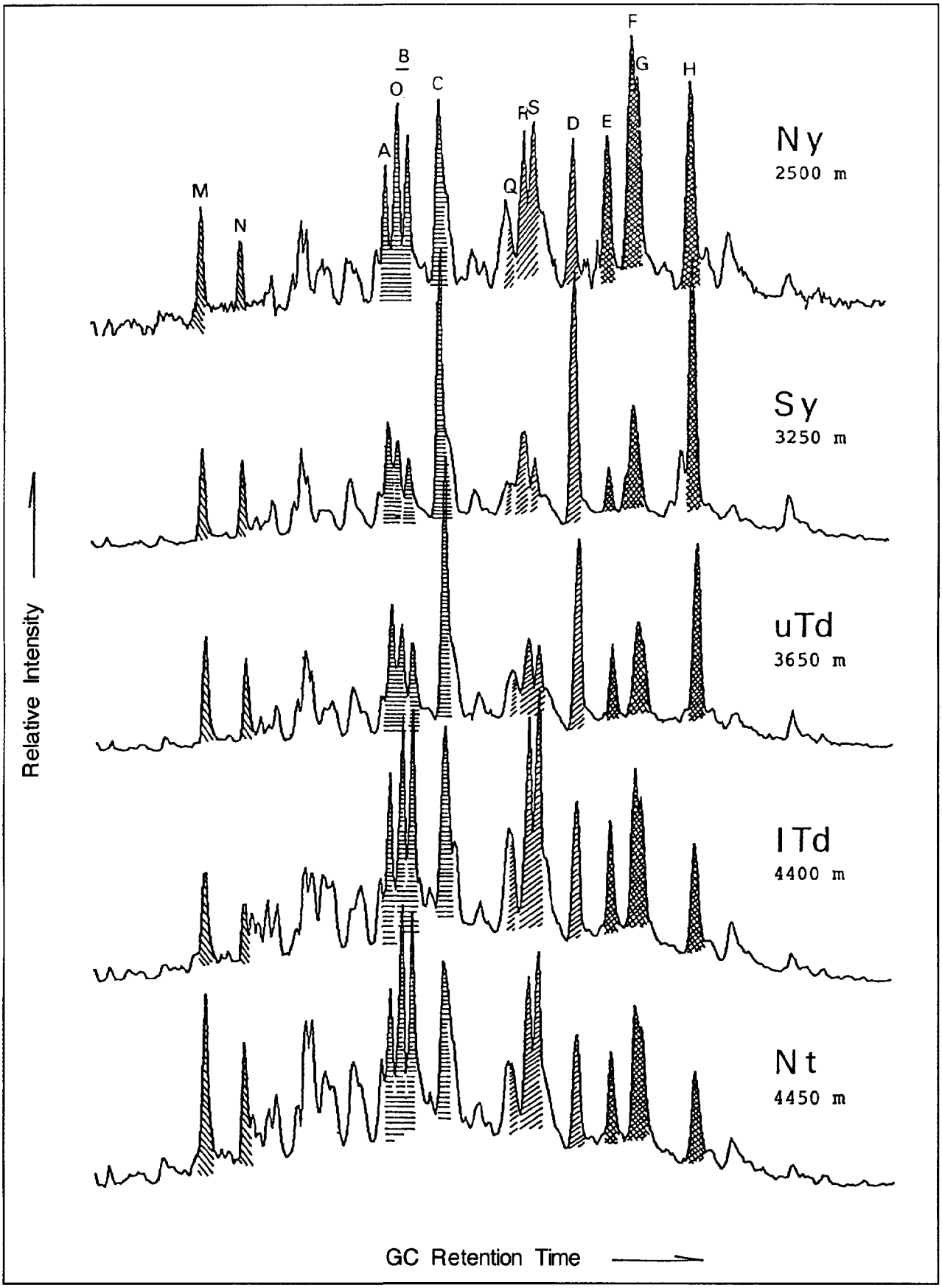


Figure 25—M/z 217 (sterane) mass chromatograms for five rock extracts from the Higashi Niigata NS-6 well, Niigata basin, Japan. Sample depths are given in meters. Formation names and ages are: Ny = Nishiyama (Pliocene-Pleistocene); Sy = Shiiya (late Miocene-Pliocene); uTd = upper Teradomari (middle-late Miocene); lTd = lower Teradomari (middle Miocene); and Nt = Nanatani (early-middle Miocene). The shallowest sample shows the highest biomarker maturity, probably as a result of the presence of reworked organic matter eroded from older rocks. See text for further discussion, and Table 2 for peak identifications. As in Figure 23, the poor resolution is due to the quality of the gas-chromatograph column. From Omokawa and Machihara (1984).

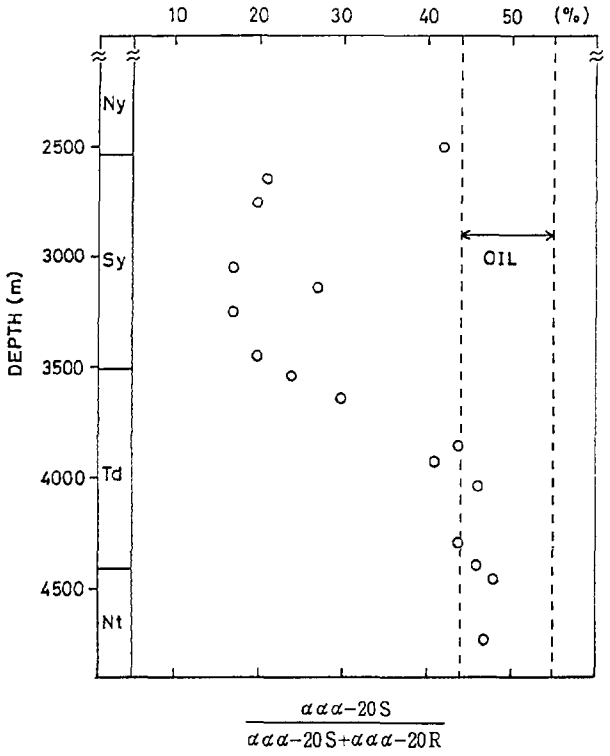


Figure 26—Plot of 20S/(20S+20R) for C_{29} regular steranes in rock extracts in the Higashi Niigata NS-6 well, Niigata basin, Japan. Formation abbreviations are explained in the caption for Figure 25. The anomalous maturity of the shallowest sample is discussed in the caption for Figure 25 and in the text. From Omokawa and Machihara (1984).

line. That of Sakata et al. (1987) was based on ten measurements of Neogene samples from the Niigata basin, Japan. The line of Goodarzi et al. (1989) represents data for 23 extracts from the Triassic Schei Point Formation of the Sverdrup basin, Canadian Arctic.

It is important to have an idea of the uncertainty in making maturity estimates from sterane ratios using Figure 27. If we assume that the "true" sterane-Ro relationship lies somewhere between the extremes shown in Figure 27, we see that for a measured 20S/(20R+20S) ratio of 0.25, for example, we would estimate vitrinite reflectance to be 0.51 ± 0.02% Ro, depending on which correlation line we choose. This uncertainty in Ro is obviously insignificant. However, if we recognize that we might have an additional error of ±0.03 in the measurement of the biomarker ratio, the uncertainty in Ro becomes somewhat greater: 0.51 ± 0.05% Ro. While this uncertainty is not negligible, it would not lead in most cases to greatly different exploration decisions.

At higher maturity, the uncertainty is greater. For example, when the 20S/(20R+20S) ratio = 0.45 ± 0.03, vitrinite reflectance would be estimated to be somewhere between 0.65% and 0.79% Ro. The closer we get to equilibrium, the more sensitive our estimate becomes to uncertainties and measuring errors. Thus near equilibrium (when 20S/(20R+20S) is 0.5 or higher), sterane epimerization interpreted from Figure 27 is not very reliable as a quantitative estimator of Ro values.

The three published sterane-Ro trends in Figure 27 are rather similar, especially when sterane epimerization is not near equilibrium. Other data, however, do not follow this trend. Figure 28 shows sterane and Ro data from the Akita basin of Japan (geologically very similar to the Niigata basin, from which the line of Sakata et al. (1987) in Figure 27 was obtained). Although there are no obvious errors in either the sterane or Ro data, there is a large amount of scatter, and the sterane-Ro trend defined by these samples is quite different from those in Figure 27. If we had used the sterane trends from Figure 27 to estimate Ro from these measured 20S/(20R+20S) values, we would have consistently overestimated Ro by about 0.2%. An error this large could affect exploration decisions.

In summary, the trend shown in Figure 27 is reasonably well defined when steranes are far from equilibrium, but as equilibrium is approached, the correlation between 20S/(20R+20S) becomes less secure. Furthermore, because data scatter and consistent deviations from the trend lines in Figure 27 are well known (e.g., Figure 28), we should not expect 20S/(20R+20S) ratios to give accurate Ro values in all cases. Causes for these deviations are not known, but may include differences in rock age as well as errors in measuring both sterane ratios and vitrinite reflectance.

Moreover, the maturity range covered in Figure 27 does not include very-low-maturity rocks (Ro < 0.35%), and the change in sterane ratios ends before peak oil generation. Furthermore, destruction of steranes at high maturities can make quantitation difficult, and may even lead to changes in the 20S/(20R+20S) ratio through preferential destruction of the 20S epimer (Marzi and Rullkötter, 1989) or the 20R epimer (Peters et al., 1990). Thus there are a number of potentially serious weaknesses of the 20S/(20R+20S) sterane maturity parameter.

In spite of the difficulties discussed above, a general consensus (e.g., Rullkötter and Marzi, 1988) exists that the 20S/(20R+20S) ratio is the most reliable and useful biomarker-maturity parameter. It can usually be measured reasonably accurately, the 20R-20S conversion is in most cases not complicated very much by diagenetic or lithologic variations, and the transformation occurs at maturity levels that are of interest in evaluating oil generation. Our biggest problem is using this ratio may be time (age) differences. The best ways to attempt to overcome such problems are

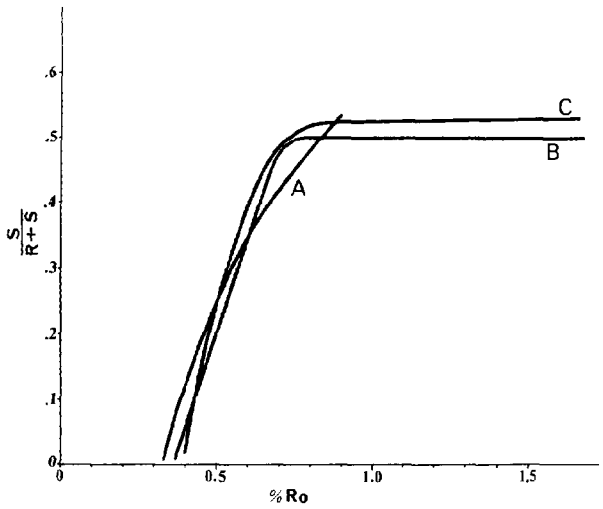


Figure 27—Plot of 20S/(20R+20S) for C_{29} regular steranes versus vitrinite reflectance (% Ro) for three data sets. (A): Derived from an equation attributed to Zumberge by Bein and Sofer (1987). The data set used in deriving the line was unspecified. (B): Interpolated by us from measured data of Goodarzi et al. (1989) for the Triassic Schei Point Formation, Sverdrup basin, Canadian Arctic. (C): Interpolated by us from measured data of Sakata et al. (1987) for Neogene rocks of the Niigata Basin, Japan. Adapted from Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology.*

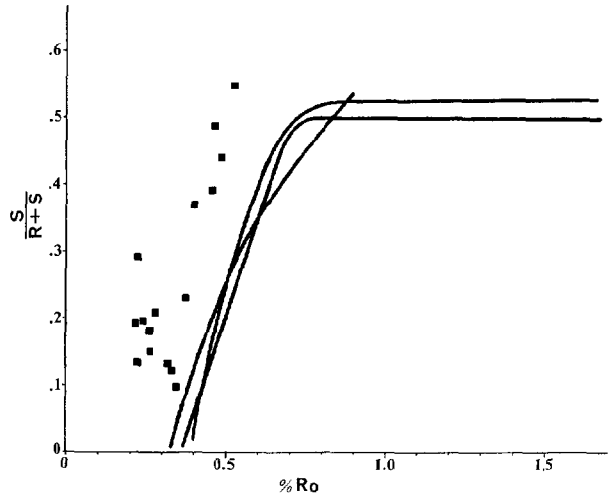


Figure 28—Plot of 20S/(20R+20S) C_{29} regular steranes versus vitrinite reflectance for rock extracts from the Akita basin, Japan (black squares), compared with the three trend lines from Figure 27.

(1) development of a local Ro-sterane relationship that is already calibrated for the rocks of interest, and (2) use of a kinetic model for sterane epimerization (discussed later in this chapter).

ββ/αα ratios

Another maturity parameter derived from steranes is the proportion of 14β(H),17β(H) and 14α(H),17α(H) forms. As we have seen, the αα form is produced biologically, but gradually converts to a mixture of αα and ββ (Figure 7, shown as ααα and αββ). This transformation involves the poorly understood but apparently nearly simultaneous change of two hydrogen atoms from alpha positions to beta. Because 20S and 20R diastereomers exist for each of the αα and ββ forms, four distinct species (αα-20R, αα-20S, ββ-20R, and ββ-20S) appear in the C_{29} sterane family (Figures 22, 23, and 25: peaks E, F, G, and H). They also exist for the C_{27} and C_{28} steranes, but are often obscured by coelution with other compounds. The progress of the transformation of αα to ββ is shown in Figures 22 and 25 (peaks E and H to F and G for C_{29} steranes), but is not as well defined in Figure 23.

The proportion of ββ and αα forms is usually expressed as the ratio ββ/αα, although descriptions like "ββ/20R" are also encountered. Seifert and Moldowan (1981) showed values as high as about 2.5, and Mackenzie (1984) stated that the equilibrium value is about 3.0.

Although in the past the ββ/αα ratio for regular steranes was frequently used as a maturity parameter, there are serious doubts today about its validity. In some cases where facies changes are minor it seems to yield reasonable results (e.g., Figure 29), though data scatter may be greater than with 20S/(20R+20S) ratios. However, it is now known that the ββ/αα ratio can be as strongly affected by diagenetic conditions as it is by maturity (ten Haven et al., 1986; Peakman and Maxwell, 1988; Peakman et al., 1989). In particular, under hypersaline conditions the ββ/αα ratio may be abnormally high (Rullkötter and Marzi, 1988). These facies or diagenetic influences on ββ/αα ratios are usually most pronounced in low-maturity samples (e.g., Dahl and Speers, 1985). As a result of these facies interferences, the ββ/αα ratio has declined greatly in importance as a maturity indicator, and is not recommended by most biomarker specialists.

20S/20R ratios have sometimes been plotted against ββ/αα ratios to aid in estimating maturity (Figure 30), although a calibration of %Ro along the "Maturation" line has never been published. With our recent loss of confidence in ββ/αα ratios as maturity parameters, there seems to be no advantage of Figure 30 over Figure 27.

If Figure 30 is used, it is inevitable that some data points will fall off the ideal maturation line. Seifert

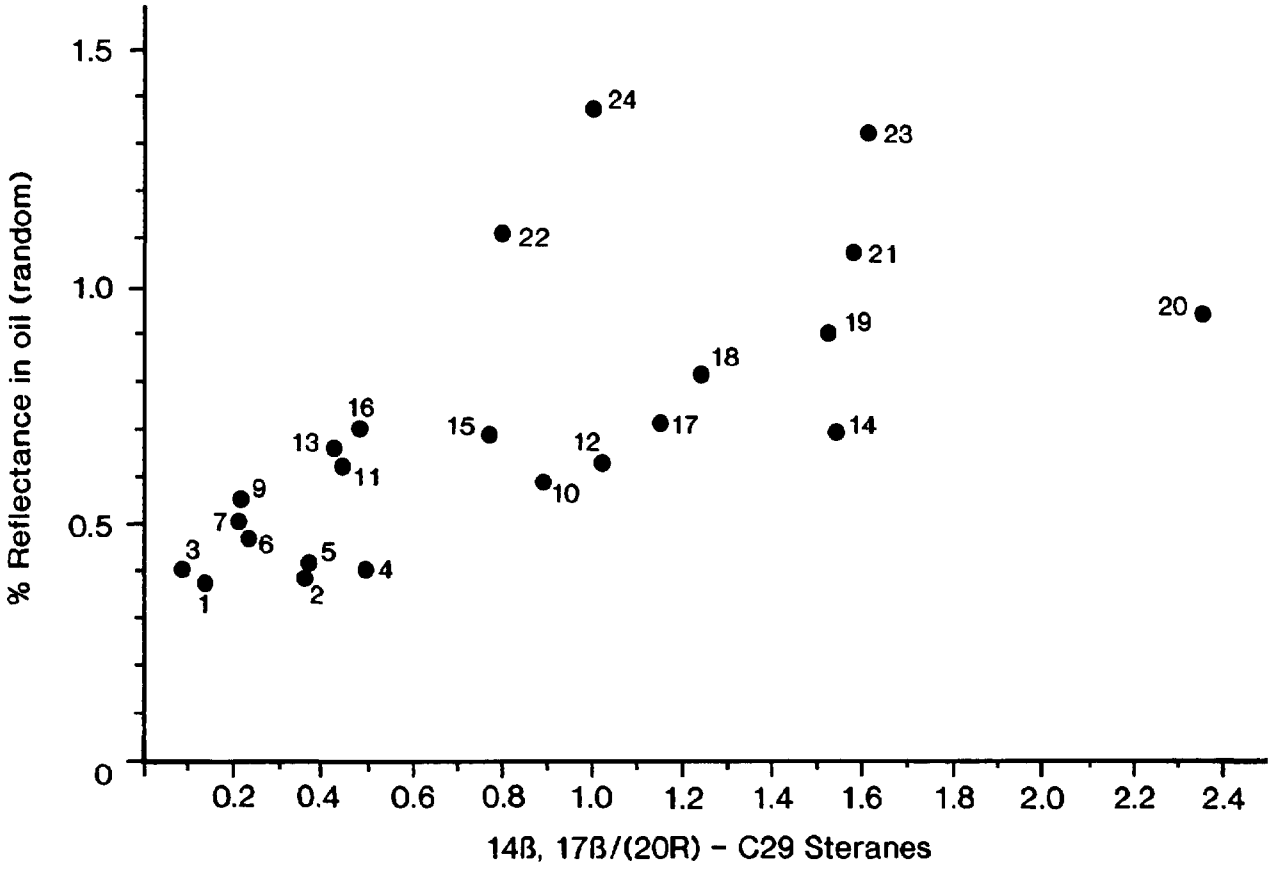


Figure 29—Plot of vitrinite reflectance versus the ratio of ββ to αα regular C_{29} steranes for rock extracts from the Schei Point Group (Triassic) of the Canadian Arctic. Numbers are for sample identification, but they are not discussed here. From Goodarzi et al. (1989); reprinted with permission of Butterworth & Co. (Publishers) Ltd.

and Moldowan (1981, 1986), who first published this type of plot, suggested that deviation from the ideal maturation line was caused by differential migration of the various sterane isomers. The amount of deviation was seen as an indication of the difficulty or length of migration. Based on laboratory simulations, some workers (e.g., Fan and Philp, 1987; Jiang et al., 1988) believe that expulsion, migration, or both can cause measurable changes in biomarker ratios, at least under certain conditions.

However, given the evidence that molecules as different in size and mobility as n-C_{15} and n-C_{25} are expelled with nearly equal efficiency from source rocks (e.g., Leythaeuser et al., 1984; Mackenzie et al.,

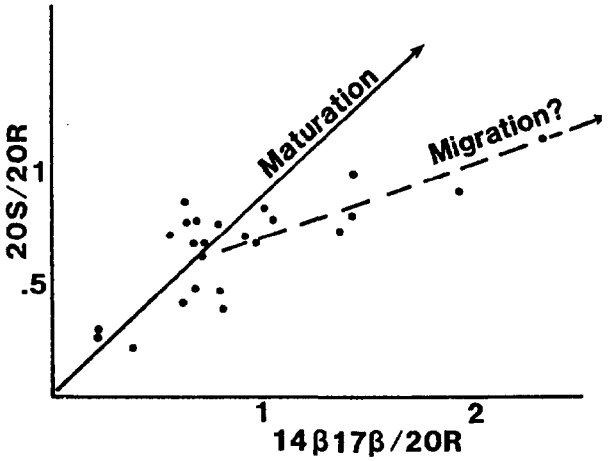


Figure 30—Sterane maturation line based on both 20S/(20R+20S) and ββ/αα ratios. No calibration of the maturation line to vitrinite reflectance is available. Samples are crude oils from the Beaufort-Mackenzie area of the Canadian Arctic. In general, samples falling off the ideal maturation line have often been considered to have been affected by migration, as shown by the line labeled "Migration?" In this case, however, there is no evidence that these oils have suffered an unusual migration history. See text for discussion of the reasons for deviation from the maturation line. From Snowdon (1988); reprinted with permission from the *Bulletin of Canadian Petroleum Geology*.

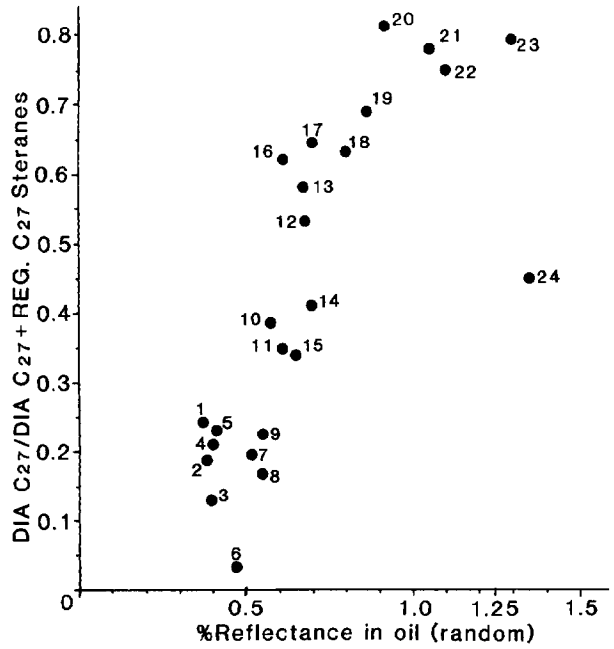


Figure 31—Plot of the ratio of C_{27} diasteranes to total C_{27} steranes versus vitrinite reflectance for extracts of rock samples of the Schei Point Group (Triassic) of the Canadian Arctic. Samples all represent a limestone to marly facies. Numbers are for sample identification, but they are not discussed here. From Goodarzi et al. (1989); reprinted with permission of Butterworth & Co. (Publishers) Ltd.

1987), and that separation of structurally similar biomarkers does not occur during migration (Cornford et al., 1983; Hoffman et al., 1984), we are doubtful whether migration effects can be seen in molecules as similar as the various C_{29} steranes. Robinson and Kamal (1988) agree, stating that fractionation is unlikely if migration is along an open pathway such as through a porous sandstone or a fault. Philp and Engel (1987) noted that no observable fractionation occurred in laboratory simulations employing geologically plausible conditions; fractionation only took place under conditions appropriate to an analytical chemistry laboratory. Other workers (e.g., Walters and Kotra, 1990; Peters et al., 1990) also are skeptical about the importance of migration-induced changes in ratios of closely related biomarkers.

The most plausible explanations for deviation from the sterane-maturation line in Figure 30 include errors in calculating ratios due to low concentrations or overlapping peaks, and the dependence of the $\beta\beta/\alpha\alpha$ ratio on diagenetic conditions, as discussed above and by Snowdon (1988). We do not recommend using Figure 30 to estimate migration distances, and prefer to use Figure 27 for maturity estimates. However, once again we caution that any use of biomarker ratios to determine either kerogen maturity or hydrocarbon generation is only approximate. We recommend a kinetic approach (discussed later in this chapter) to compare measured and calculated biomarker ratios as a check on the burial and thermal history.

Diasteranes/regular steranes

The proportion of diasteranes compared with regular steranes is known to be dependent upon maturity, because the original regular steranes are isomerized gradually to a mixture of diasteranes and regular steranes. For example, Hughes et al. (1985) noted that diasterane contents in Ekofisk oils (North Sea) were controlled by maturity. Goodarzi et al. (1989) showed that for a lithologically homogeneous set of dominantly carbonate samples there was a good correlation between measured vitrinite reflectance and the ratio of diasteranes to total steranes (Figure 31).

However, the ratio of diasteranes to regular steranes (or diasteranes to regular steranes plus diasteranes) has not generally been used quantitatively as a maturity indicator, because lithology is also believed to influence the rate of isomerization. Moreover, the exact calibration between %Ro and diasterane ratio is likely to vary with lithology, and thus will require local calibration. The correlation shown in Figure 31 is not likely to be valid in all cases, and in any such case a correlation can only be used where the samples represent the same lithology. Facies effects on diasterane contents are discussed more fully in Chapter 5.

TRITERPANES

22S/(22R+22S) epimer ratios

Transformation of the biologically produced 22R form of the C_{31}-C_{35} extended 17α(H)-hopanes to the 22S epimer (Figure 6) occurs in the same manner as the 20R/20S conversion for the steranes, but at a different rate. The proportions of 22R and 22S can be calculated for any or all of the C_{31} through C_{35} 17α(H)-hopanes, but for simplicity C_{31} or C_{32} is usually used. Figure 32 shows a pair of m/z 191 mass chromatograms illustrating the changes in proportions of C-22 epimers (peaks f through p) with increasing maturity. At equilibrium the approximate proportions are 55-60% 22S and 40-45% 22R. (Identities of the triterpanes in this figure and others are given in Table 3.)

A major problem in calculating 22S/(22R+22S) ratios can occur in samples in which the C_{31} extended hopanes (peaks f and g) are unusually abundant. The reasons for this unusual abundance will be discussed

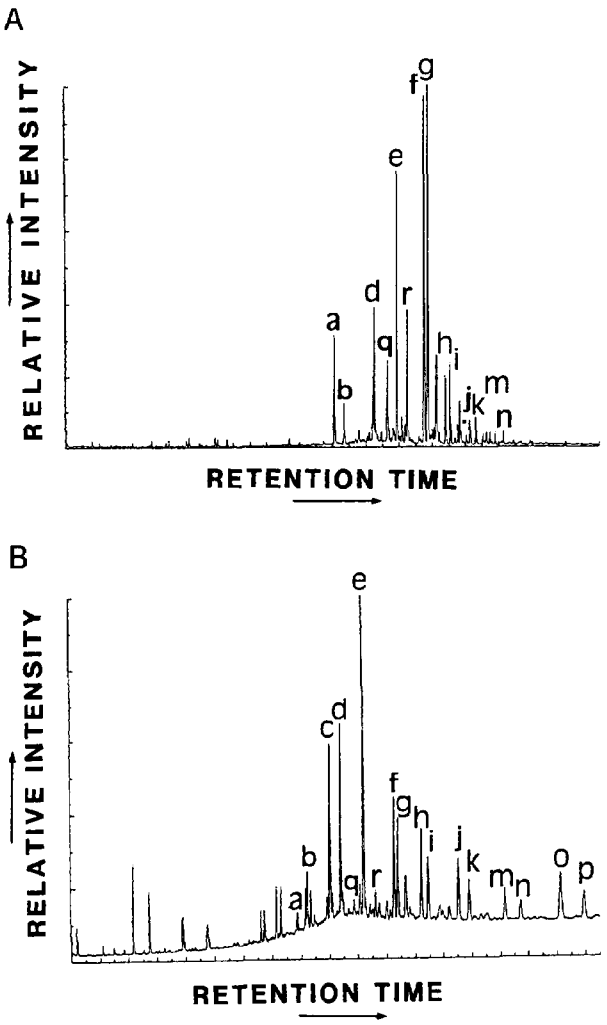


Figure 32—M/z 191 (triterpane) mass chromatograms showing the conversion of 17α(H)-extended hopanes with 22R configuration to the 22S configuration, and the decrease in moretanes relative to hopanes with increasing maturity. Sample in (A) is less mature than that in (B). Identities of peaks are given in Table 3.

in Chapter 5. For some reason, the C_{31} extended hopanes, when present in unusually high abundance compared with other extended hopanes, reach equilibrium much more rapidly than do the other extended hopanes (Villar et al., 1988). In cases where the C_{31} extended hopanes are anomalous compared with the other extended hopanes, the C_{32} homolog should be used in calculating the 22S/(22R+22S) ratio.

We have also noted cases where the C_{35} extended hopanes (peaks o and p) epimerize more slowly than the others, as illustrated in Figure 33. This phenomenon has been observed in carbonate facies, in which the C_{35} species are more abundant than usual. However, since the C_{35} homologs are seldom used for calculating 22S/(22R+22S) ratios, this discrepancy causes no major problems in maturity estimations.

The 22S/(22R+22S) ratio for 17α(H)-extended hopanes can usually be measured with great accuracy, but once the transformation begins, equilibrium is reached rapidly. Figure 34 shows the rapidity of this transformation in the MITI Rumoi well from Hokkaido, Japan, where within 400 meters (2284 m to 2682 m) the 22S/(22R+22S) ratio for the C_{31} extended hopanes goes from very immature to the equilibrium value. However, in the samples from 2682.7 m and 2683.2 m, epimerization of the C_{32} extended hopanes (peaks h and i) are lagging behind the C_{31} homologs (peaks f and g). The reason for this lag, like that for the C_{35}homologs mentioned above, is not known.

Because equilibrium in the extended hopanes is reached very rapidly, and at Ro values less than 0.6%, the useful range for 22S/(22R+22S) ratios is limited to very immature samples. Extended hopanes in oils have generally reached equilibrium, although cases are known where they are not (e.g., Fu Jiamo et al., 1986).

Peters and Moldowan (1991) have noted that as maturity increases, the proportion of heavy homohopanes (e.g., C_{35}) decreases, whereas the proportion of lighter (e.g., C_{31}) species increases. However, this observation has not yet been developed as a quantitative maturity indicator.

Moretane/hopane ratios

Moretanes are much less stable than 17α(H)-hopanes, and thus decrease in concentration more rapidly with increasing maturity (e.g., Kvenvolden and Simoneit, 1990). It is often supposed that moretanes are gradually converted to hopanes (e.g., Grantham, 1986b), but direct evidence for this transformation is lacking. The ratio of moretanes to hopanes (also sometimes expressed as hopanes/moretanes) thus serves as a maturity indicator (e.g., Seifert and Moldowan, 1980; Cornford et al., 1983; Curiale, 1986; Grantham, 1986b; Bazhenova and Arefiev, 1990).

Sometimes the C_{29} and C_{30} moretanes (peaks q and r) and hopanes (peaks d and e) are used; in other cases only the C_{29} or C_{30} species are calculated. Figure 32 shows the decrease in moretane/hopane ratios from the very-immature sample at the top to the more-mature sample at the bottom.

Seifert and Moldowan (1980) reported moretane/hopane ratios of about 0.03 to 0.06 in a series of mature crude oils. Cornford et al. (1983) reported values as low as 0.01 in the North Sea. However, Grantham (1986b) noted that oils from Tertiary sources often have higher ratios (0.1-0.3, with values of 0.15-0.2 being common) than do older samples, which are

Table 3. Identities of triterpanes in the m/z 191 mass chromatograms in most of the illustrations in this book.

Designation	Identity	Number of Carbon Atoms
	Hopanes	
y	25,28,30-trisnorhopane	27
a	Ts	27
b	Tm	27
c	28,30-bisnorhopane	28
d	C_{29} 17α(H)-hopane (norhopane)	29
e	C_{30} 17α(H)-hopane (hopane)	30
f	22S C_{31} 17α(H)-hopane	31
g	22R C_{31} 17α(H)-hopane	31
h	22S C_{32} 17α(H)-hopane	32
i	22R C_{32} 17α(H)-hopane	32
j	22S C_{33} 17α(H)-hopane	33
k	22R C_{33} 17α(H)-hopane	33
m	22S C_{34} 17α(H)-hopane	34
n	22R C_{34} 17α(H)-hopane	34
o	22S C_{35} 17α(H)-hopane	35
p	22R C_{35} 17α(H)-hopane	35
	Moretanes	
q	normoretane	29
r	moretane	30
	Other	
s	gammacerane	30
t	18α(H)-oleanane	30
u	18β(H)-oleanane	30
x	C_{30}-pentacyclic (compound X)	30

generally less than 0.1. He suggested that the short time available for maturation in Tertiary samples may play a role in controlling moretane/hopane ratios. (The problem of time in biomarker maturation will be discussed more at the end of this chapter.) It is not known whether the lowest values (i.e., 0.01-0.06) reported for moretane/hopane ratios represent the attainment of some sort of equilibrium.

Another problem with moretane/hopane ratios as maturity indicators is that the origin and geochemical behavior of the moretanes are poorly understood. Because there is evidence that the initial moretane/hopane ratios are variable (0.5 to 1.0 or more), they generally are not used quantitatively. Data scatter may be as large as the observed changes in ratios (Figure 35).

Furthermore, because all or most moretane loss occurs at very low maturities (Ro < 0.6%), moretane/hopane ratios, like 22S/(22R+22S) ratios for extended hopanes, are only useful in limited situations. Their value is therefore mainly as a qualitative indicator of immaturity: if the moretane/hopane ratio is above about 0.15, the maturity level of the sample is less than 0.6% Ro.

22S/(22R+22S) Moretane ratios

According to Larcher et al. (1987), the extended moretanes (Figure 13), which are analogous to the extended hopanes and also have a chiral center at C-22, epimerize at that site as a function of maturity. The starting 22R form eventually equilibrates with 22S in a ratio of 60% 22R and 40% 22S. This ratio is essentially the inverse of that observed for the extended hopanes, in which the 22S form is more stable. However, although the actual 22S/(22R+22S) ratio at equilibrium is different in the extended moretanes than in the extended hopanes, the epimerization in extended moretanes seems to proceed essentially simultaneously with hopane epimerization. Although a quantitative relationship between moretane epimerization and vitrinite reflectance could probably be constructed, at the present time 22S/(22R+22S) ratios of extended moretanes are not used routinely for maturity estimation.

Tm/Ts ratios

With increasing maturity, the 17α(H)-trisnorhopane Tm (peak b) gradually disappears and the 18α(H)-tris-

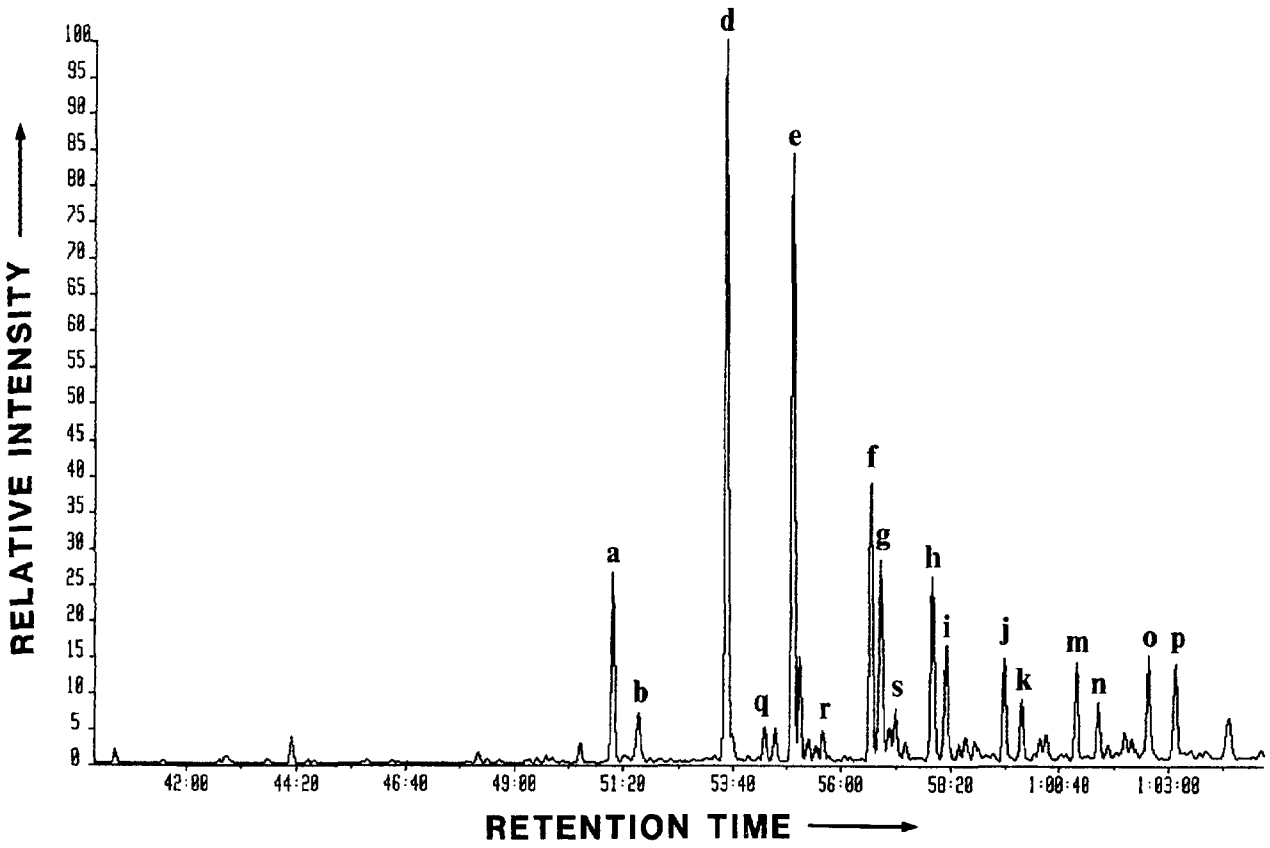


Figure 33—M/z 191 (triterpane) mass chromatogram of a crude oil from a marine carbonate source rock. Epimerization of the C_{35} extended hopanes (peaks o and p) has not progressed as far as for the C_{31}-C_{34} homologs. The extract from the source rock for this oil shows the same anomalous behavior of the C_{35} species.

norneohopane, Ts (peak a), increases in relative concentration (Figure 13). In contrast to moretane/hopane and 22S/(22R+22S) ratios, the Tm/Ts ratio begins to decrease quite late during maturation (>0.9% Ro: van Graas, 1990). Original values persist with little change even after the 20S/(20R+20S) sterane transformation is essentially complete. Thus, in principle, Tm/Ts (or Ts/Tm) ratios should be able to supplement the sterane maturation lines in Figure 27 at maturity levels above 0.75% Ro.

In practice, however, facies effects (possibly due to natural variation in original Ts content) make this parameter somewhat imprecise (Cornford et al., 1983; Schou et al., 1985; Palacas et al., 1986; Snowdon et al., 1987; Rullkötter and Marzi, 1988). Figure 32 illustrates the problem: according to both 22S/(22R+22S) and moretane/hopane ratios, the top sample is very immature, while the bottom sample is more mature. Tm/Ts ratios, however, lead to the opposite conclusion, presumably because the two unrelated samples represent greatly different facies.

The biggest problems seem to occur in hypersaline facies, in which the initial content of Ts is higher than normal (Fan Pu et al., 1984; Rullkötter and Marzi, 1988). Moreover, Volkman et al. (1983a) have suggested that another unidentified compound may sometimes coelute with Tm, giving spuriously high Tm/Ts ratios.

Thus the Tm/Ts ratio does not appear to be appropriate for quantitative estimation of maturity. However, within a series of rock or oil samples representing the same facies, a decrease in Tm/Ts may be a useful nonquantitative indicator of relative maturity (e.g., Jones and Philp, 1990).

Tricyclics/pentacyclics

The ratio of tricyclic triterpanes to pentacyclics has been used by some workers as a qualitative indicator of maturity (e.g., van Graas, 1990). Tricyclics seem to be more stable than pentacyclics, leading to an increase in the tricyclic/pentacyclic ratio at maturity levels approaching or past peak oil generation (Kruge, 1986; Snowdon et al., 1987). In some cases (e.g., Buchardt et al., 1989) the complete absence of penta-

cyclics has been attributed to maturity. However, any quantification of the tricyclic/pentacyclic ratio would probably require local calibration, since tricyclic and pentacyclic contents are controlled by facies as well as by maturity.

Oleananes

No routine application of oleananes (Figure 15) has been made for estimating maturity, but recent work suggests that they may have considerable potential (Riva et al., 1988; Ekweozor and Udo, 1988; Ekweozor and Telnaes, 1990). The ratio of two of the oleanane isomers (18α(H)/18β(H)) has been shown to increase over a maturity range from approximately 0.6% Ro to about peak oil generation (Figure 36). It has also been suggested (Figure 37) that the ratio of 18α(H)+18β(H) oleananes to the sum of those two compounds plus C_{30} hopane (called the oleanane parameter, or OP: Ekweozor and Telnaes, 1990) varies with maturity, reaching a maximum value at vitrinite-reflectance values between 0.46% and 0.58% Ro in the Niger Delta (Ekweozor and Telnaes, 1990). Those workers claimed that the maximum in the OP value correlated very well with the top of the oil-generation window.

However, oleanane ratios are still relatively little studied and controversial as maturation parameters. For example, Brown (1989) did not observe a change in oleanane concentrations with maturity in Indonesian coals and mangrove shales. Facies effects may play an important role, although Ekweozor and Telnaes (1990) found that the OP values peaked at the same Ro value in two different facies.

At the present time the main limitations to the use of oleananes are that (1) no kinetic parameters are available for oleanane transformations (or alternatively, no calibration of oleanane ratios to other reliable maturity parameters such as vitrinite reflectance has yet been published); (2) our present concepts are based on very limited data that require further corroboration; (3) oleananes do not appear to be applicable at maturities beyond early oil generation; and (4) oleananes are somewhat limited in their geological occurrence (they have been reported primarily in deltaic sediments of Late Cretaceous age and younger). This last point, the age and facies limitations, will be discussed further in Chapter 5.

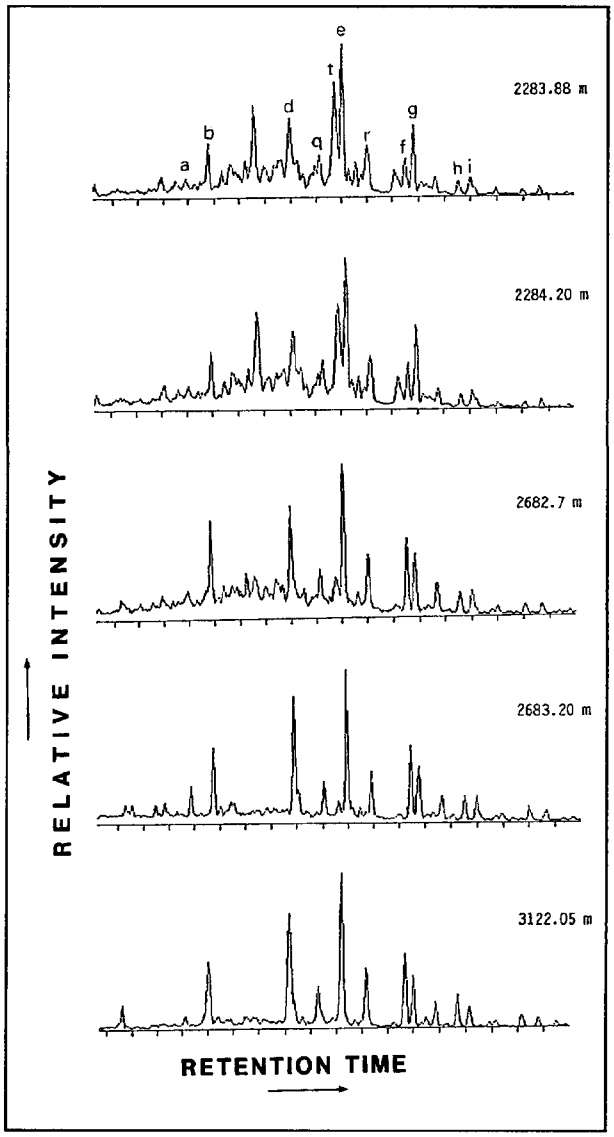


Figure 34—M/z 191 (triterpane) mass chromatograms for five rock extracts from the MITI Rumoi well, Hokkaido, Japan. The top two samples are from the Chikubetsu Formation of early-middle Miocene age; the next two are from the Sankebetsu Formation of early Miocene age; and the deepest is from the Haboro Formation of Eocene age.

KINETIC MODELING OF BIOMARKER TRANSFORMATIONS

Modeling of organic maturation as estimated by vitrinite-reflectance values has been carried out for a long time. Most early modeling was done using the TTI method (e.g., Waples, 1980), but kinetic models for Ro change (e.g., Burnham and Sweeney, 1989) are now replacing TTI. Biomarker transformations have also been modeled by kinetic equations (e.g., Mackenzie and McKenzie, 1983; Dahl et al., 1987; Walters and Kotra, 1990). This modeling yields predicted values of biomarker ratios that can then be compared with measured values (Figure 38). An acceptable fit between measured and calculated biomarker ratios can then be achieved by adjusting the proposed thermal or burial history of the section being modeled (e.g., Suzuki, 1990).

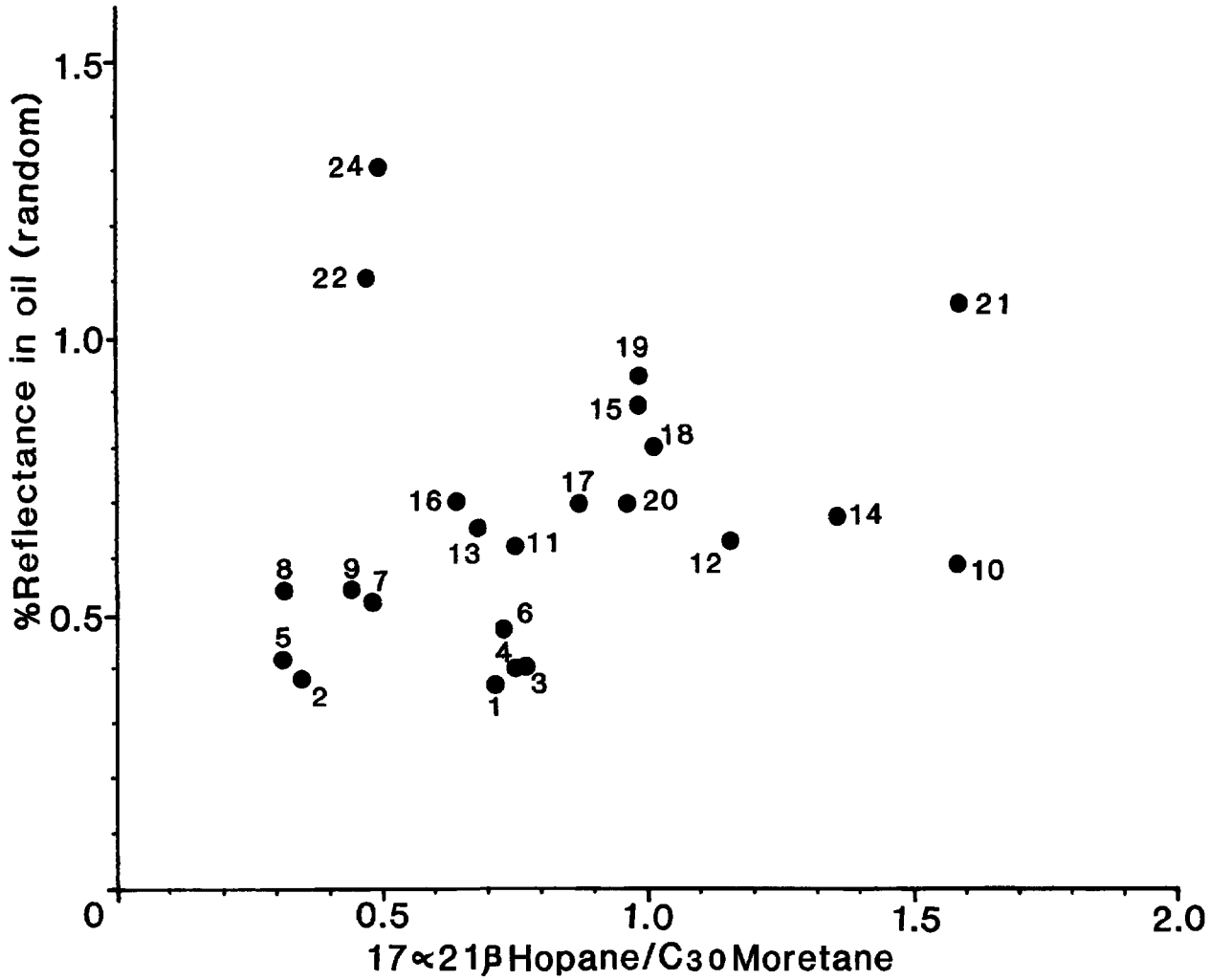


Figure 35—Vitrinite reflectance versus C_{30} hopane/moretane ratios for rock extracts from the Schei Point Group (Triassic) of the Canadian Arctic. Numbers are for sample identification, but they are not discussed here. From Goodarzi et al. (1989); reprinted with permission of Butterworth & Co. (Publishers) Ltd.

In principle, biomarker ratios could be used instead of vitrinite-reflectance values in modeling simulations. However, it is more common to model both biomarker transformations and Ro changes (Figure 38), since the relative sensitivities of Ro and biomarker ratios to time and temperature are different. Thus by modeling both processes one may be able to constrain the burial and thermal history of the rocks even more closely than by using Ro alone.

Unfortunately, although the concept of modeling biomarker transformations is quite clear, the kinetic models and parameters to be used in such modeling are in dispute. Most published data have focused on the transformation of 20R to 20S in steranes. It has generally been assumed that the conversion of 20R to 20S involves a simple reversible epimerization reaction, but recent work (e.g., Curiale and Odermatt, 1989; Strachan et al., 1989; Abbott et al., 1990; Peters and Moldowan, 1991) suggests that the actual process may be much more complex. If so, the simple reversible first-order reactions assumed in most kinetic analyses to date may be in error.

The following discussion assumes that traditional reversible first-order kinetics are applicable. The earliest work by Mackenzie and McKenzie (1983) based on well data gave an activation energy of 91 kJ/mol, with an Arrhenius factor of 0.006 sec^{-1}. Alexander et al. (1986) reinterpreted some of the data of Mackenzie and McKenzie, and obtained similar values (activation energy = 84 kJ/mol and Arrhenius factor = 0.0066 sec^{-1}). In another study data from a very young petroleum yielded an activation energy of 91 kJ/mol and an Arrhenius factor of 1.9×10^5 $year^{-1}$ (Kvenvolden et al., 1988).

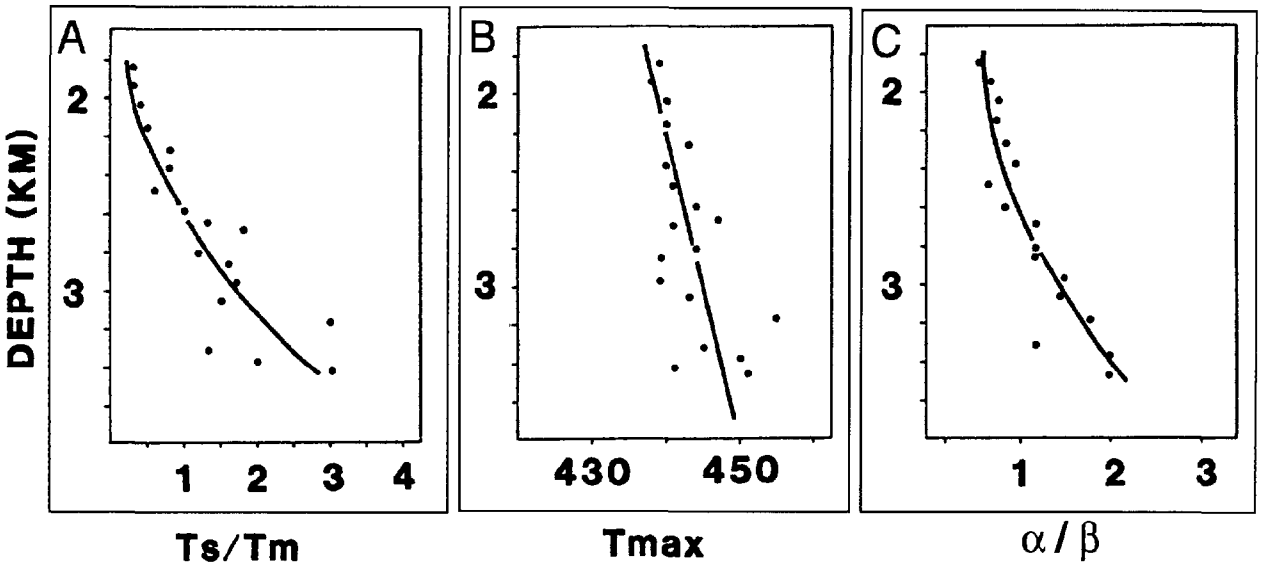


Figure 36—Plot showing increase in ratio of 18α(H)/18β(H) oleanane as a function of burial depth (C). A and B plots show changes in Ts/Tm and pyrolysis T_{max} in the same well. From Riva et al. (1988); reprinted with permission of Pergamon Press PLC.

Pyrolysis experiments have also provided valuable data on the kinetics of sterane isomerization. Dry pyrolysis gave an activation energy of 147 kJ/mol and an Arrhenius factor of 6.5 x 10^7 sec^{-1} (Suzuki, 1984), although that author noted some problems in applying his results successfully to natural systems. Hydrous pyrolysis gave an activation energy of 131 kJ/mol and an Arrhenius factor of 2 x 10^5 sec^{-1} (Rullkötter and Marzi, 1988).

Interpretation of hydrous-pyrolysis data and natural data together yields an activation energy of 170 kJ/mol and an Arrhenius factor of 6 x 10^8 sec^{-1} (Rullkötter and Marzi, 1988). This last value may be the best one publicly available today, since it includes data from both short-time/high-temperature experiments and natural data from long-time/low-temperature samples. However, further work is needed to confirm these values.

Hopane epimerization (22R to 22S) has also received some attention. Mackenzie and McKenzie (1983) and Kvenvolden et al. (1988) both indicate that the activation energy for hopane epimerization at C-22 is the same (91 kJ/mol) as for sterane epimerization at C-20, but that the Arrhenius factor for hopane epimerization is slightly higher (5.1 x 10^5 $year^{-1}$). According to this model, hopane and sterane epimerization would have the same temperature dependence, but hopanes would epimerize more rapidly. Suzuki (1984), however, found quite different results for hopanes and steranes in dry pyrolysis experiments. He reported an activation energy of 98 kJ/mol and an Arrhenius factor of 2.0 x 10^4 sec^{-1} for hopane epimerization, in contrast to his sterane parameters listed above.

The discrepancy between these two data sets has not yet been resolved. However, if we accept, as do most others, that the activation energies for sterane and hopane epimerization are likely to be similar, and combine this idea with the activation energy and frequency factor for steranes derived by Rullkötter and Marzi (1988) from both natural samples and laboratory experiments, we might estimate the activation energy for hopane epimerization to be about 170 kJ/mol and the Arrhenius factor to be about 1.6 x 10^9 sec^{-1}.

Kinetics of sterane aromatization, equilibration of methylphenanthrenes, and destruction of biphenyls, compounds and processes which are not covered in this book, have also received some attention. The interested reader is referred to Mackenzie and McKenzie (1983), Mackenzie (1984), Alexander et al. (1986), Kvenvolden et al. (1988), Abbott and Maxwell (1988), Alexander et al. (1988, 1990), and Tupper and Burckhardt (1990) for further information.

GENERAL PROBLEMS WITH BIOMARKER MATURITY DATA

The various transformations we have just discussed all represent distinct chemical reactions, each with its own energy requirements. As we have seen, they do not all proceed simultaneously; rather, each transformation occurs over its own range of maturity. In order to make the best possible use of biomarker maturity data, we must know not only the reliability

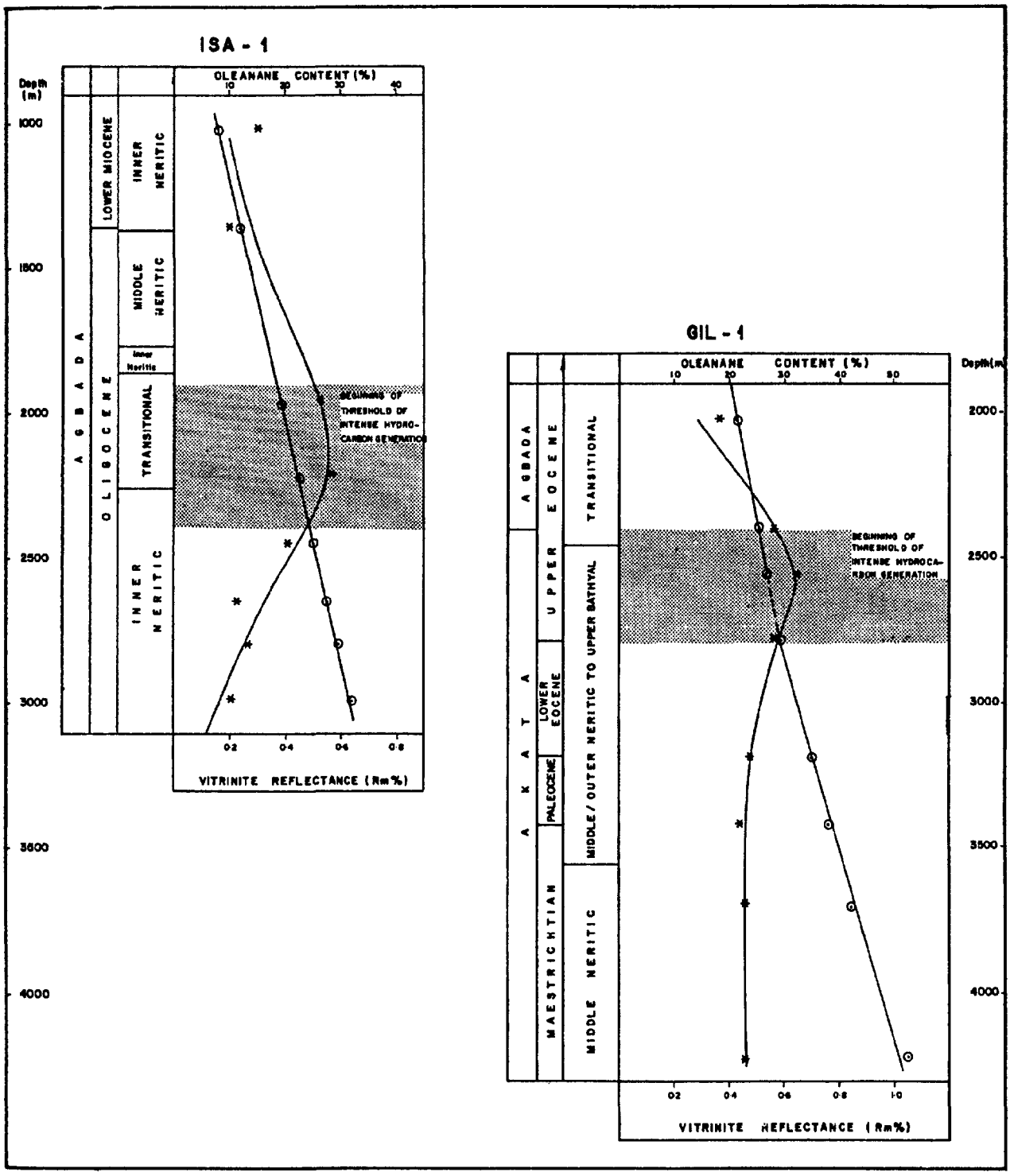


Figure 37—Plot of oleanane content or oleanane parameter (OP: defined here as [18α(H) oleanane + 18β(H) oleanane]/[18α(H) oleanane + 18β(H) oleanane + C_{30} hopane]) versus depth for two wells from the Niger Delta. Oleanane contents (*) reach a maximum near the onset of intense oil generation and then decrease. Vitrinite-reflectance values (open circles) are plotted for reference. Shaded areas represent approximate range for onset of oil generation. From Ekweozor and Udo (1988); reprinted with permission of Pergamon Press PLC.

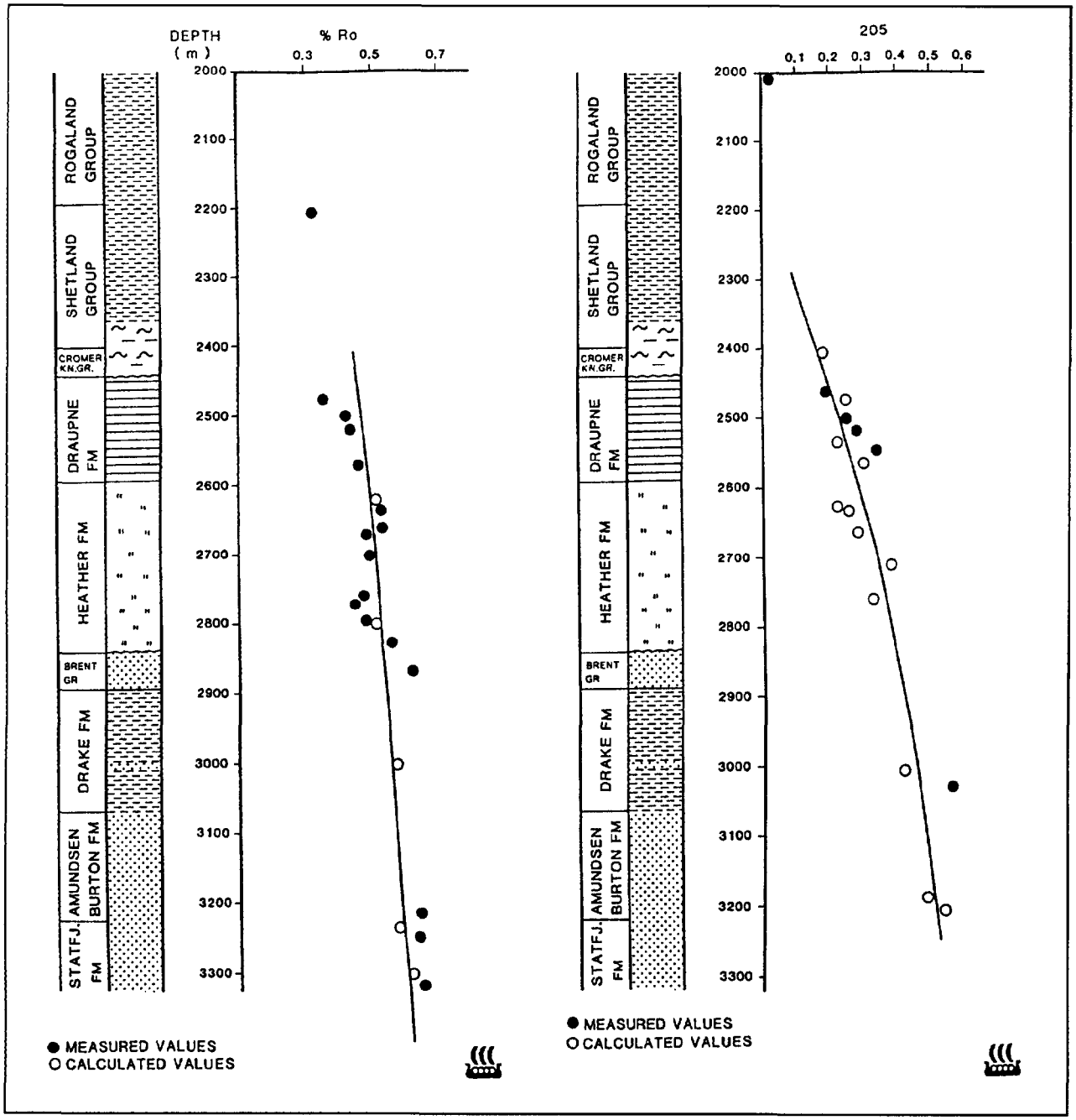


Figure 38—Plots of measured (dark circles) and calculated (open circles) vitrinite-reflectance values (left) and sterane epimerization (right; expressed as 20S/[20R+20S]) in the 30/6-5 well, Oseberg area, offshore Norway. By modeling both Ro changes and sterane epimerization, one can constrain the burial and thermal history of the section more tightly than by modeling Ro alone. From Dahl et al. (1987); reprinted with permission of Graham and Trotman Limited.

of each measurement and the maturity range within which each biomarker transformation occurs, but also the weaknesses associated with biomarker maturities in general.

One problem is that biomarker maturities may not be universally valid, because the relative roles of time and temperature can vary among the various biomarker transformations (Mackenzie, 1984). These variations can lead to discrepancies in biomarker data between young, hot basins and old, cool basins (Mackenzie and McKenzie, 1983). Mackenzie (1984) has suggested that it would be impossible to construct a standard biomarker maturity scale of universal validity. The data of Shi et al. (1982) and Grantham

(1986b) for low levels of sterane and moretane isomerization in young (Tertiary) samples support the view of Mackenzie.

However, the problem of lack of universal validity is intrinsic to all kerogen-maturity parameters when they are applied to predicting hydrocarbon generation, and is probably best viewed as a complication in biomarker interpretation rather than as a complete condemnation of the technology. Because of these limitations, the maturation lines in Figures 27 and 30 should be used with particular caution in estimating maturities wherever time or temperatures are extreme. A kinetic approach, in which calculated biomarker ratios are compared with measured data to test proposed burial and thermal histories, is really preferable to diagrams like Figures 27 and 30.

Several criticisms of the use of biomarkers as maturity indicators that we discussed earlier in this chapter include contamination, reworking, possible migration effects, diagenesis, analytical error, low concentrations, and coelution. Other potential problems also exist. For example, Tannenbaum et al. (1986a) pointed out that the presence of mineral catalysts, particularly smectite, can affect the rate of biomarker transformations in laboratory heating experiments. However, because the effects of such catalysts in nature are likely to be quite different from those in the laboratory, laboratory experiments may not be relevant to modeling natural hydrocarbon generation. We therefore should base our models for biomarker maturity parameters more on empirical data from natural geological situations than on data from laboratory simulations.

Anomalous maturity behavior of biomarkers is well documented in natural samples. Figures 25 (top) and 26 showed an example of natural contamination of steranes by mature biomarkers in reworked sedimentary organic material. Other examples of such contamination were cited by Farrimond et al. (1988, 1989, 1990), who noted that many of the organic-lean samples analyzed in studies of the Toarcian and Cenomanian-Turonian anoxic events in Europe showed anomalously high hopane maturities. They concluded that the hopanes in the lean samples were dominated by reworked material, whereas in the rich samples indigenous hopanes were dominant. Rullkötter et al. (1986) noted that various maturity parameters used in a study of oils in the Michigan basin gave discrepant results, and attributed this problem to mixing. However, it is quite possible that they were simply observing a variety of facies-caused differences in parameters that at that time were still believed to be purely maturity controlled.

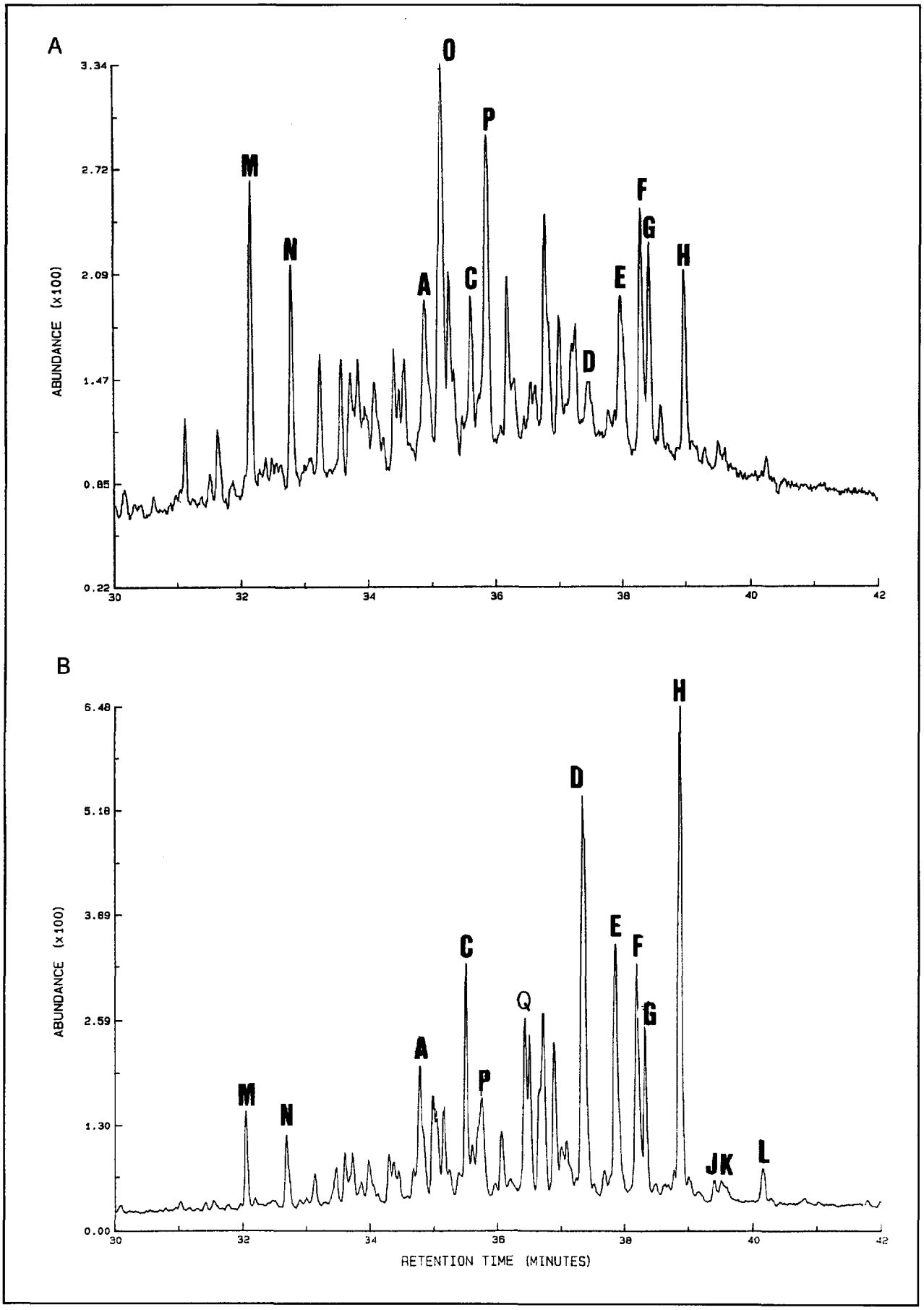
Figure 39 shows retardation of biomarker transformations in an organically lean carbonate rock. The two samples shown are from the same well in the Michigan basin, U.S.A. Measured vitrinite reflectance for the organic-rich Antrim sample (TOC = 3.7%) is 0.7% Ro, a value with which the sterane biomarkers are in agreement. The more deeply buried Al Carbonate sample (TOC = 0.31%) is much more mature (1.7% Ro), yet the steranes (e.g., peaks E and H) indicate the rock to be immature. Triterpanes (not shown) yield maturities that are in agreement with those of the steranes.

Two explanations are possible for the apparent retardation of biomarker transformations in the A1 Carbonate: either the absence of clay catalysts in the carbonate has prevented formation of the more-stable biomarker epimers from less-stable ones, or the poor source quality of the lean rock has prevented generation of new hydrocarbons that would bear the signature of mature biomarkers. Until these questions are answered we should be cautious about using biomarker maturities derived from clay-free rocks and from very lean rocks.

Another quite different but intriguing example of a difficulty with biomarker maturities is shown in Figure 40. Four genetically related oils from the Gippsland basin of Australia were analyzed by gc-ms (Philp and Gilbert, 1986). The Hapuku oil has a normal appearance compared with most other oils in the area, but the other three show very high concentrations of the C_{31} extended hopanes (peaks f and g) and the C_{29} hopane (peak d). More alarmingly, the 22S/(22R+22S) ratio in the Perch and Dolphin oils is extremely low, and disagrees with the ratio calculated from the C_{32} extended hopanes (peaks h and i) in the same samples. This result indicates either that these oils were formed at very low levels of maturity, or that there is some problem with the biomarker analysis.

Philp and Gilbert (1986) explained these changes in triterpane distribution, the immature appearance of the C_{31} extended hopanes (peaks f and g), and the discrepancy in 22S/(22R+22S) for the C_{31} and C_{32} extended hopanes by suggesting that these three oils had leached (dissolved) biomarkers out of rich, immature

Figure 39—Sterane distributions (m/z 217 mass chromatograms) in two rock extracts from a single well in the Michigan basin. The Devonian-age Antrim Shale (A) is at a much lower maturity (as measured by vitrinite reflectance) than is the deeper Silurian-age Salina A1 Carbonate sample (B), yet the sterane distributions indicate the A1 Carbonate to be much less mature. Identities of peaks are given in Table 2. See text for further discussion. From Waples and Machihara, 1990; reprinted with permission from *Bulletin of Canadian Petroleum Geology*.


A
3.34
2.72
2.09
1.47
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0.22
ABUNDANCE (x100)
M
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30
32
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36
38
40
42
B
6.48
5.18
3.89
2.59
1.30
0.00
ABUNDANCE (x100)
M
N
A
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RETENTION TIME (MINUTES)

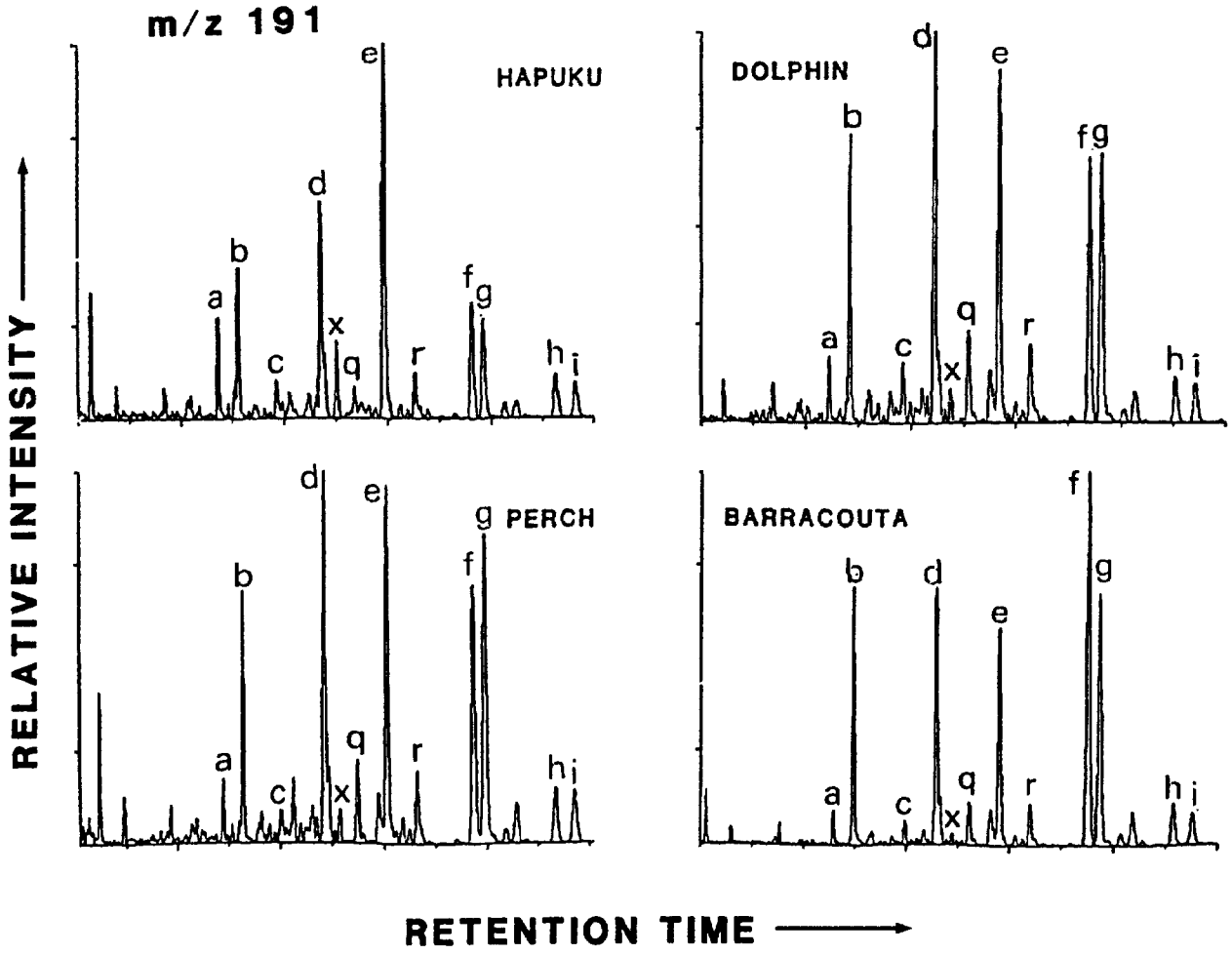


Figure 40—Triterpane distributions (m/z 191 mass chromatograms) in four oils from the Gippsland basin. The distribution in the Hapuku oil is normal, but the other three show contamination by immature hopanes leached from lignites through which the oils migrated. Identities of peaks are given in Table 3. From Philp and Gilbert (1986); reprinted with permission of Pergamon Press PLC.

coal or lignite beds through which they passed during vertical migration. The coals were unusually rich in the C_{31} extended hopanes and the C_{29} hopane, whose characteristics then came to dominate the m/z 191 mass chromatograms of the oils. A further discussion of the reasons for the high C_{31} extended-hopane concentrations is found in Chapter 5.

Fortunately, this type of phenomenon is relatively rare. In the Gippsland case, the beds through which the oils were percolating were very rich and had particularly high concentrations of a few biomarkers. When added to the oils these nonindigenous biomarkers strongly affected the total biomarker distribution of the oils. In normal horizontal migration through reservoir rocks there seldom would be much opportunity for contact with such an organic-rich facies.

In another example, however, we found a light condensate that contained significant amounts of extremely immature biomarkers (Figure 41). The 20R form of the C_{29} sterane is virtually the only sterane present (peak H, Figure 41B), whereas the triterpane chromatogram (Figure 41A) is dominated by extremely immature ββ hopanes and hopenes (not labelled). These compounds had been added to the condensate during vertical migration along deepseated faults through large volumes of immature shale. They completely dominated the biomarker spectrum because the light condensate itself probably contained almost no biomarkers.

Wielens et al. (1990) proposed a similar explanation for the anomalous distribution of biomarkers in a condensate thought to have been derived from a Paleozoic source rock. They suggested it had been contaminated in some unspecified way by biomarkers from

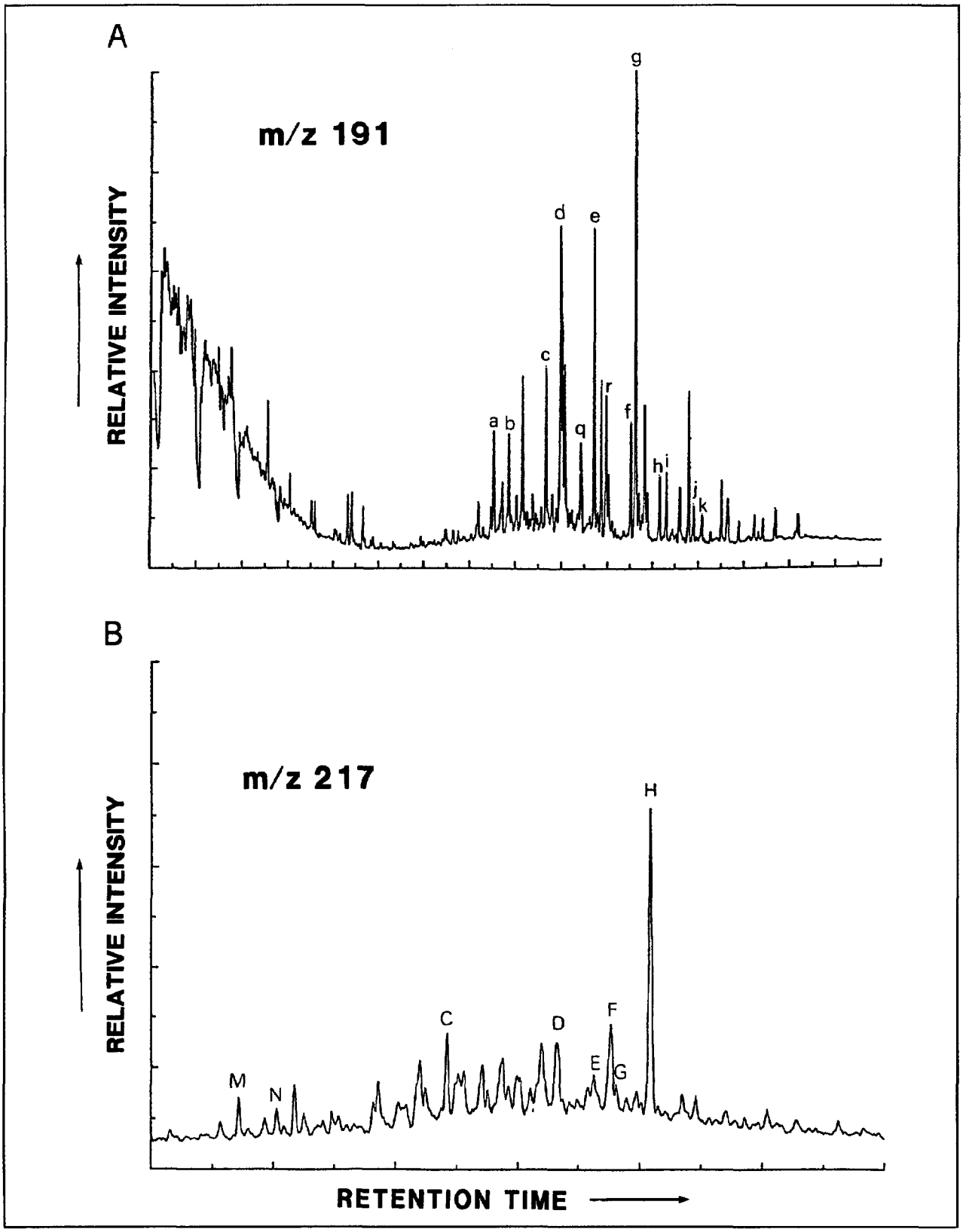


Figure 41—Triterpanes (m/z 191: A) and steranes (m/z 217: B) in a condensate. The high concentrations of these heavy compounds and their immature distributions indicate that these biomarkers were leached from immature shales through which the condensate passed during vertical migration through a fault zone. Identities of some peaks are given in Tables 2 and 3. Unidentified compounds in the m/z 191 chromatogram are probably ββ hopanes found only in samples of very low maturity.

nearby immature Cretaceous rocks. Mattavelli and Novelli (1990) suggested leaching of organic material from Tertiary rocks during vertical migration as a possible explanation for the presence of oleanane in Italian oils thought to be sourced from Jurassic-age sediments, where oleanane is unknown.

In spite of the wide popularity of biomarkers today, van Graas (1990) is generally skeptical about the utility of biomarker ratios as maturity parameters, because he did not find them very sensitive or reliable in the maturity range of his study (0.6-1.0% Ro). He found absolute concentrations of biomarkers (normalized to the saturated-hydrocarbon content) to be more reliable, although he had to establish different empirical trends for different facies. His view is still a minority one at present, but may well be an indication of a future trend toward greater skepticism regarding maturity information obtained from biomarkers.

SUMMARY

In our view, the following statements provide reasonable guidelines for applying biomarker data to estimate maturities of extracts and oils:

1. Any application of biomarkers to predict vitrinite reflectance (i.e., kerogen maturity) or hydrocarbon generation must be viewed as only approximate. A much better general approach is to use kinetic modeling to compare predicted and measured biomarker ratios as a test of proposed thermal and burial histories.

2. If one wishes to use biomarkers to estimate vitrinite reflectance, the most useful results from 0.45% Ro to about 0.75% are usually obtained by using Figure 27, which plots the changes in 20S/(20R+20S) ratios (peak E/[peak H + peak E]) for C_{29} regular steranes.

3. Of lesser value is the plot in Figure 30, in which both the 20S/20R and $\beta\beta/\alpha\alpha$ ratios for C_{29} regular steranes are plotted. The main problem with Figure 30 lies in the effects of diagenesis on $\beta\beta/\alpha\alpha$ ratios.

4. At lower maturity levels, the 22S/(22R+22S) ratio in 17α(H)-extended hopanes (peak f/[peak g + peak f]) is of qualitative value. However, once the transformation of 22R to 22S begins, this ratio changes so rapidly that it cannot be used to estimate maturity precisely. This ratio is thus mainly of value as a qualitative measure of immaturity.

5. The C_{32} extended hopanes (peaks h and i) are more reliable than the C_{31} hopanes (peaks f and g) in calculating 22S/(22R+22S) ratios for hopanes.

6. Moretane/hopane ratios (e.g., peak q/peak d) are of some value, mainly in a qualitative sense, as indicators of immaturity. However, they may be affected by source as well as maturity.

7. Tm/Ts ratios from m/z 191 mass chromatograms (peak b/peak a) can in principle extend the maturity scale beyond 0.9% Ro, but natural variations from sample to sample generally make them less precise than the sterane curve in Figure 27. They are of greatest value in estimating relative maturities of samples from the same facies.

8. Oleananes and tricyclics show promise as qualitative or possibly even quantitative maturity indicators. At the present time, however, these parameters have not been adequately quantified and tested.

9. All maturity data obtained from biomarkers in rock extracts should be compared carefully with kerogen-maturity data because of the possibility of contamination of extracts by migrated material. However, we should not expect perfect agreement, since the relative influences of time and temperature on biomarkers are different from those on kerogen maturation. Furthermore, biomarkers can show internal discrepancies for the same reasons.

10. Because of many unknowns about the chemical processes involved in biomarker maturation, we should exercise care in interpreting biomarker-maturity data, especially in carbonates and organic-lean rocks. A recent discussion by Zumberge (1987) summarizes many of these points for a series of low-maturity oils.

11. Concentrations of all biomarkers decrease with increasing maturity. Thus in highly mature samples biomarker concentrations may be too low for accurate quantification.

12. In addition to the saturated steranes discussed here, aromatic steranes and methylphenanthrenes have also been used for a number of years as maturity indicators. The interested reader could refer to Mackenzie (1984), Riolo et al. (1986), Sakata et al. (1987), Radke and Welte (1983), or Tupper and Burckhardt (1990) for further information. Biphenyls are a new addition to the list of maturity indicators (Alexander et al., 1990), and their potential needs to be evaluated further.

Chapter 5

Biomarkers as Organic-Facies Indicators

INTRODUCTION

Because biomarkers are derived from biological precursor molecules in specific organisms, and because each of these organisms lives only under certain conditions, it is logical to attempt to use biomarkers as indicators of those life conditions. Steranes are in general indicators for photosynthetic biota, both terrestrial and aquatic. Triterpanes, which are derived mainly from bacteria, much more frequently are indicators of depositional and diagenetic conditions. Together, therefore, steranes and triterpanes can provide information about most parts of the system we call "organic facies."

However, any application of biomarkers for organic-facies interpretations should be made with a full awareness that organic facies (and hence biomarker distributions) can change rapidly, both vertically and laterally (Moldowan et al., 1986; Curiale and Odermatt, 1989; Farrimond et al., 1990). If one is working with a typical sample of cuttings material, the biomarker signature will be an average for all facies present in the sample, and thus may be much harder to interpret.

Furthermore, if only a few samples of core material are available, one cannot be sure that these samples are representative of the complete rock unit. In some source rocks, particularly lacustrine beds, lateral changes in organic facies can yield oils that look quite different (Katz and Mertani, 1989). Oil samples themselves will almost certainly represent some kind of averaging of input from various localities.

Another problem is that we now realize that there is no definite and unique facies interpretation for most biomarkers. It is likely that there are multiple precursors for many biomarkers, and that these precursors may come from very different kinds of organisms that can live in a wide range of environments. This point is discussed in detail later in this chapter. The proper use of biomarkers in organic-facies interpretations is analogous to the use of microfossils in age dating or paleoenvironmental interpretation, in which the presence or absence of a single variety is not completely diagnostic. Just as micropaleontologists base their interpretations on assemblages of fossils, geologists and geochemists interpreting biomarker data should look at assemblages of biomarker data. In this sense, the term "biomarkers" refers to many other types of compounds than steranes and triterpanes: for example, n-alkanes, isoprenoids, diterpanes, sesquiterpanes, and porphyrins.

Finally, biomarkers, even in the broad sense of the word, represent but one part of the total geological and geochemical information we have available. If biomarker data disagree with other information, they may be revealing some new and hitherto unsuspected truths about the samples. On the other hand, the biomarker data or interpretation may simply be wrong. Any successful facies analysis must evaluate and integrate all available information to make a single, consistent story. Biomarkers should not be given undue consideration simply because they represent relatively expensive, high technology.

These complications have led to a certain amount of pessimism about the use of biomarkers for organic-facies interpetations (e.g., Moldowan et al., 1985). However, if an assemblage approach is taken to interpreting biomarkers, and if biomarkers are integrated with all other geochemical and geological data, they are very useful (e.g., Murchison, 1987). A certain amount of restraint must simply be exercised in interpreting biomarker distributions in terms of organic facies.

STERANES

C_{27}-C_{29} Regular steranes

The steranes inherited directly from higher plants, animals, and algae are the 20R epimers of the 5α(H),14α(H),17α(H) forms of the C_{27}, C_{28}, C_{29}, and C_{30} steranes (Figure 9). The relative proportions of each of these "regular" steranes can vary greatly from sample to sample, however, depending upon the type of organic material contributing to the sediment (Figure 42).

Huang and Meinschein (1979) provided the first evidence that the relative proportions of the C_{27}-C_{29} regular sterols in living organisms were related to specific environments (Figure 43), and suggested that steranes in sediments might provide valuable pale-

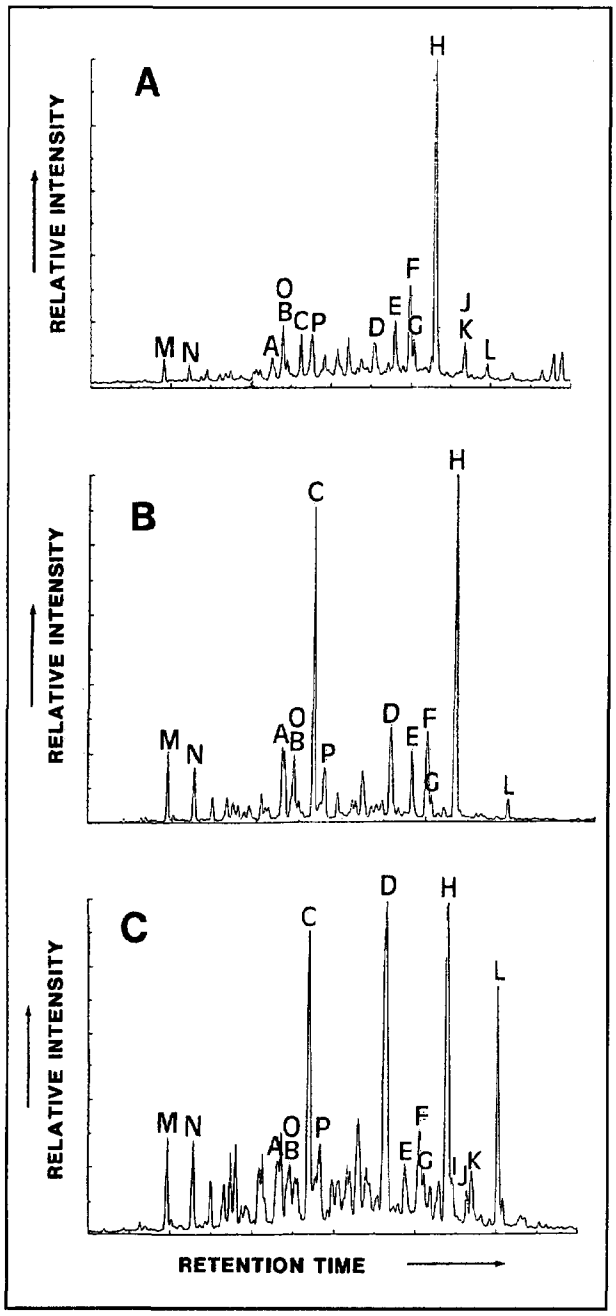


Figure 42—M/z 217 (sterane) mass chromatograms of three very-immature samples showing a variety of C_{27}-C_{29} sterane distributions. Immature samples were selected to avoid complications caused by maturation. Identities of peaks are given in Table 2. From Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology*.

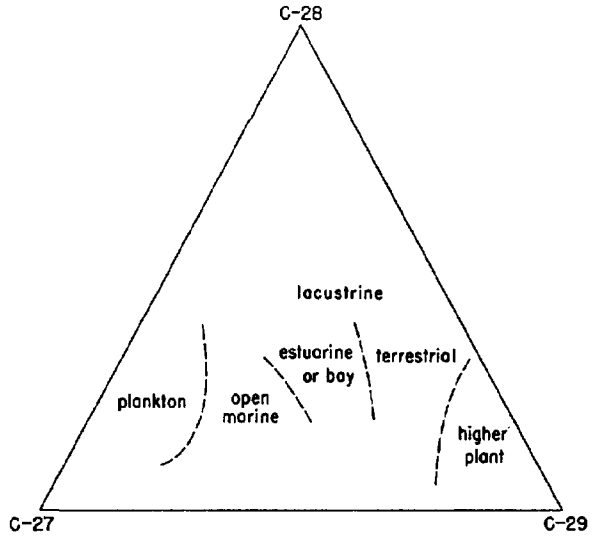


Figure 43—Triangular diagram showing initial proposal of environmental dependence of the sterol composition in organisms. Further data indicate that the simple patterns implied by this diagram often are not valid, and that great care must be taken in using sterol and sterane distributions for environmental interpretations. From Huang and Meinschein (1979); reprinted with permission of Pergamon Press PLC.

oenvironmental information. They proposed that a preponderance of C_{29} sterols (or steranes) would indicate a strong terrestrial contribution, whereas a dominance of C_{27} would indicate a dominance of marine phytoplankton. C_{28} was found in general to be the lowest of the three steranes, but where relatively abundant it might indicate a heavy contribution by lacustrine algae. Since these suggestions were first made, triangular diagrams (e.g., Figure 44) have often been employed to represent the relative proportions of these three steranes.

The proposal of Huang and Meinschein has been used with some success. For example, Figure 45 shows the sterane distributions for two facies within the Elko Formation (Eocene) of Nevada. The continental lignitic siltstones show a very strong predominance of the C_{29} steranes, as expected. In contrast, the oil shales, which were deposited in a lacustrine environment, show much larger proportions of the C_{27} and C_{28} steranes, which presumably are contributed by nonmarine algae. Robinson (1987) noted that in Indonesia, C_{29} regular steranes and diasteranes dominate among fluvio-deltaic oils, reflecting the strong contribution of terrestrial plant material. Humic and waxy coals generally display a strong dominance of the C_{29} steranes.

In spite of such successes, however, one must be cautious when applying these oversimplified rules. Volkman (1986, 1988) has commented that most marine sediments, including those deposited in pelag-

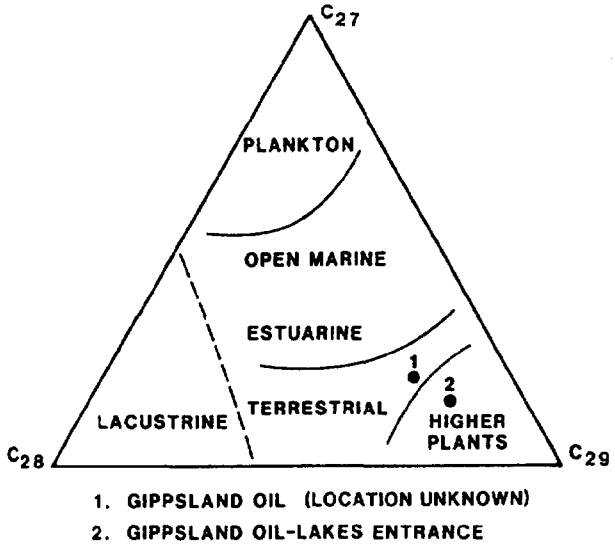


Figure 44—Triangular diagram showing interpretation of environment from sterane distributions. This type of diagram has been adapted from that in Figure 43, but is subject to the same cautions discussed for that figure. From Shanmugam (1985).

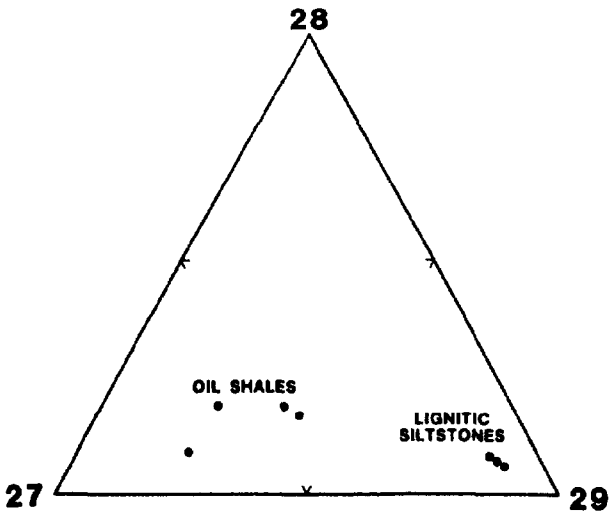


Figure 45—Triangular diagram showing proportions of C_{27}, C_{28}, and C_{29} regular steranes in two facies of the Elko Formation, Eocene, of Nevada. The terrestrially dominated lignitic siltstones show a strong predominance of the terrestrially derived C_{29} sterane, whereas the oil shales, deposited in lacustrine environments where nonmarine algal material dominated, have more C_{27}. From Palmer (1984); reprinted with permission of the Rocky Mountain Association of Geologists.

ic environments far from terrestrial influence, show predominances of C_{29} steranes (peaks E, F, G, and H). Furthermore, lower Paleozoic and Precambrian sediments often contain substantial amounts of the C_{29} sterane, even though land plants could not have contributed (e.g., Grantham, 1986a [see Example 4 in Chapter 7]; Rullkötter et al., 1986; Vlierboom et al., 1986; Longman and Palmer, 1987; Fowler and Douglas, 1987; Buchardt et al., 1989). Volkman concluded that there must be unproven marine sources of the C_{29} sterane; Matsumoto et al. (1982) and Fowler and Douglas (1984, 1987) suggest it could come from cyanobacteria (blue-green algae). Nichols et al. (1990) showed that large amounts of C_{29} sterols are produced by marine diatoms during the spring bloom in cold Antarctic waters.

Recently an extremely interesting and radically new interpretation of regular-sterane distributions has been put forth by Grantham and Wakefield (1988). They showed that the ratio of C_{28}/C_{29} regular steranes (e.g., peak D/peak H) in marine environments is controlled not by facies but by geologic age. The C_{28}/C_{29} ratio increases from past to present, as shown in Figure 46. They attributed this change to evolutionary trends within living organisms. Use of this ratio offers a unique way to date oils, and thus to make a better first guess about their source rocks. However, Grantham and Wakefield cautioned against overly enthusiastic use of this method for precise age dating, at least at our present state of knowledge.

In one example, the C_{28}/C_{29} ratio was used to distinguish between possible source rocks of Eocene and Albian age for oils in the Zagros Orogenic Belt of Iran (Bordenave and Burwood, 1990). In a second example, we see in Figure 47 the m/z 217 mass chromatogram of an extract of a cuttings sample that was believed to be from a reasonably mature Paleozoic interval in the Middle East. The low maturity indicated by 20S/(20R+20S) (peak E/[peak H + peak E]) and BB/aa ([peak F + peak G]/[peak E + peak H]) ratios was very surprising, and suggested contamination by caving. The high C_{28}/C_{29} sterane ratio (peak D/peak H) supported the interpretation that the steranes came mainly from immature Cretaceous or Tertiary strata above the Paleozoic.

In a third study, both Cretaceous and Jurassic source rocks were suspected to be present. We predicted on the basis of the C_{28}/C_{29} sterane ratio (Figure 48: peak D/peak H, about 1.4) that an oil found in the area had come from the Cretaceous source, because Figure 46 indicates that Jurassic samples are more likely to have C_{28}/C_{29} ratios less than 1.0. This delicate

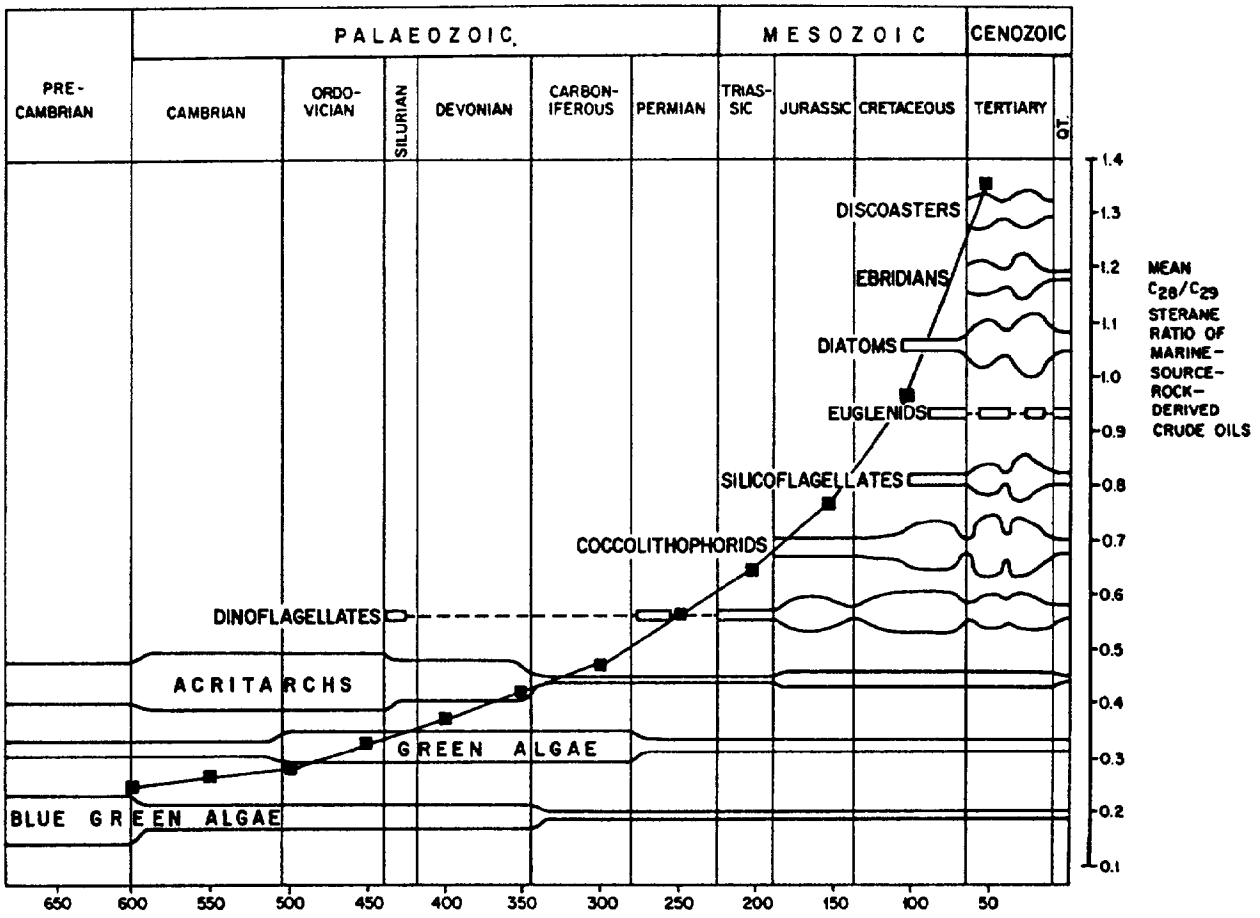


Figure 46—Plot of the ratio of C_{28}/C_{29} regular steranes as a function of geologic time, showing that as a result of evolutionary changes in photosynthetic organisms, the C_{28}/C_{29} ratio has increased from past to present, particularly since the Jurassic. From Grantham and Wakefield (1988); reprinted with permission of Pergamon Press PLC.

distinction may be appropriate for Mesozoic and younger rocks, but because the C_{28}/C_{29} ratio begins to change dramatically only in the Mesozoic, it will be of limited value in distinguishing one Paleozoic period from another. For example, Jones and Philp (1990) found no difference among oils from at least two distinct Paleozoic sources in the Anadarko basin.

The hypothesis of Grantham and Wakefield applies only to marine sediments. Hall and Douglas (1983) reported lacustrine shales of Devonian age from Scotland with a strong predominance of C_{28} steranes over C_{27} and C_{29}. McKirdy et al. (1984) found similar distributions in oil shows attributed to playa-lake source rocks of Cambrian age in the Officer basin of Australia. Furthermore, exceptions to the hypothesis of Grantham and Wakefield have been noted. For example, an extract of Ordovician rock from the Anadarko basin showed a very high ratio (0.91) more typical of Jurassic or Cretaceous samples (Jones and Philp, 1990). Thus we should be cautious in applying C_{28}/C_{29} ratios until they are verified further.

In spite of these recent advances in our understanding of sterane distributions, any simplistic interpretation of C_{27}–C_{29} sterane ratios, especially in terms of paleoenvironment, is still risky. Use of the triangular diagram in Figure 45 without reference to facies implications is now common because it is a useful way to display sterane data. However, there is at least a minor concern that C_{27}–C_{29} distributions may be influenced by maturity as well as facies (Curiale, 1986). In any case, all interpretations of sterane distributions must be consistent with other geological evidence and with common-sense logic.

C_{30} Regular steranes

Recently Moldowan et al. (1985) proposed that the previously neglected C_{30} steranes (Figure 9) are present only in post-Silurian samples deposited in marine environments. Mello et al. (1988a,b) have con-

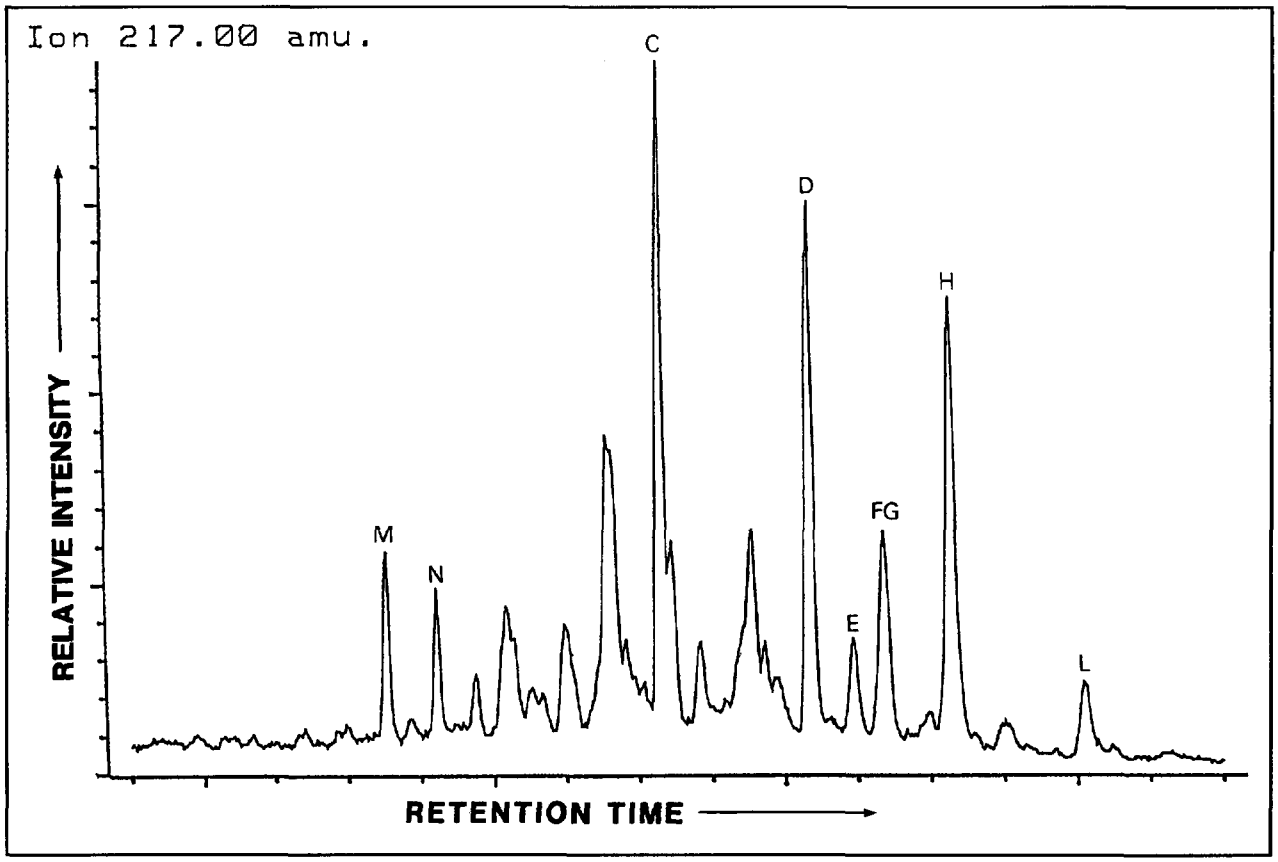


Figure 47—M/z 217 (sterane) mass chromatogram from an extract of a moderately mature Paleozoic rock from the Middle East, showing a very immature sterane distribution (mainly ααα-20R) and a dominance of C_{28} over C_{29}, a characteristic normally associated with much younger samples. Identities of peaks are given in Table 2. See text for discussion.

firmed these conclusions based on work in Brazilian basins. It is not yet known whether the converse is true; i.e., that all marine environments contain C_{30} steranes. It has also been suggested that C_{30} steranes will eventually be identified in lacustrine algae as well as marine (Volkman, 1988).

The precise time in the past at which the C_{30} steranes evolved is also not known. The data set of Moldowan and coworkers included samples of Cambrian age from which the C_{30} steranes were missing, and samples of Devonian age in which they were present.

The C_{30} steranes reported by Moldowan, Mello, and coworkers are believed to contain their extra methyl group in the longest side chain. They can therefore be called 24-propylcholestanes, and can be seen in the m/z 217 mass chromatogram (peaks I, J, K, and L in Figure 42, for example). However, they are more unambiguously identified in the m/z 414 to m/z 217 metastable transition using SMIM. In contrast, the two families of 4-methylsteranes mentioned previously (dinosteranes and 4-methylcholestanes) have their extra methyl group attached to ring A. The m/z 231 fragment ion is more dominant for 4-methylsteranes than is the m/z 217 ion, because the additional methyl group is attached to the fragment that bears the positive charge.

However, 4-methylsteranes (see discussion below) also give a modest m/z 217 peak, and thus can be confused with regular steranes in the m/z 217 mass chromatogram. In particular, some of them elute at about the same time as the C_{30} steranes (Moldowan et al., 1985; see also Figure 49). Figure 42 (A and B) shows the presence of minor amounts of C_{30} steranes (conclusively identified from other mass-spectral evidence). 4-Methylsteranes are absent. Figure 42C, however, shows a very large amount of material that could be either the 14α(H),17α(H)-20R epimer of the C_{30} sterane, or one of the 4-methylsteranes. More detailed analysis of this compound by the mass spectroscopist would be required for positive identification.

Jones and Philp (1990) observed in their study of the Anadarko basin that the ratios of the C_{29}/C_{30} ββ regular steranes ([peak E + peak F]/[peak J + peak K]) varied between oils from different Paleozoic sources. This ratio played an important role in grouping the oils into genetic families and in correlating oils with source

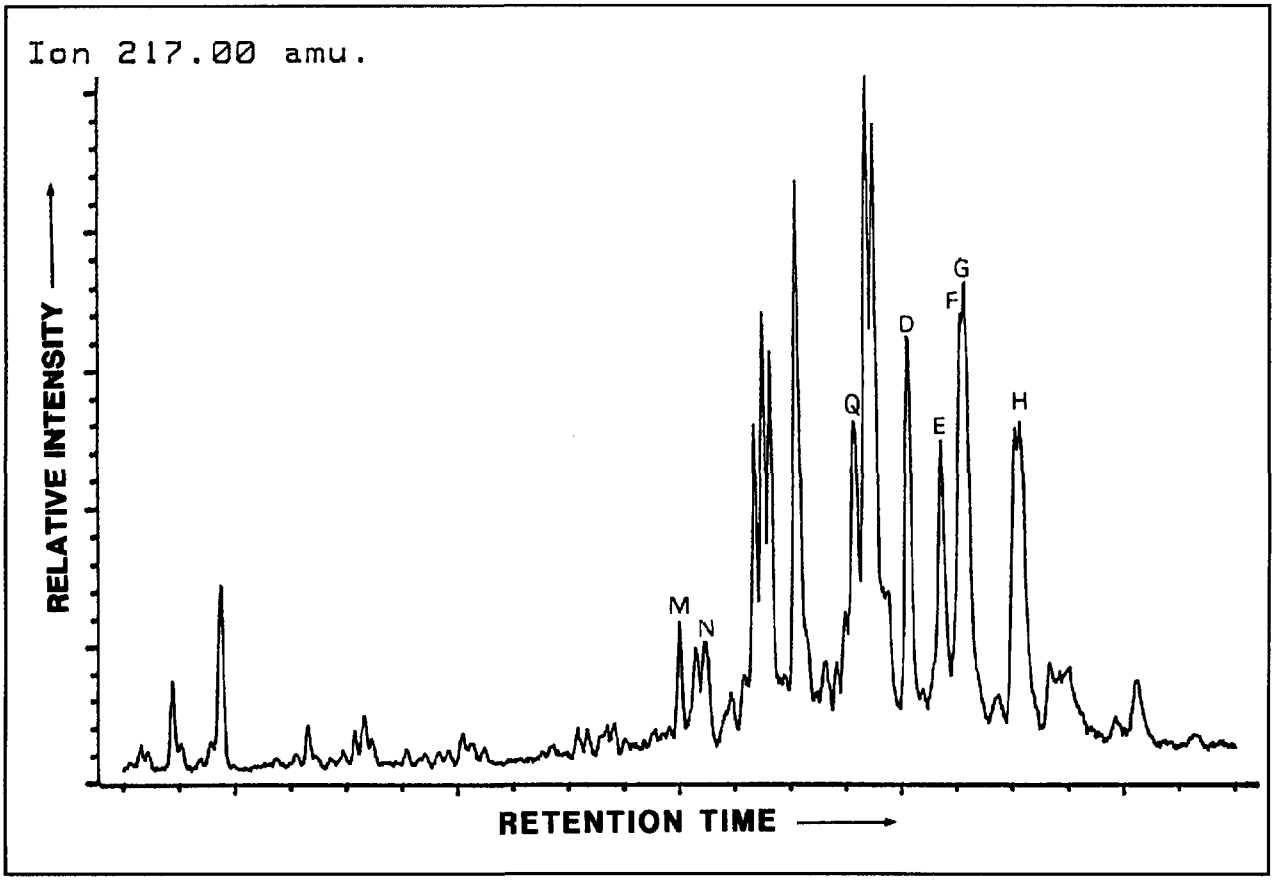


Figure 48—M/z 217 (sterane) mass chromatogram of an oil with a dominance of the C_{28} steranes over C_{29}. Identities of peaks are given in Table 2. See text for discussion.

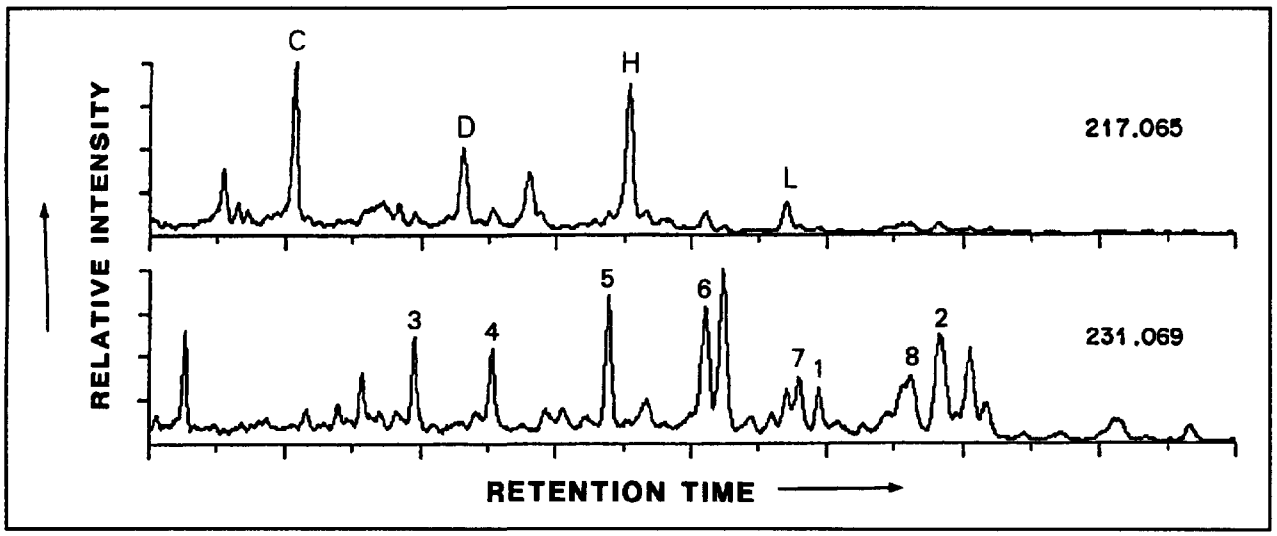


Figure 49—M/z 217 and 231 (sterane) mass chromatograms of an extract from an immature Upper Jurassic sample of marine origin in which dinoflagellate cysts were abundant. Peaks C, D, H, and L are, respectively, the αα-20R forms of the C_{27}, C_{28}, C_{29}, and C_{30} regular steranes, as in Table 2. Peaks 1 and 2 are, respectively, the 4α-methyl and 4β-methyl forms of dinosterane. The other numbered peaks represent the various 4-methylcholestanes: peaks 3 and 4 are the 4-methylcholestanes (4α-methyl and 4β-methyl versions of peak C); peaks 5 and 6 are the 4-methyl-24-methylcholestanes (4α-methyl and 4β-methyl versions of peak D: and peaks 7 and 8 are the 4-methyl-24-ethylcholestanes (4α-methyl and 4β-methyl versions of peak H. Adapted from Goodwin et al. (1988) with permission of Pergamon Press PLC.

rocks. However, since all the plausible source rocks were marine, the cause for the variation was not clear.

4-Methylsteranes

Until recently it was thought that all 4-methylsteranes were dinosteranes, but it has now been shown that both C_{30} dinosteranes and a series of C_{28}-C_{30} 4-methylcholestanes exist (Figure 11). Both are best detected using the m/z 231 chromatogram (Figure 49).

The dinosteranes, which are found mainly in marine environments, are believed to be derived from dinosterol in dinoflagellates, but the origin of the 4-methylcholestanes, which are common in both marine and freshwater samples, is still a mystery. Dinosteranes and 4-methylcholestanes frequently occur together in marine samples. Probable precursors for the 4-methylcholestanes have been reported in microscopic prymnesiophyte brown algae of the genus *Pavlova* (Volkman et al., 1989, 1990). Prymnesiophytes date back to the Carboniferous and are common in both marine and brackish waters (Volkman et al., 1990), but it is not yet clear how widely distributed through space and time the *Pavlova* genus is. Goodwin et al. (1988) suggested freshwater dinoflagellates, algae, or bacteria as possible sources for the 4-methylcholestanes found in nonmarine environments.

Until more data are available, C_{28}-C_{30} 4-methylcholestanes should not be used as paleoenvironmental indicators, and in any case the 4-methyl-24-ethylcholestanes should not be confused with dinosteranes. Much of the pre-1989 literature in which 4-methylsteranes were always interpreted as indicating a dinoflagellate origin should therefore be viewed skeptically.

Diasteranes

Diasteranes (also called rearranged steranes: Figure 10) are present in significant quantities in most samples that are at least moderately mature. They are well known as C_{27}, C_{28}, C_{29}, and C_{30} species. Figure 39A shows the 20S and 20R forms of the C_{27} and C_{29} diasteranes, which are usually the most dominant and easily observed. The C_{27} diasteranes (peaks M and N) are well separated from other important peaks, but the C_{29} 20S diasterane (peak O) frequently overlaps badly with the $\beta\beta$ C_{27} (20S + 20R) regular steranes (peak B).

The relative amount of diasteranes compared with regular steranes seems to depend on both sediment lithology and maturity. Diasteranes seem to form most readily in clastic sediments, where clay catalysts can play a role in their formation from other steranes. They are therefore frequently used to distinguish carbonate facies (low diasteranes) from clastic ones (e.g., Hughes, 1984; Zumberge, 1984; Mello et al., 1988b; Czochanska et al., 1988; Mattavelli and Novelli, 1990; Riediger et al., 1990; Alajbeg et al., 1990). Brown (1989) noted that Indonesian shales containing mangrove-derived organic matter had lower diasterane contents than did closely related shale-poor coals.

However, the facies dependence must be more subtle than simply one of clastic/nonclastic or of clay content. Moldowan et al. (1986) suggested there might be some redox control on the diasterane/sterane ratio. Clark and Philp (1989) found significant differences in diasterane contents between oils sourced exclusively from evaporitic carbonates, and those containing a contribution from deep-water micritic carbonates. Connan et al. (1986) found diasteranes to be abundant in some organic-lean Guatemalan anhydrites. Palacas et al. (1984) observed abundant diasteranes in clay-free samples of the Sunniland Limestone (Florida) and saw no correlation between clay content and diasterane content in that formation. Clark and Philp (1989) have summarized the published occurrences of high diasterane contents in carbonates, and suggest that there may be other as-yet-unidentified mechanisms for forming diasteranes in at least some carbonate environments.

The application of diasteranes as facies indicators is further complicated by their dependence on maturity as well as environment. Diasteranes seem to be more stable than regular steranes, and thus become more dominant with increasing maturity. Figure 50 shows the increase in diasteranes relative to regular steranes in three extracts of different maturities from the same facies. The ratio of C_{27}/C_{29} $\alpha\alpha$ diasteranes (peaks [M+N]/[O+P]) parallels the ratio of C_{27}/C_{29} $\alpha\alpha$ regular steranes (peaks [A+C]/[E+H]), a trend that is not surprising in view of the proposed genetic relationship between regular steranes and diasteranes.

Finally, diasteranes seem to be unusually abundant in many lower Paleozoic oils, compared with regular steranes (e.g., Moldowan et al., 1985; Vlierboom et al., 1986; Reed et al., 1986; Longman and Palmer, 1987), even where no clay minerals are evident. Although these oils are not all of high maturity, it is possible that time has played a role in the conversion. Alternatively, there may be some as-yet-unrecognized facies affect that is not related to clay minerals.

Resin-derived cycloalkanes

Compounds believed to be cycloalkanes derived from resin have been observed in oils derived from coals and in extracts from coals in the Indonesian Archipelago (Thompson et al., 1985; Comet et al., 1989; Jamil et al., 1990). These compounds are not steranes, but may be confused with steranes because they yield large m/z 217 peaks (Figure 51). They are discussed more fully later in this chapter under "TRITERPANES."

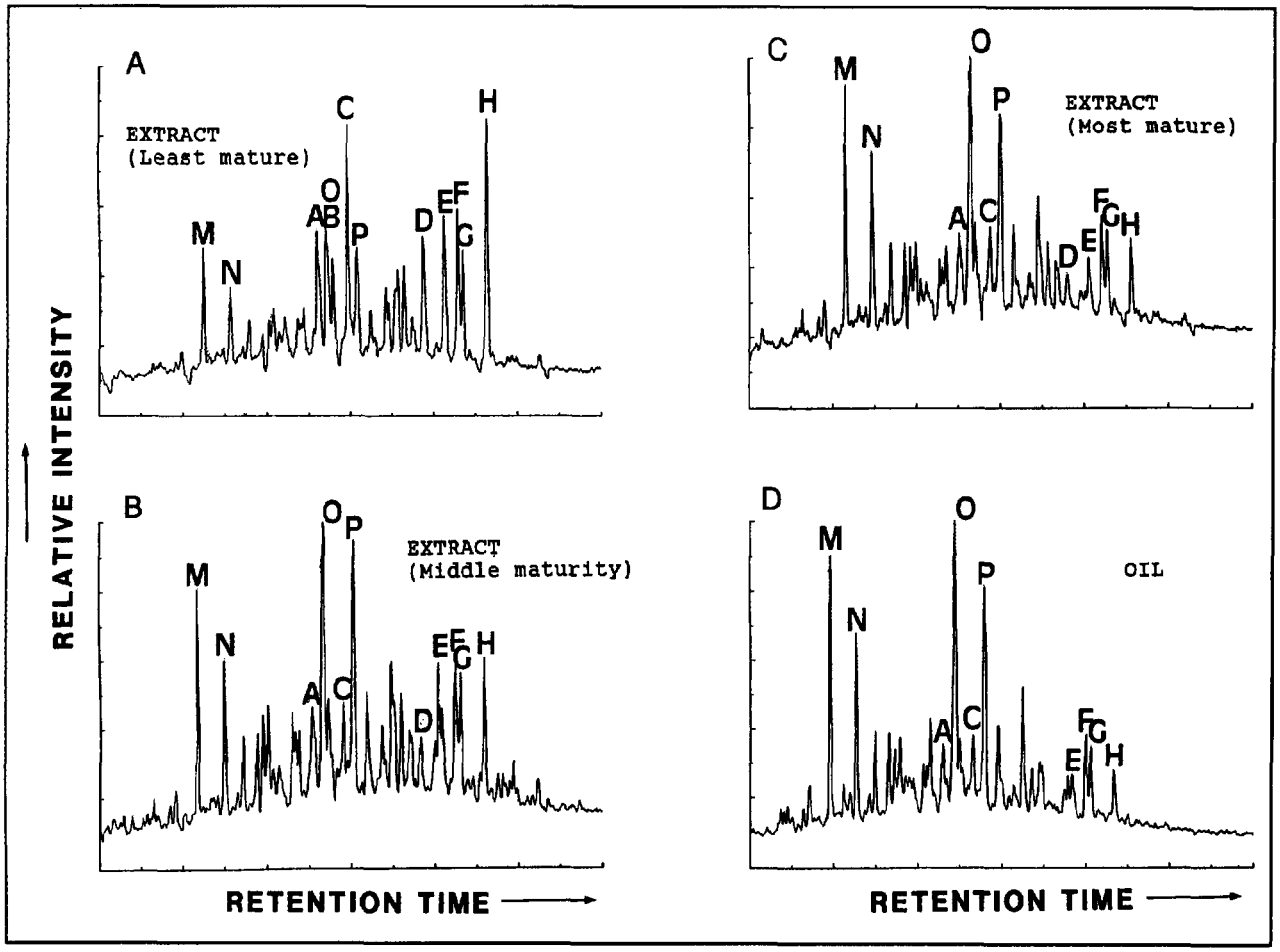


Figure 50—M/z 217 (sterane) mass chromatograms for three extracts from the same facies at different levels of maturity. The extract in (A) is least mature, followed by (B) and (C). With increasing maturity, the proportions of the αα-20S sterane and the ββ steranes increase, as expected. The relative increase in diasteranes with increasing maturity could be due either to formation of new diasteranes during maturation, or to a greater stability of early-formed diasteranes. The oil in (D) was sourced from this facies. Identities of peaks are given in Table 2.

TRITERPANES

Introduction

Although we do not yet understand all the details of the influence of depositional and diagenetic conditions on triterpane distributions, because of their dominantly microbial origin these compounds are potentially powerful markers for diagenetic conditions. As such they differ fundamentally from the steranes, which reflect principally the type of primary photosynthetic organic material.

C_{29} and C_{30} Hopanes

Hopanes are almost certainly derived primarily from bacteria. The C_{29} and C_{30} 17α(H)-hopanes, the two dominant triterpanes in most samples, are not used extensively as environmental indicators, because the ratio of the height of the C_{30} 17α(H)-hopane peak to that of the C_{29} (norhopane) is usually about 2:1 (for example, Figure 32: peak d/peak e). However, oils and extracts from organic-rich carbonates (Zumberge, 1984; Connan et al., 1986; Price et al., 1987) and some evaporites (Connan et al., 1986) may have unusually high concentrations of the C_{29} 17α(H)-hopane (Figures 33 and 52). Riva et al. (1989) have suggested that the C_{29}/C_{30} hopane ratios might provide a scale of "carbonaticity," but further work will be required to quantify this idea.

However, high norhopane contents are not always associated with carbonates. Brooks (1986) noted that high C_{29} hopane contents can occur in samples containing oleanane and bisnorlupanes (Figure 53), both of which are considered to be terrestrial indicators (see below). Furthermore, nonmarine Jurassic coals from the Western Desert of Egypt (Bagge et al., in

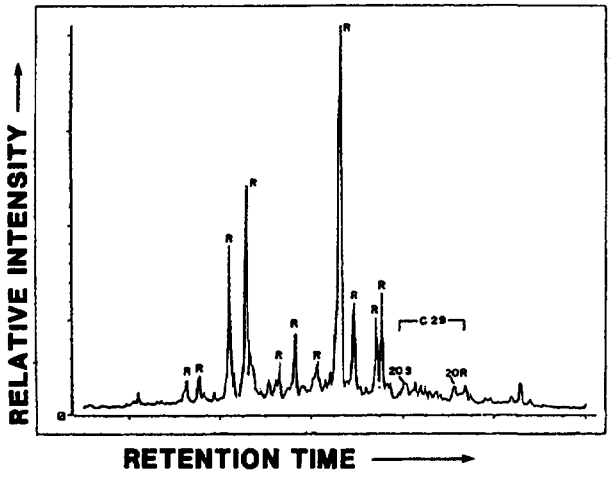


Figure 51—M/z 217 mass chromatogram of saturated hydrocarbons in an Indonesian oil generated from a coaly source rock. Peaks marked "R" are due to resin-derived compounds. αα-20R and 20S forms of C_{29} regular sterane are indicated, but are present in very low concentration. From Robinson and Kamal, 1988; reprinted with permission of Indonesian Petroleum Association.

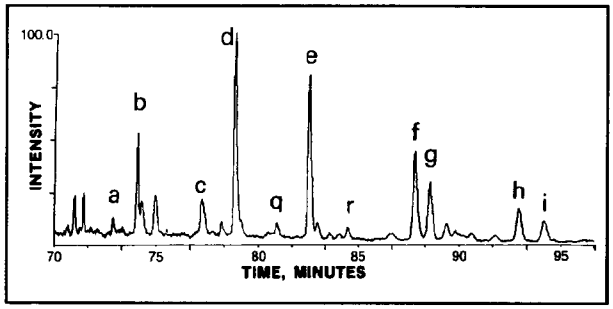


Figure 52—M/z 191 (triterpane) mass chromatogram of triterpanes from an extract from the organic-rich, calcareous La Luna Formation (Upper Cretaceous of Colombia). Note the presence of 28,30-bisnorhopane (peak c) and the dominance of C_{29} 17α(H)-hopane (peak d) over C_{30} 17α(H)-hopane (peak e). Identities of other peaks are given in Table 3. From Zumberge (1984).

press) and Upper Carboniferous coals from Madagascar (Ramanampisoa et al., 1990) can have high norhopane/hopane ratios.

Extended hopanes (homohopanes)

In contrast to the C_{29} and C_{30} hopanes, the concentration of 17α(H)-extended hopanes varies considerably from sample to sample (Figure 54). Therefore, they are valuable as paleoenvironmental indicators. The C_{31}-C_{35} extended hopanes all probably are derived from the C_{35} bacteriohopanetetrol (Peters and Moldowan, 1991).

The most common distributions, with a regular decrease in peak height from the C_{31} members to C_{35} (Figure 54A), usually represent clastic facies. Unusually large amounts of the C_{35} 17α(H)-extended hopanes (Figures 33 and 54B: peaks o and p) seem to be associated with marine carbonates or evaporites (Philp and Gilbert, 1986; Connan et al., 1986; Fu Jiamo et al., 1986; Mello et al., 1988b; Clark and Philp, 1989; Jones and Philp, 1990; Riediger et al., 1990). This phenomenon can be displayed conveniently as the ratio of C_{35}/C_{34} extended hopanes (peaks [o+p]/peaks [m+n]: e.g., Jones and Philp, 1990). However, Peters and Moldowan (1991) prefer to correlate high C_{35}/C_{34} ratios in marine environments with low redox potential rather than with lithology, particularly since not all carbonate rocks have high concentrations of C_{35} extended hopanes (Palacas et al., 1984; Jones and Philp, 1990). Peters and Moldowan (1991) noted, however, that the correlation between redox potential and homohopane distribution in lacustrine facies is less certain. They believe that sulfur, which is often limited in lacustrine environments, may play an important role in homohopane diagenesis.

Abnormally large amounts of the C_{32} and C_{34} 17α(H)-extended hopanes have also been reported in some marine carbonates (e.g., Figures 33 and 54C: peaks h, i, m, and n), in lacustrine evaporites (Fu Jiamo et al., 1986; Brassell et al., 1988), and, most surprisingly, in nonmarine coals (Bagge et al., in press).

High concentrations of the C_{31} hopanes (Figure 32A, peaks f and g) have been correlated with peats and coals (Villar et al., 1988). The precise concentrations of the C_{31} hopanes seem to depend on diagenetic conditions in the peat-forming environment, since the C_{31} hopane concentrations correlate well with pristane/phytane ratios (which in turn have been related to diagenetic conditions in coal swamps: ten Haven et al., 1987).

Tm/Ts ratios

Tm/Ts ratios (also expressed as Ts/Tm), previously believed to be affected only by maturity, are now recognized to be related at least as much to diagenetic conditions. Several authors have noted that Tm/Ts ratios (peak b/peak a) are lowest in hypersaline facies (Fan Pu et al., 1984; Philp and Fan, 1987; Rullkötter and Marzi, 1988). Riva et al. (1989) observed Tm/Ts ratios to increase as the proportion of shale in calcareous facies decreased. However, high Tm/Ts values have also been reported in oils sourced from carbonates (e.g., McKirdy et al., 1983, 1984; Rullkötter et al., 1985; Mattavelli and Novelli, 1990). Price et al. (1987) stated that high Tm/Ts ratios in carbonate-sourced

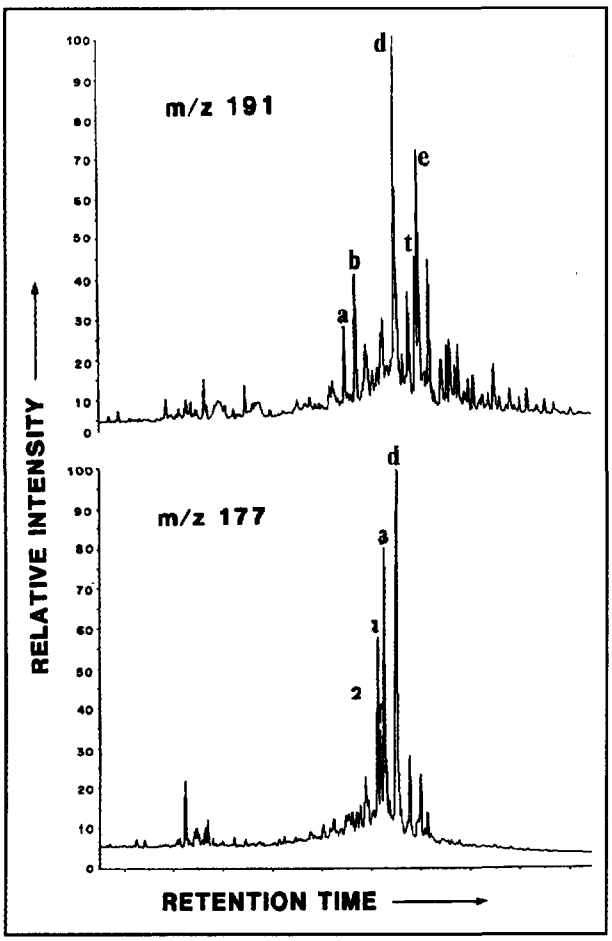


Figure 53—M/z 191 (top) and 177 mass chromatograms of triterpanes in the Koakoak oil from the Beaufort Mackenzie Delta, Canadian Arctic. The m/z 191 chromatogram shows a dominance of the C_{29} hopane (norhopane, peak d) over the C_{30} hopane (peak e) even though oleanane (peak t) is present. The m/z 177 chromatogram shows the presence of three 23,28-bisnorlupanes (peaks 1, 2, and 3), which elute prior to the C_{29} hopane. Identities of other peaks are given in Table 3. From Brooks (1986); reprinted with permission of Pergamon Press PLC.

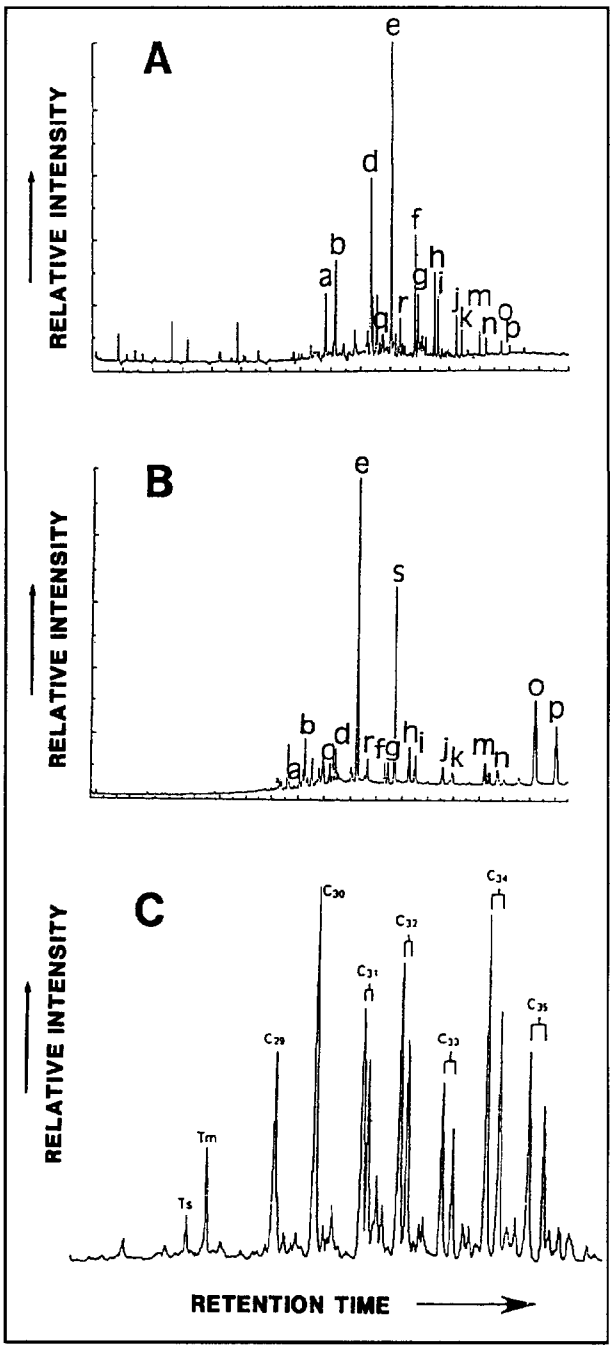


Figure 54—M/z 191 (triterpane) mass chromatograms showing variations in distributions of 17α(H)-extended hopanes (C_{31}-C_{35}). The profile in (A) is the most common type, with a gradual decrease in peak height from C_{31} to C_{35}. The fragmentogram in (B), from an organic-rich marine carbonate, shows an anomalously large concentration of the C_{35} species, while that in (C) (from Palacas et al., 1984) shows high concentrations of C_{32} and C_{34} 17α(H)-extended hopanes in another carbonate. Identities of peaks are given in Table 3. From Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology*.

oils from Seram, Indonesia, were probably related to source rather than to maturity.

Robinson (1987) noted trends of Tm/Ts values in Indonesian oils from high in terrestrial (fluvio-deltaic) oils, to medium in marine oils, to low in lacustrine oils. However, the relationship between Tm/Ts ratios and lithology is not yet clear. Moldowan et al. (1986) suggested as an alternative explanation that Tm/Ts ratios are higher in oxic sediments than in anoxic ones. Because of these uncertainties, no quantitative guides are currently available for interpreting paleoenvironments from Tm/Ts ratios.

28,30-Bisnorhopane

The C_{28} 17α(H)-hopane (usually called 28,30-bisnorhopane) is usually absent or present only in trace amounts (Figure 15: peak c). Occasionally, however, it is an important component (Figures 32B, 51, and 55), and may even be so abundant that it appears as a prominent peak on the gas chromatogram (Figure 56).

It is currently believed that sediments containing large amounts of the 28,30-bisnorhopane were all deposited under anoxic conditions (Katz and Elrod, 1983; Mello et al., 1988b). Bisnorhopane is nearly ubiquitous in the Kimmeridge Clay and related oils from the North Sea (e.g., Grantham et al., 1980; Cornford et al., 1983; Hughes et al., 1985; Schou et al., 1985; Dahl and Speers, 1985). Connan et al. (1986) observed it in Guatemalan evaporites. It has frequently been reported in the Monterey Formation of California and in other biogenic siliceous rocks of the circum-Pacific region (e.g., Katz and Elrod, 1983; Williams, 1984; Bazhenova and Arefiev, 1990). Curiale and Odermatt (1989) noted higher concentrations of 28,30-bisnorhopane in phosphate/carbonate facies of the Monterey Formation than in siliceous (diatomaceous) ones. Katz and Elrod (1983) and Williams (1984) proposed that 28,30-bisnorhopane is associated with bacterial mats.

Murchison (1987), on the other hand, suggests that 28,30-bisnorhopane is common in oil with terrestrial affinities. However, there is no evidence that it actually originates in land plants (Philp, 1985).

Many other anoxic sediments do not contain any 28,30-bisnorhopane. Since there is no evidence for an origin in algae or higher plants, its occurrence is probably dependent upon a peculiar bacterial population (perhaps one present in bacterial or algal mats) whose environment we do not yet fully understand. Its higher relative concentration in immature sediments than in crude oils and the decrease in its concentration relative to hopane (e.g., Cornford et al., 1983; Moldowan and Seifert, 1984; Schou et al., 1985) indicate either that it is destroyed easily by thermal reactions (Moldowan et al., 1985), or that its concentration is diluted by preferential generation of other triterpanes.

Tannenbaum et al. (1986b) found 28,30-bisnorhopane in extracts but not in kerogen pyrolysates from the Monterey Formation. They concluded that this compound probably was not incorporated into the kerogen structure, and thus its concentration would not increase with maturation.

A direct relation between 28,30-bisnorhopane and sulfur content has been reported for oils from the North Sea (Grantham et al., 1980). This observation is consistent with an origin in certain anoxic or euxinic environments. However, Hughes et al. (1985) pointed out that the relationship between 28,30-bisnorhopane and sulfur could also be due to maturity. Within a homogeneous organic facies, changes are due to maturity, since both 28,30-bisnorhopane and sulfur contents decrease with increasing maturity, but at different rates. In a nonhomogeneous sample set, however, the facies differences may dominate over the maturity differences.

25,28,30-Trisnorhopane

25,28,30-Trisnorhopane has been detected in many of the same samples as bisnorhopane (Bjorøy and Rullkötter, 1980; Katz and Elrod, 1983; Noble et al., 1985; Mello et al., 1988a, b). Because this compound lacks the C-25 methyl group, it is detected using the m/z 177 mass chromatogram (Figure 57: peak y). It probably indicates anoxic depositional conditions similar to those favoring its cousin, 28,30-bisnorhopane. Like 28,30-bisnorhopane, 25,28,30-trisnorhopane and other 25-nortriterpanes enter the sediments directly as hydrocarbons during diagenesis, and are not cleaved from kerogen during thermal maturation (Noble et al., 1985).

Moretanes

The origin of the moretanes has not been extensively studied, and they generally are little used in organic-facies interpretations. However, it has been suggested that they are more abundant in organic material of terrestrial origin (Connan et al., 1986; Mann et al., 1987), and are present in low amounts in carbonates (Rullkötter et al., 1984; Connan et al., 1986). It is not known whether they come from terrestrial plants or from microorganisms associated with those particular depositional environments.

Gammacerane

Gammacerane (structure shown in Figure 15; occurrence in Figure 54B as peak s) was originally reported in lacustrine sediments. High gammacerane

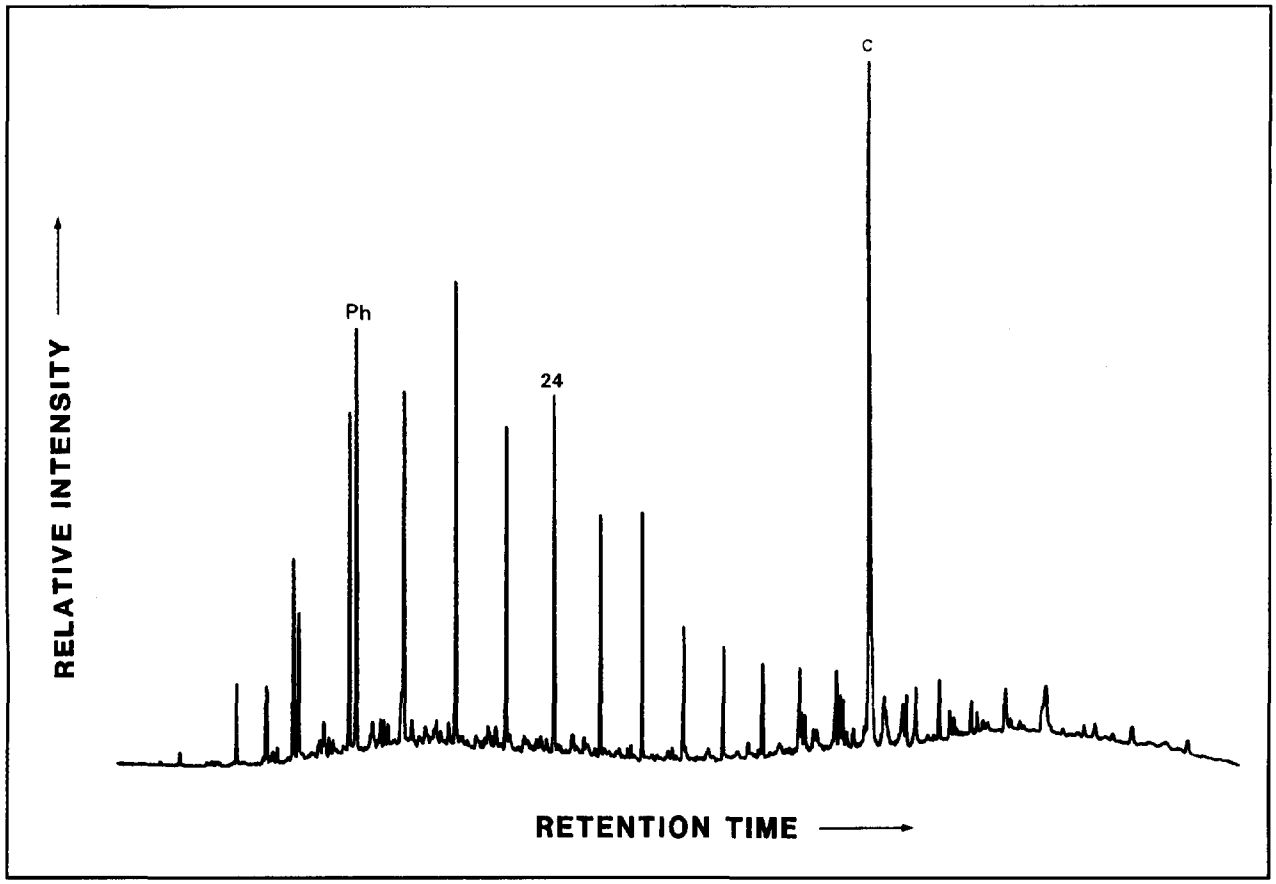


Figure 55—M/z 191 (triterpane) mass chromatogram of an oil containing a large amount of 28,30-bisnorhopane (peak c). The apparently anomalous abundance of the 22R epimer of the C_{31} extended hopane (peak g) in this case may be due to coelution of that compound with gammacerane. The precise position at which gammacerane appears on gc/ms traces (relative to the C_{31} extended hopanes) varies depending on the nature of the chromatographic column. Identities of other peaks are given in Table 3. From Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology.*

concentrations were therefore originally considered to be markers for lacustrine facies (e.g., Poole and Claypool, 1984). However, gammacerane can also occur in major or minor amounts in many rocks that are definitely not of lacustrine origin. Carbonates of the Gulf of Suez and evaporites in the Brazilian Atlantic-margin basins are examples of marine rocks in which gammacerane can be a dominant component (Rohrback, 1983; Mello et al., 1988b).

More recent work indicates that the lacustrine environments in which gammacerane is particularly abundant are not freshwater lakes (e.g., Fu Jiamo et al., 1986, 1988; Brassell et al., 1988). Mann et al. (1987) reported an inverse correlation between gammacerane content and pristane/phytane ratio, suggesting that its abundance might depend on unusual oxygen levels or salinities (ten Haven et al., 1987). It now appears that gammacerane is a marker for unusual salinities, and that the lakes from which it was first reported were not truly freshwater lakes.

Gammacerane is believed to be derived from tetrahymanol, a triterpenoid found ubiquitously in recent sediments (Venkatesan, 1989; ten Haven et al., 1989). Tetrahymanol occurs in protozoa of the genus *Tetrahymena*, although other sources cannot yet be excluded. An origin for gammacerane in primitive organisms is supported both by its ubiquitous presence in Phanerozoic samples, and by its occurrence in late Proterozoic rocks (Summons et al., 1988).

Oleananes

Various oleananes (Figure 15) have been reported in extracts of shales and coals from deltaic sequences, and in oils from deltaic sediments, particularly from Nigeria and from Southeast Asia (e.g., Grantham et al., 1983; Hoffmann et al., 1984; Thompson et al., 1985; Riva et al., 1986; Talukdar et al., 1986; Grantham,

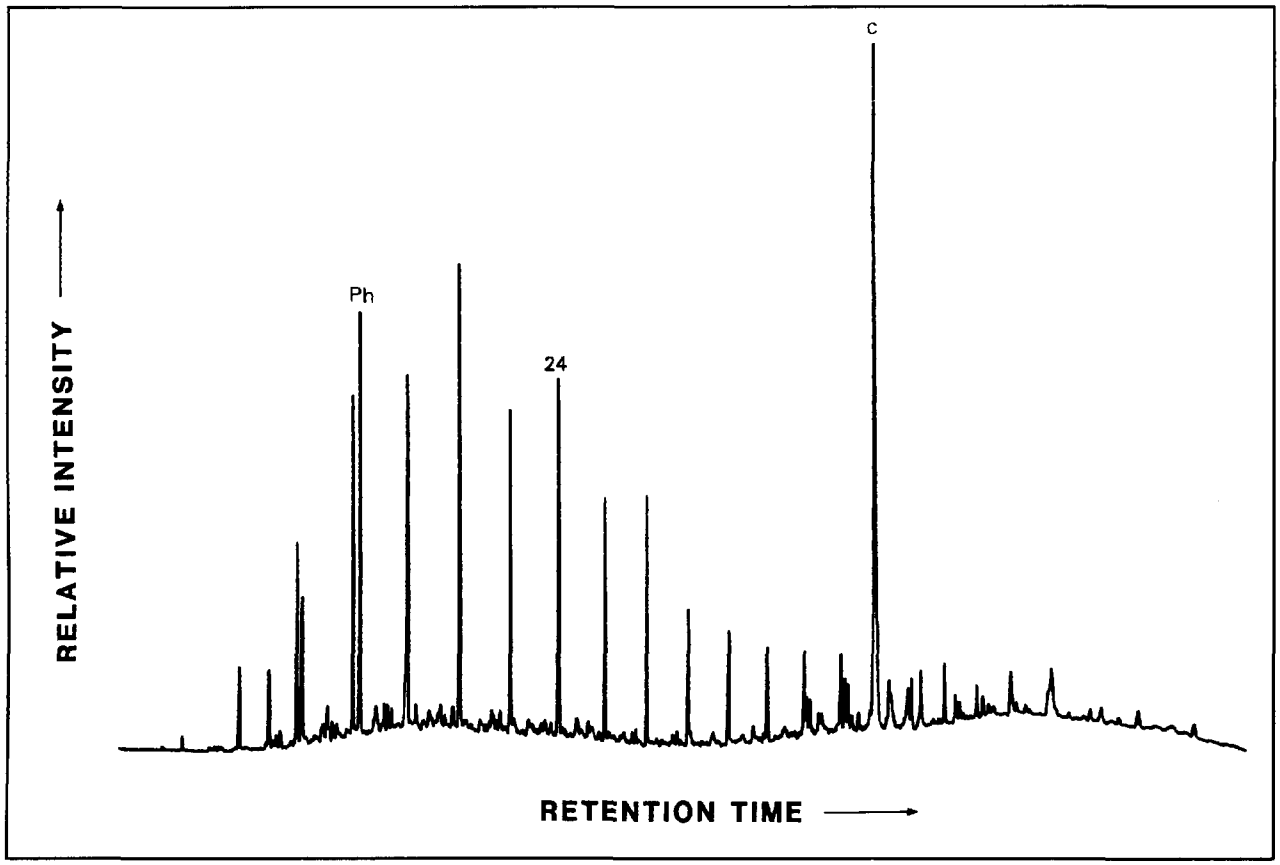


Figure 56—Gas chromatogram of a Monterey oil (Miocene of southern California) showing an extremely large amount of 28,30-bisnorhopane (c). Ph = phytane, 24 = n-C_{24}.

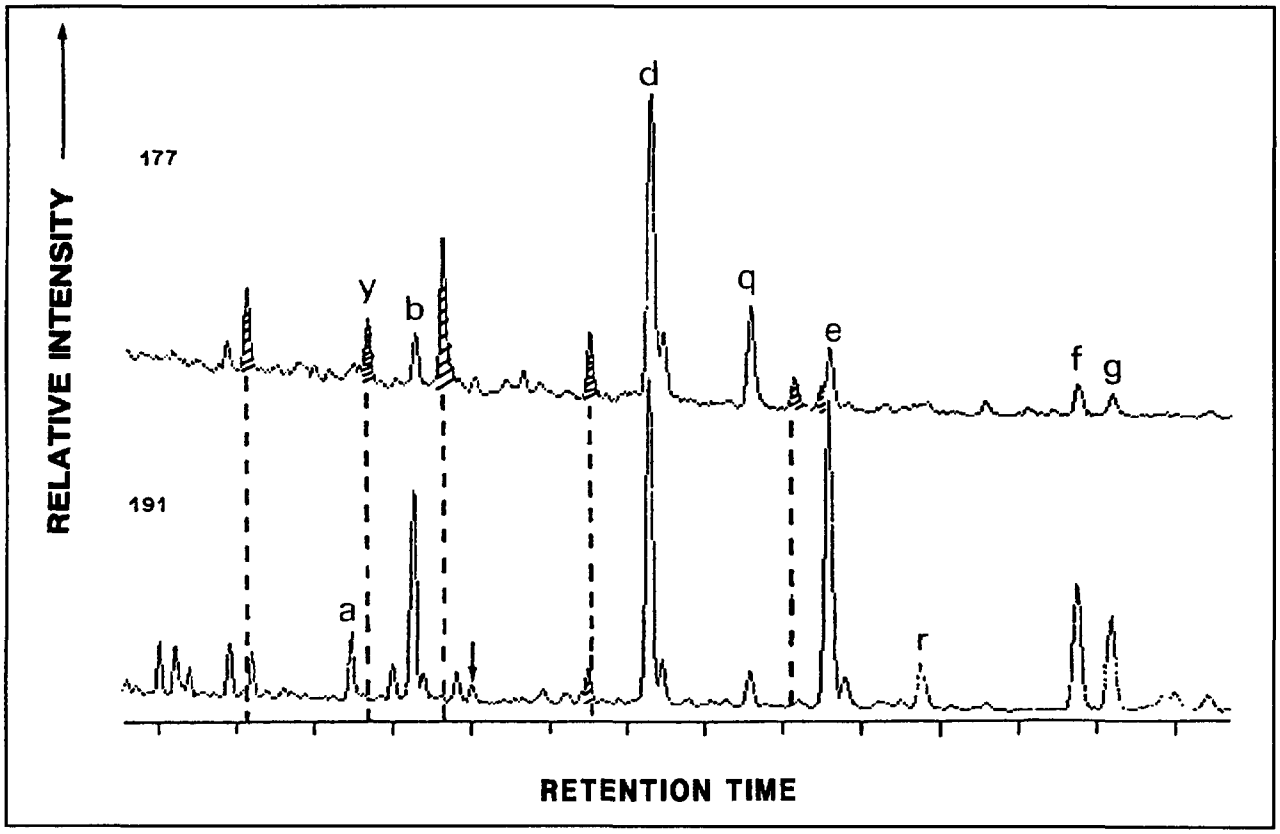


Figure 57—M/z 177 and 191 (triterpane) mass chromatograms for a sample containing 25,28,30-trisnorhopane (peak y). It appears in the m/z 177 chromatogram (top) but not in the m/z 191. Identities of selected peaks are given in Table 3. From Noble et al. (1985); reprinted with permission of Pergamon Press PLC.

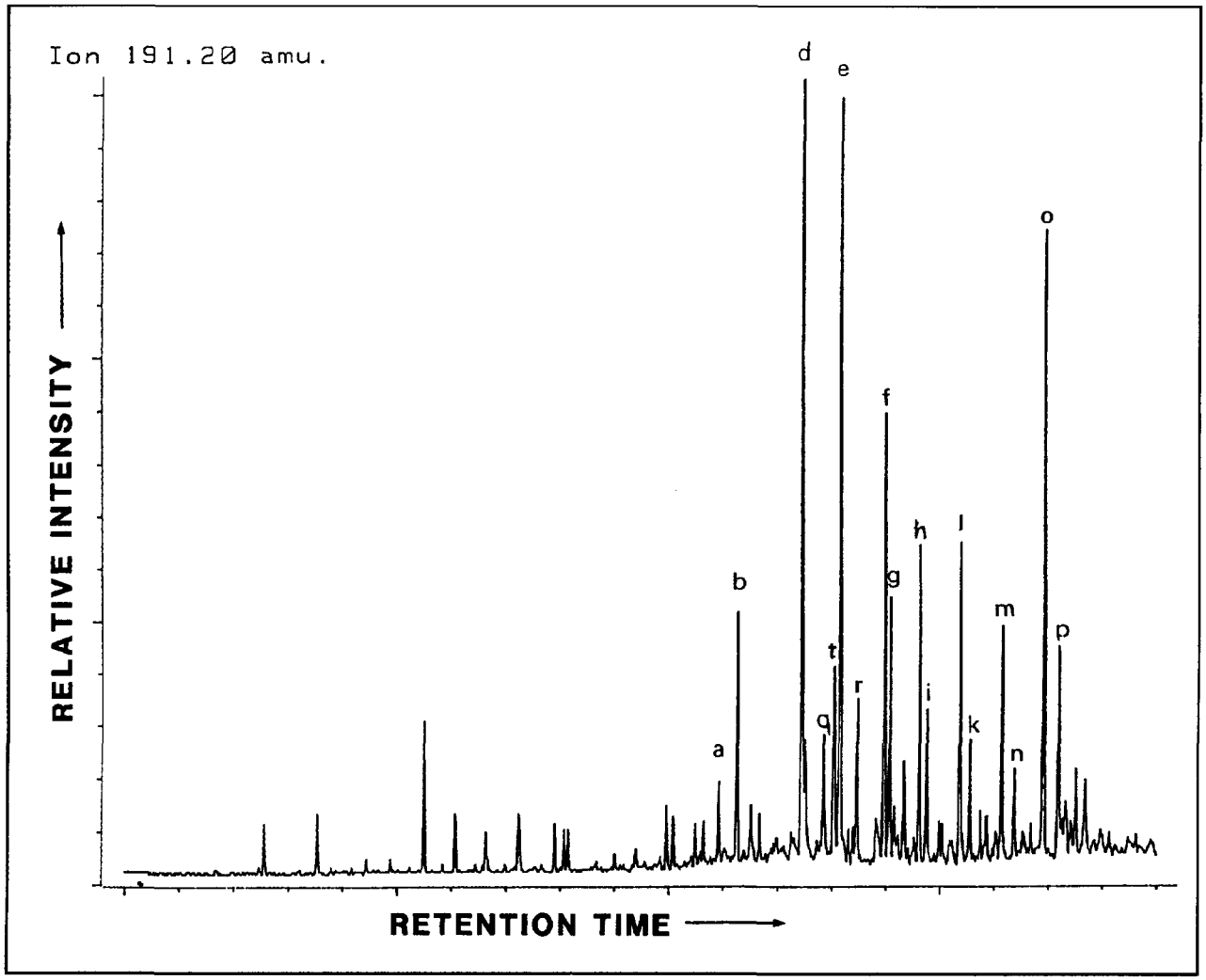


Figure 58—M/z 191 (triterpane) mass chromatogram of an extract from the Nishikurosawa Formation (middle Miocene) of the Akita basin, Japan. Note the presence of oleanane (peak t), together with evidence of a carbonate environment (high C_{29} hopane [peak d] and high C_{35} homohopanes [peaks o and p]).

1986b; Robinson, 1987; Ekweozor and Udo, 1988; Czochanska et al., 1988). Other studies have found oleananes in lake beds (Mann et al., 1987) or in marine shales in Indonesia (Phoa and Samuel, 1986). All reported occurrences are in sediments of Tertiary or Late Cretaceous age.

Oleananes are thought to be derived from a variety of terrestrial precursors, especially angiosperms that produce abundant resin (Ekweozor and Udo, 1988; Riva et al., 1988). Their presence in marine environments probably represents in most cases transport from terrestrial sources.

Because angiosperms are believed to have evolved in Late Cretaceous time, the absence of oleananes in Lower Cretaceous and older sediments is understandable (e.g., Bagge et al., in press). However, oleananes are also absent from many terrestrially influenced sediments and oils of Tertiary age, perhaps because their precursors only occur in certain families of terrestrial plants. Thompson et al. (1985) showed that coals and oils sourced from coals in the Kutai basin of Indonesia both contain abundant oleanane, whereas it is absent in oils sourced from the shales of similar age and environment. Oleanane is more abundant in mangrove shales of Indonesia than in associated coals (Brown, 1989).

However, 18α(H)-oleanane has been found in abundance in an evaporitic lake bed (where input from terrestrial plants might be expected to be minor) from the Renqiu oil field of China (Brassell et al., 1988). Oleanane is also rather common in samples from the Miocene-age Monterey Formation in California, which is generally of pelagic origin (J.D. King, personal communication, 1988) and in other similar

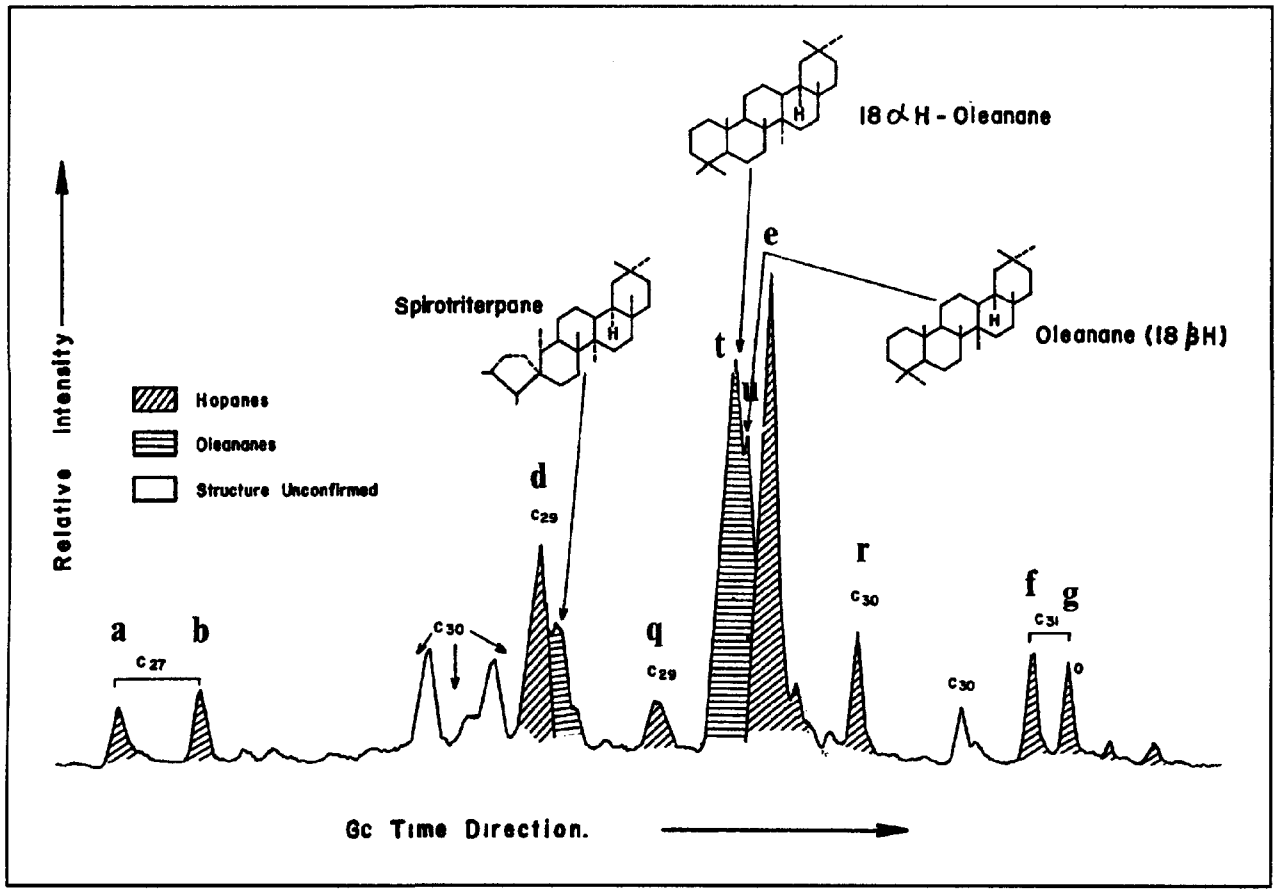


Figure 59—Part of the m/z 191 (triterpane) mass chromatogram of a crude oil from the Niger Delta, showing the elution positions of three members of the oleanane family with respect to the C_{29} and C_{30} hopanes. Peak identities are given in Table 3. From Ekweozor and Udo (1988); reprinted with permission of Pergamon Press PLC.

facies (e.g., Figures 34 and 58: peak t)). None of these rocks show other strong sedimentological or geochemical evidence for terrestrial input. It therefore seems possible that there could also be an aquatic origin for oleanane, perhaps from some type of microorganism or phytoplankton.

The two dominant oleananes, 18α(H) and 18β(H), elute as a single peak (peak t) or a poorly separated pair of peaks immediately before the C_{30} hopane (Figure 59). When abundant, oleananes can often be among the most dominant triterpanes.

Compound X

An unidentified but common triterpane eluting after the C_{29} norhopane (compound X in Figure 60), suggested by Philp and Gilbert (1986) to have a C_{30} pentacyclic structure, has been observed in many samples that bear a strong terrestrial imprint (Philp and Gilbert, 1986; Bagge et al., in press; Taher et al., in press). Further work is required to verify that this compound is indeed a useful marker of terrestrial input (Philp and Gilbert [1986] have also suggested that it may have a bacterial source), to determine its structure, to identify its precursors, and to determine how strongly it is affected by maturity.

The relative proportion of compound X in a sample probably depends strongly on maturity (Bagge et al., in press). Figure 61 shows three oils from the Cooper/Eromanga basin of Australia. Compound X is present in at least two of them, ranging from dominant in the Karmona oil (A) to minor in the Merrimelia oil (B).

Although no direct information about the maturities of these oils is available, we have two indirect ways of estimating their relative maturities. The first way is to use the Tm/Ts ratio (peak b/peak a), although a close genetic relationship among the three oils has not been established. The decrease in Tm/Ts from (A) to (C) suggests that the oil in (A) is the most mature, followed by the oil in (B) and then the oil in (C) (Jackson) oil.

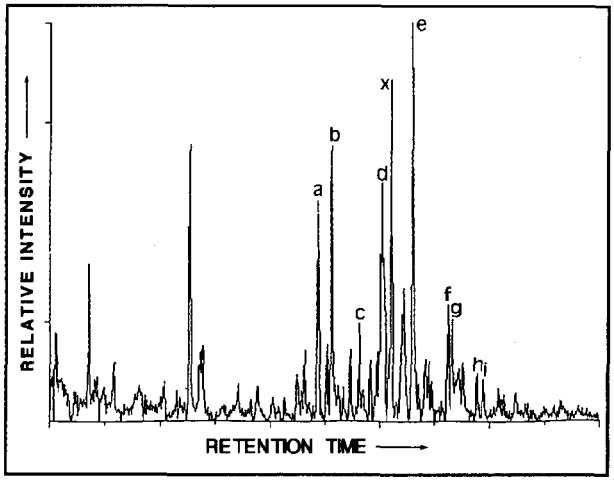


Figure 60—M/z 191 (triterpane) mass chromatogram of a coal extract from the Sydney basin, Australia, showing large amounts of compound X, identified as a C_{30} pentacyclic triterpane. Compound X has been proposed as a marker for terrestrial input. Identities of other peaks are given in Table 3. From Philp and Gilbert (1986); reprinted with permission of Pergamon Press PLC.

A second way of estimating maturity is to use the hopane concentrations as a maturity indicator, because hopanes are known to be sensitive to thermal destruction. However, information on absolute concentrations is not available, because in each case the tallest peak is simply normalized to 100%. Nevertheless, the noisy baseline in the Karmona oil chromatogram suggests that it was run at higher sensitivity, and thus that the absolute amount of triterpanes in that sample is low. The mass chromatogram of the Merrimelia oil is much less noisy, while the chromatogram for the Jackson oil has a very smooth baseline, suggesting the highest concentration of triterpanes. Compound X is most dominant when absolute concentrations are lowest (Karmona), and is present as at most a trace component when the hopanes are most abundant (Jackson). The change in relative abundance of compound X in the three oils could therefore be due to its greater thermal stability. Until details of the effect of maturity on concentrations of compound X are available, compound X should not be used as a quantitative indicator of anything.

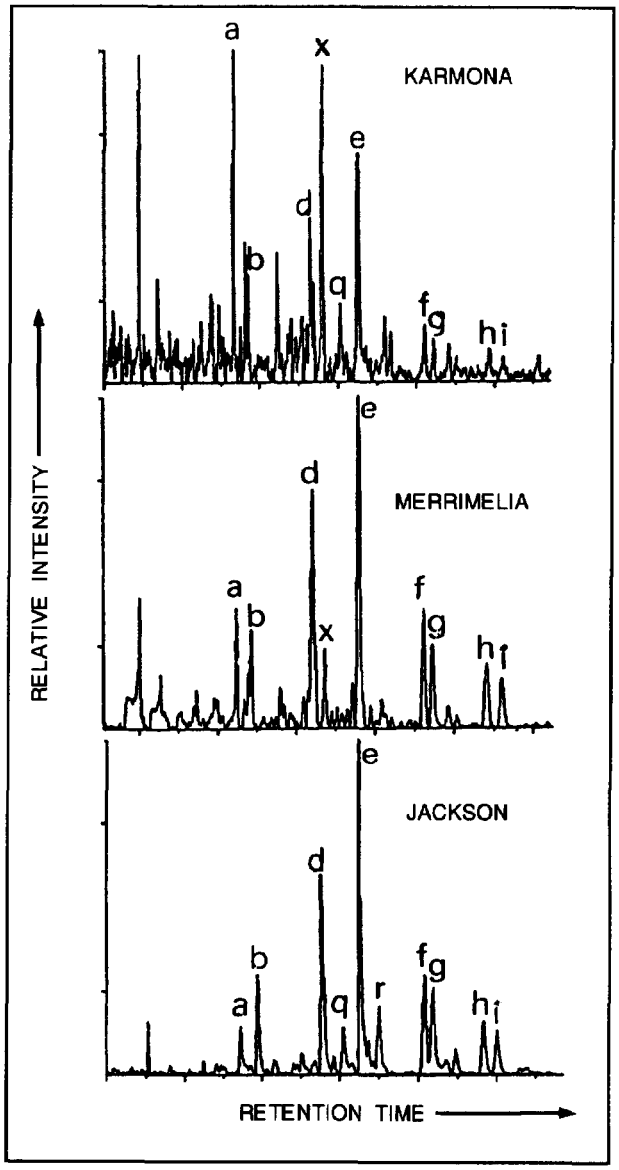


Figure 61—M/z 191 (triterpane) mass chromatograms of three oils from the Cooper/Eromanga basin, Australia, showing the presence of compound X. The highest relative concentration occurs in the oil that apparently has the lowest concentration of other triterpanes (Karmona). See text for further discussion. From Philp and Gilbert (1986); reprinted with permission of Pergamon Press PLC.

Lupanes

23,28-Bisnorlupanes, pentacyclic triterpanes with a nonhopanoid structure (see Figure 2 for a lupane structure in which the A ring has been opened), have been reported a few times from sediments and oils of Tertiary age (e.g., Rullkötter et al., 1982; Brooks, 1986; Freeman et al., 1990). The probable parent structure, lupane, is believed to originate in terrestrial plants (possibly in sapotaceous trees, which are angiosperms: Murchison, 1987) and has been reported from brown coals (Petrov et al., 1985; Wang and Simoneit, 1990). We do not know the mechanism for demethylation, nor do we know whether it occurs in the source organisms themselves or in sediments.

Bisnorlupanes are best analyzed using the m/z 177 fragment ion, since they are missing one methyl group from the A ring. They elute as a series of compounds before the C_{29} hopane (Figure 53, bottom).

Bicadinanes

In 1983, Grantham et al. reported a series of three unidentified compounds that they called compounds R,T, and W in oils from Southeast Asia. These compounds have since been identified as bicadinanes, which are technically pentacyclic triterpanes since they have five rings and a skeleton composed of three terpene units. However, the structures of bicadinanes (Figure 62) are quite distinct from those of any of the other triterpanes discussed here (Cox et al., 1986).

It has since been proposed that bicadinanes are formed within sediments by cyclization of precursors found only in dammar resin (van Aarssen et al., 1990). Dammar resin is obtained from trees of the *Dipterocarpaceae* family, angiosperms which are abundant in parts of Southeast Asia today (Alam and Pearson, 1990). Their ancient distribution may have been similar. Earliest occurrences, like those of oleananes, are limited by the evolution of angiosperms in general and *Dipterocarpaceae* in particular.

In a study of oils from Bangladesh, bicadinanes were found to be abundant in oils bearing other typical signatures of strong terrestrial influence, such as high wax content and high concentrations of oleananes (Alam and Pearson, 1990). However, the lack of covariance between oleanane and bicadinane concentrations indicated that the source materials for oleananes and bicadinanes were different.

In spite of their distinctive structures, bicadinanes still give a dominant m/z 191 peak like that of other pentacyclic triterpanes. However, the m/z 95 peak, which is actually larger, was found to be more useful for quantification (Alam and Pearson, 1990). Bicadinanes elute prior to the hopanes (Figure 63).

Resin-derived cycloakanes

As noted previously in the sterane section of this chapter, a family of compounds believed to be cycloalkanes derived from resin has been reported in samples from Indonesia and East Malaysia (Thompson et al., 1985; Robinson and Kamal, 1988; Comet et al., 1989; Jamil et al., 1990). Details of the structures of these compounds are not known. They are not steranes or triterpanes, but can easily be confused with both those classes of compounds because they give large m/z 217 and 191 peaks. However, they can be readily distinguished from triterpanes because they also give major peaks in the m/z 259 and 163 mass chromatograms, in addition to m/z 217 (Figure 64).

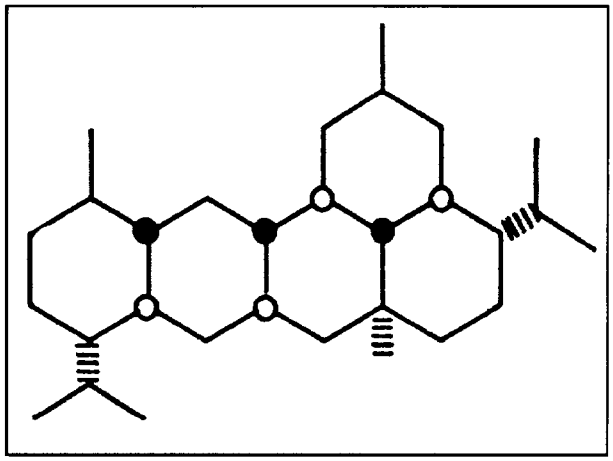


Figure 62—Structure of compound T, a bicadinane (after Cox et al., 1986).

They are in fact the only compounds known to give major peaks in both m/z 217 and m/z 191. Comet et al. (1989) have suggested that some of these compounds may be bicadinanes, although other structures are probably also represented.

These cycloalkanes were found to be present only in coals and coal-derived oils; they were absent in noncoaly samples from the same areas (Thompson et al., 1985; Robinson and Kamal, 1988). They have been documented in sediments and oils of Miocene (Thompson et al., 1985; Jamil et al., 1990), and pre-Miocene age (Robinson and Kamal, 1988). Because resins of Tertiary and Late Cretaceous age are known from a variety of locations in Southeast Asia, Australia, and New Zealand, it is likely that these cycloalkanes will eventually be reported from a much larger area and longer stratigraphic range than is presently known.

Hexacyclic hopanoids

A series of four hexacyclic hopanoid triterpanes has been reported from a number of oils and source rocks, all of which represented anoxic evaporitic facies containing sulfur-rich kerogens (Connan and Dessort, 1987). These compounds appear as modest peaks between the extended hopanes in the m/z 191 mass chromatograms (Figure 65). More conclusive identifications can be obtained using SMIM.

Tetracyclic terpanes

The C_{24} tetracyclic terpane (Figure 66) has been found in abundance in oils and extracts from a number of evaporitic and carbonate sequences (Aquino Neto et al., 1983; Palacas et al., 1984; Connan et al., 1986; Connan and Dessort, 1987; Mann et al., 1987;

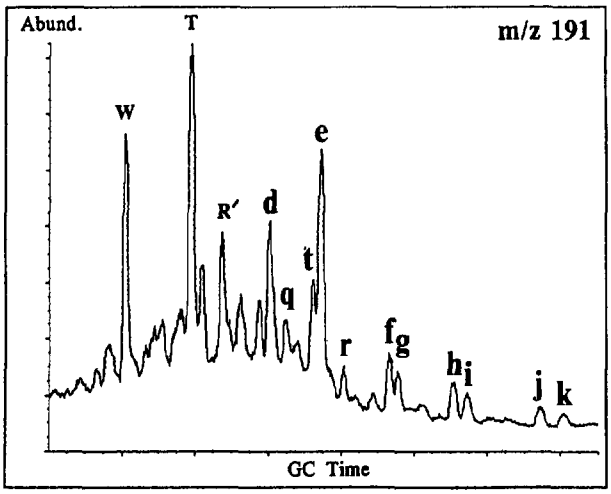


Figure 63—M/z 191 mass chromatogram showing elution of three bicadinanes (compounds R, T, and W) compared with other triterpanes, which are identified in Table 3. From Alam and Pearson (1990); reprinted with permission of Pergamon Press PLC.

Clark and Philp, 1989; Jones and Philp, 1990). In those examples it is probably of microbial origin.

However, Wielens et al. (1990) noted an abundance of the C_{24} tetracyclic in a Cambrian-age alginite (similar to kukersite) derived from *Gloeocapsamorpha prisca* or its evolutionary ancestor, and in a bitumen thought to have been sourced from the alginite. Philp and Gilbert (1986) found the C_{24} tetracyclic in Australian oils that were believed to be sourced mainly from terrestrial organic matter.

Thus it is not clear whether there is a single origin for this compound, or two or more unrelated sources. Although found in association with alginites or terrestrial organic matter, the C_{24} tetracyclic could still be of microbial origin. No data have been reported on its thermal stability, although its abundance does not appear to be related to selective preservation during maturation.

The C_{25} to C_{27} tetracyclic terpanes have also been reported in carbonates and evaporites (Aquino Neto et al; 1983; Connan et al., 1986). They do not appear to be present in abundance in other types of sediments.

Tricyclic triterpanes

Tricyclic triterpanes, which may come from different species of bacteria than the pentacyclics, have not been examined in as much detail as the pentacyclics. They are usually present in much lower concentrations than the pentacyclics are (Figures 32 and 54 to the left of peak a, for example), but they may occasionally be present in large (Figure 67B and 67C) or even dominant (Figure 67A) amounts.

Few data are available linking the rare, high concentrations of tricyclics to specific paleoenvironments. Samples rich in *Tasmanites* contain large amounts of tricyclics and only minor amounts of pentacyclics (Simoneit et al., 1986; Aquino Neto et al., 1989). The high tricyclic/pentacyclic ratios reported in lacustrine black shales of Early Jurassic age in the eastern United States (Kruge et al., 1990) could come from such a source, although those authors suggested that the lake environment itself, which was alkaline and nonhypersaline, might be responsible. Tricyclics have been reported as absent or present in reduced quantities in the nonmarine oils (fluvio-deltaic and lacustrine) of Indonesia (Robinson, 1987).

The C_{23} tricyclic is always dominant (Aquino Neto et al., 1983), although it may be less dominant in terrestrial samples (Aquino Neto et al., 1983; Price et al., 1987). It has been noted that the tricyclics with 26 or more carbon atoms are scarce in carbonates, but in other environments these tricyclics are approximately equal in abundance to the C_{19}–C_{25} homologs (Aquino Neto et al., 1983; Zumberge, 1984; Price et al., 1987). Kruge et al. (1990) found homologs out to at least C_{41}, and observed that the C_{22}, C_{27}, C_{32}, and C_{42} species were missing. They also noted that those with more than 25 carbon atoms exist as the R and S epimers.

Tricyclics appear to be more stable thermally than pentacyclics are. Thus, with increasing maturity the ratio of tricyclics to pentacyclics can be expected to rise, and as the pentacyclics near total destruction in a highly-mature sample, the sample may come to be dominated by tricyclics. In such cases, it is important to look at absolute concentrations as well as tricyclic/pentacyclic ratios in an effort to separate maturity effects from facies effects. For example, if maturity effects are dominant, oils with higher tricyclic/pentacyclic ratios should show lower concentrations of both tricyclics and pentacyclics than the oils do that have lower tricyclic/pentacyclic ratios. If facies effects are dominant, concentrations and ratios may show different trends.

TRITERPANE/STERANE RATIOS

Both the absolute and relative amounts of steranes and triterpanes vary greatly from sample to sample. Absolute concentrations are strongly affected by both source and maturity, whereas the ratios of triterpanes to steranes depend primarily on facies. However, because the relationship between organic facies and triterpane/sterane ratio is complex, this ratio is not used widely or with a high degree of confidence today in interpretations. Furthermore, there is no uniformity about which compounds in each class are included in calculating the triterpane/sterane ratio.

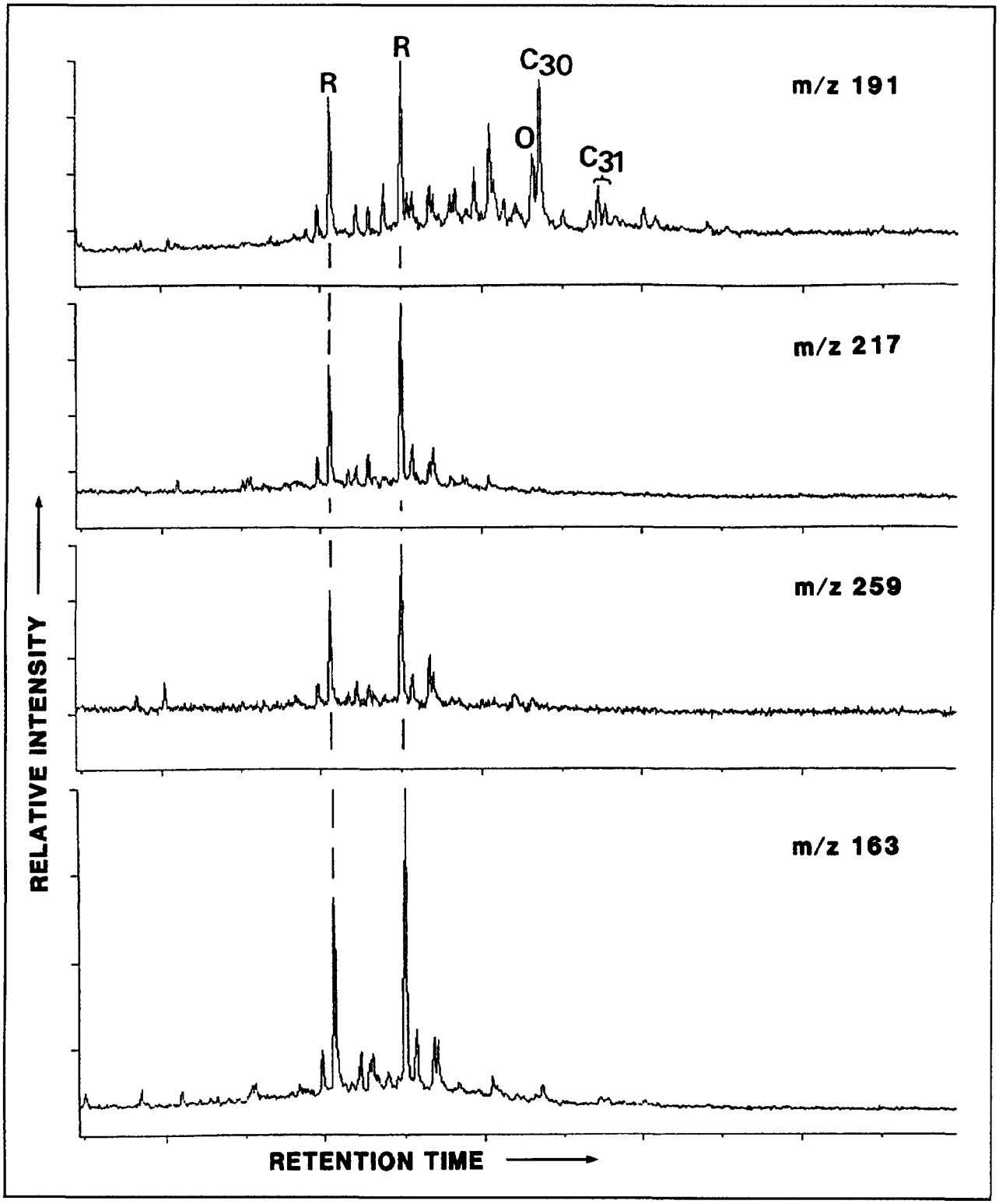


Figure 64—M/z 191, 217, 259, and 163 mass chromatograms of saturated hydrocarbons from an Indonesian oil. Compounds marked "R" are believed to be cycloalkanes derived from resin. They give strong peaks in all four mass chromatograms. Steranes are present in very low concentration in this sample. Compound "O" is oleanane; also shown are the C_{30} and C_{31} hopanes. From Thompson et al., 1985; reprinted with permission of Graham and Trotman.

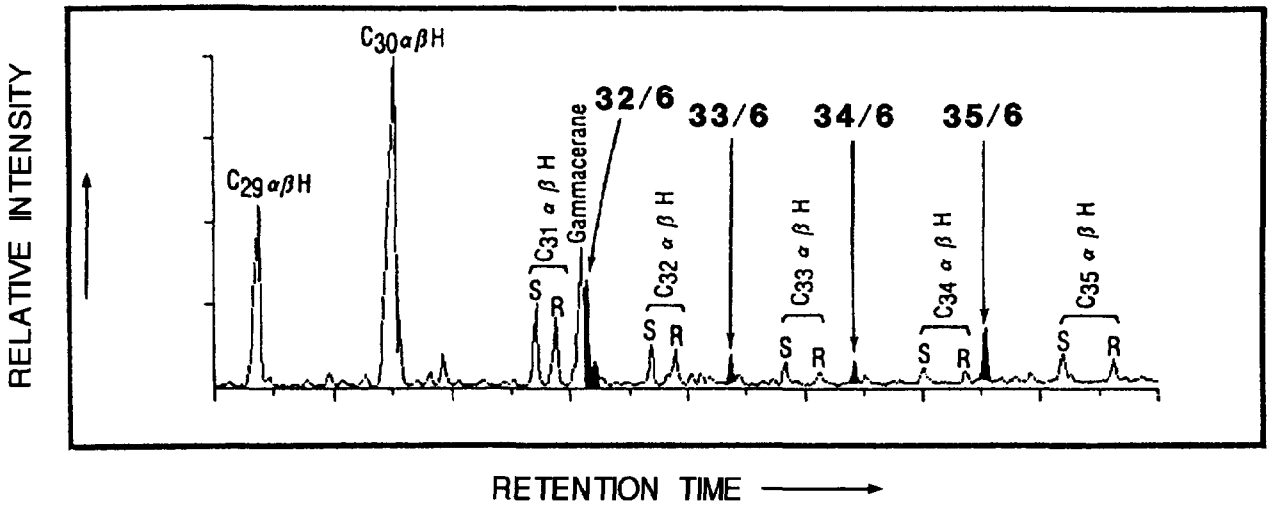


Figure 65—Part of the m/z 191 (triterpane) mass chromatogram of an oil, showing the occurrence of four hexacyclic triterpanes (labelled 32/6, 33/6, 34/6, and 35/6) whose structures are related to the hopane structure. Other compounds are the C_{29} to C_{35} hopanes and extended hopanes. From Connan and Dessort (1987); reprinted with permission of Pergamon Press PLC.

Our general ideas about triterpane/sterane ratios come from the belief that steranes come mainly from algae and higher plants, whereas triterpanes come mainly from bacteria. When absolute concentrations of biomarkers are high, high triterpane/sterane ratios (>20) have been taken to indicate a very high degree of microbial input (Connan et al., 1986). Where absolute biomarker concentrations are low, however, microbial contribution is considered to be small, and high triterpane/sterane ratios are taken to indicate greater contribution from land plants than from algae (Mann et al., 1987; Robinson, 1987; Bagge et al., in press).

In contrast, low triterpane/sterane ratios (often <10), together with high absolute biomarker concentrations, are associated with coals, shales, and oils, particularly in Southeast Asia and New Zealand (Hoffman et al., 1984; Czochanska et al., 1988). Mackenzie et al. (1984) made the reasonable suggestion that large absolute and relative amounts of steranes are usually due to high algal productivity. Supporting this idea is the fact that steranes were found to exceed hopanes in salt-lake beds from China, where terrestrial input was low (Fu Jiamo et al., 1986). Low triterpane/sterane ratios coupled with low absolute abundances may indicate a dominance of higher-plant and fungal material (Clifton et al., 1990).

A WORD OF CAUTION

Steranes and triterpanes represent only two groups of biomarker molecules, and are fallible in spite of the fact that they represent some of petroleum geochemistry's highest technology. Other groups of biomarkers, such as n-alkanes, isoprenoids, sesquiterpanes, diterpanes, and porphyrins, also can offer valuable information on organic facies that often supports or expands upon the evidence supplied by steranes and triterpanes. A geologist should use information from all these sources, together with geological data, in making organic-facies interpretations.

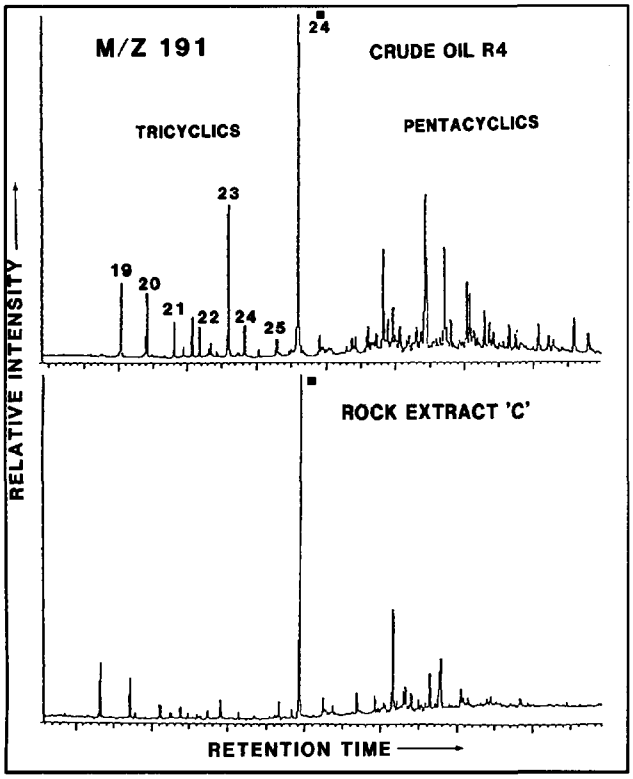


Figure 66—M/z 191 (triterpane) mass chromatogram of a crude oil and rock extract from the Black Creek basin, Alberta, Canada, showing a large abundance of the C_{24} tetracyclic terpane, marked with a solid square. See text for discussion. Numbers represent numbers of carbon atoms in the triterpanes. From Clark and Philp (1989); reprinted with permission from the *Bulletin of Canadian Petroleum Geology*.

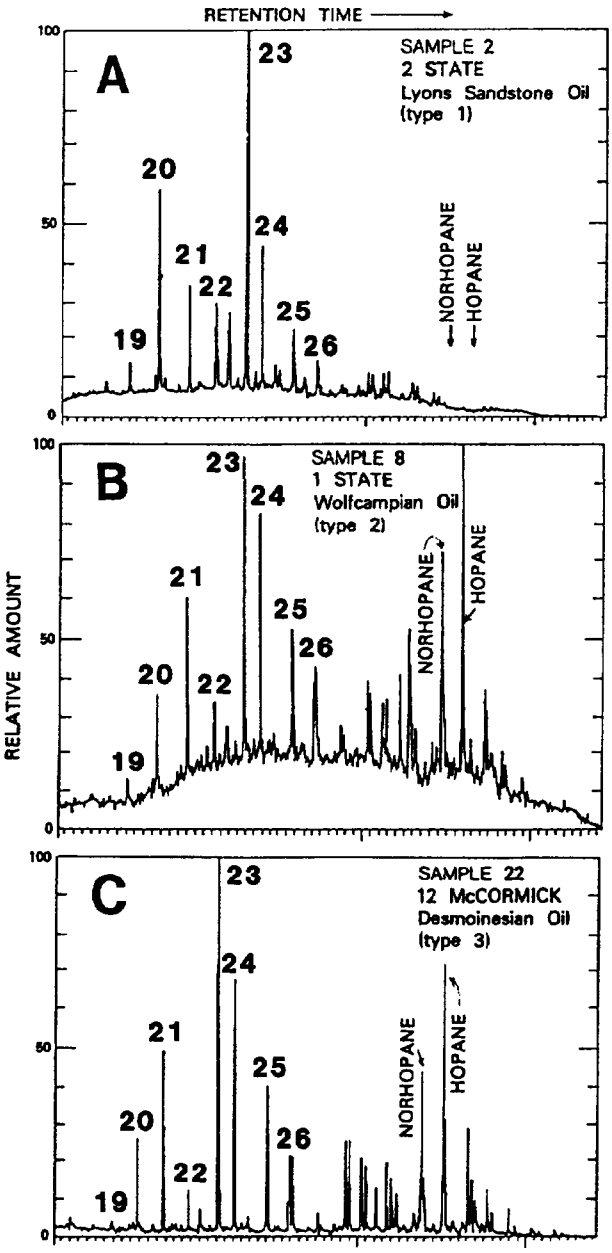


Figure 67—M/z 191 (triterpane) mass chromatograms for oils from three families in the Paleozoic of the Denver basin, U.S.A. All three oil types show large amounts of tricyclics (numbers, which represent numbers of carbon atoms per molecule), and the Lyons Sandstone oil (A), shows an almost complete dominance of tricyclics over pentacyclics. From Clayton et al. (1987).

Chapter 6

Biodegradation of Steranes and Triterpanes

Although loss of n-alkanes and isoprenoids is the most common molecular transformation that occurs as a result of bacterial attack on crude oil, it is now recognized that in certain cases steranes and triterpanes also can be affected when biodegradation is extremely severe. Biodegradation of crude oil requires molecular oxygen (O_2) and temperatures below about 80°C, with an optimum temperature around 60°C (Connan, 1984). The oxygen requirement generally means that the water in contact with the oil must be connected to the surface so that oxygen can be continually replenished through surface recharge. The temperature requirement places limits on the depths at which biodegradation can occur, although the maximum depth will vary from area to area because of differing geothermal gradients. Furthermore, biodegraded oil can be found in reservoirs whose present temperatures are above 80°C, if the biodegradation took place when the oil was at a lower temperature. It is now generally accepted that biodegradation can occur during migration as well as in the reservoir, provided that the appropriate conditions are present.

Volkman et al. (1983b) have proposed a nine-level scale for evaluating the level of biodegradation of any crude oil (Table 4). The first five levels of biodegradation are based on n-alkanes, isoprenoids, and alkylcyclohexanes, but levels 7–9 can be distinguished only by analysis of sterane and triterpane biomarkers. Prior to Level 7, steranes and triterpanes are not affected by biodegradation.

In those rare cases where biodegradation reaches Level 7, the hopanes and some of the steranes are degraded according to a reasonably predictable sequence (Table 4). The first readily observed change is a reduction in the abundance of the 20R epimer of the 14α(H),17α(H)-C_{29} sterane relative to the 20S form (McKirdy et al., 1983). This process can be recognized easily, because the 20S/(20R+20S) ratio in normal oils does not exceed about 1.2. Biodegraded crudes can have much higher values (Figure 68).

The order of ease of attack of steranes by bacteria appears to be αα-20R > αα-20S > ββ-20R = ββ-20S > diasteranes (Seifert and Moldowan, 1979; Mackenzie et al., 1983; McKirdy et al., 1983; Zhang et al., 1988). Requejo et al. (1989) showed an m/z 217 mass chromatogram of an oil in which all the regular steranes had been degraded, but in which the diasteranes had not yet disappeared. Lin et al. (1989) noted that when the regular C_{30} steranes are present, they appear to be more resistant to biodegradation than the C_{27}–C_{29} homologs are.

Goodwin et al. (1983), using laboratory cultures, have now demonstrated all or most of these biodegradation effects. Those workers also noted a slight preferential degradation of steranes with fewer numbers of carbon atoms (i.e., C_{27} regular steranes before C_{28} and C_{29}).

Samples from weathered oil seeps (Reed, 1977), asphalts and bitumens (Rullkötter and Wendisch, 1982; Robinson et al., 1986), and severely biodegraded crudes (Seifert and Moldowan, 1979; Volkman et al., 1983b; Lu et al., 1990; Peters and Moldowan, 1991) have been shown to contain a series of 25-norhopanes (regular 17α(H)-hopanes that have lost a methyl group from C-10; e.g., compound B in Figure 4). Tricyclics and tetracyclics in which the methyl at C-10 has been removed have also been reported (Jiang et al., 1990). The presence of these compounds indicates that maximum or near-maximum biodegradation (Level 8 or 9) has occurred. This series of compounds is best detected using the m/z 177 mass chromatogram (Alexander et al., 1983). Figure 69 shows the relationship between the original hopanes (top, m/z 191) for the unaltered Flinders Shoal oil and the 25-norhopanes in the heavily biodegraded Mardie oil (bottom, m/z 177). The offset in retention time in the gc-ms chromatograms is due to the ability of the smaller demethylated hopanes to move faster through the gc column than their parents can.

Several workers (e.g., Hoffman and Strausz, 1986; Brooks et al., 1988; Requejo et al., 1989; Lin et al., 1989) have noted that the 22R epimers of the homohopanes, like the 20R epimers of the regular steranes, are more easily degraded than their 22S counterparts. Disputes arise, however, about the relative ease of biodegradation of the various hopane homologs. Some details of the biodegradation sequence may depend on local reservoir conditions or bacterial populations (Peters and Moldowan, 1991). Goodwin et al. (1983) reported that the ease of biodegradation decreased from C_{35} to

Table 4. Stages of biodegradation of crude oils based on the presence or absence of certain classes of compounds. From Volkman et al. (1983b); reprinted with permission of Pergamon Press PLC.

Level of Biodegradation	Compounds Removed	Extent of Biodegradation
1	None	Undegraded
2	Short n-alkanes	Minor
3	>90% of n-alkanes	Moderate
4	Alkylcyclohexanes; isoprenoids reduced	Moderate
5	Isoprenoids	Moderate
6	Bicyclic alkanes	Extensive
7	>50% of regular steranes	Very extensive
8	Steranes; hopanes reduced; demethylated hopanes abundant	Severe
9	Demethylated hopanes predominate; diasteranes formed; steranes gone	Extreme

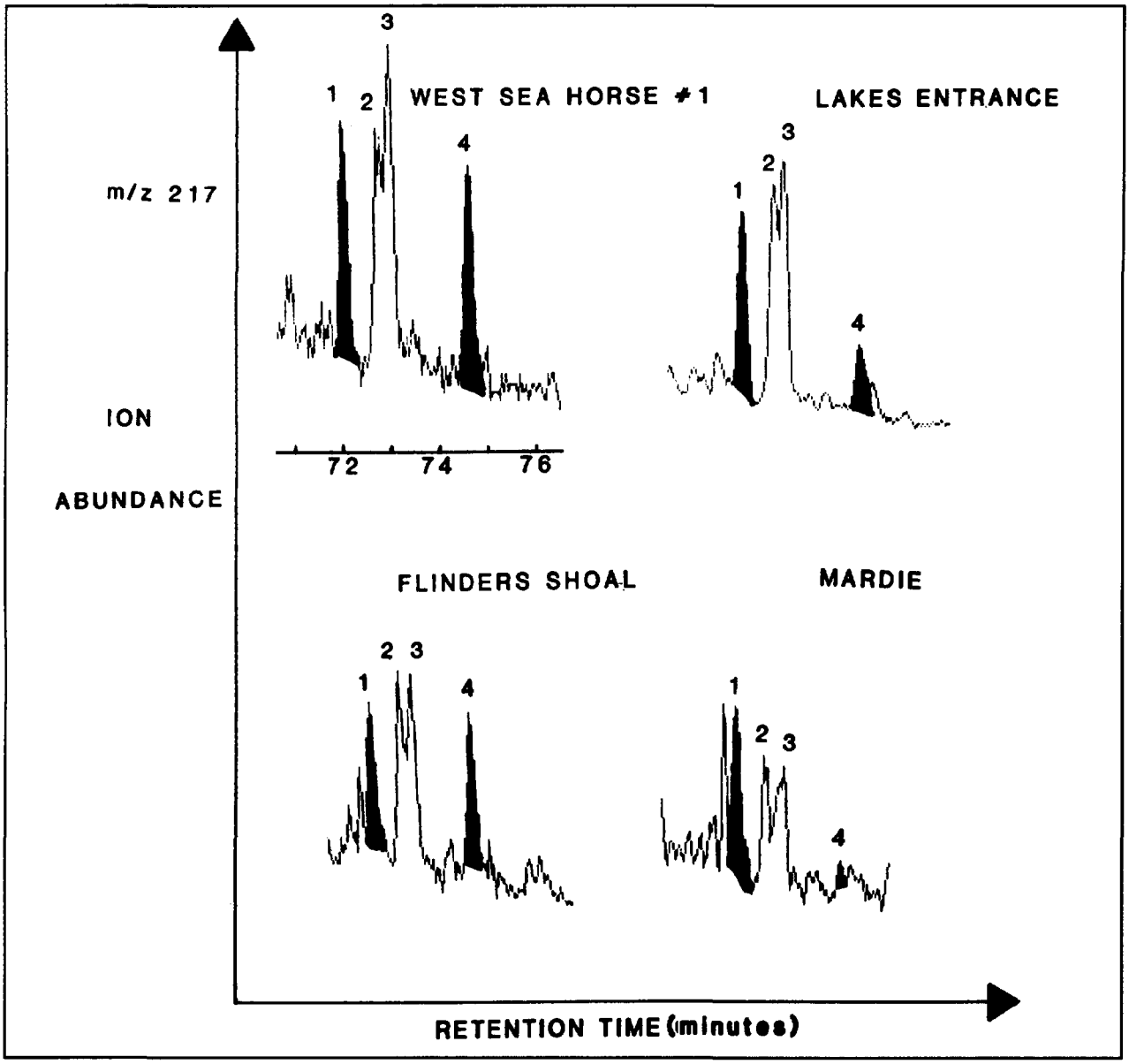


Figure 68—M/z 217 (sterane) mass chromatograms showing preferential loss of the ααα-20R epimer (peak 4) of the C_{29} regular steranes during very heavy biodegradation of crude oils. The Lakes Entrance and Mardie oil both show this phenomenon, whereas the West Sea Horse #1 and Flinders Shoal oils have not yet reached this level of extreme alteration (Level 7 in Table 4). Peak 1 is the ααα-20S; peak 2 is the αββ-20R; and peak 3 is the αββ-20S. From Alexander et al. (1983); reprinted with permission of the Australian Petroleum Exploration Association.

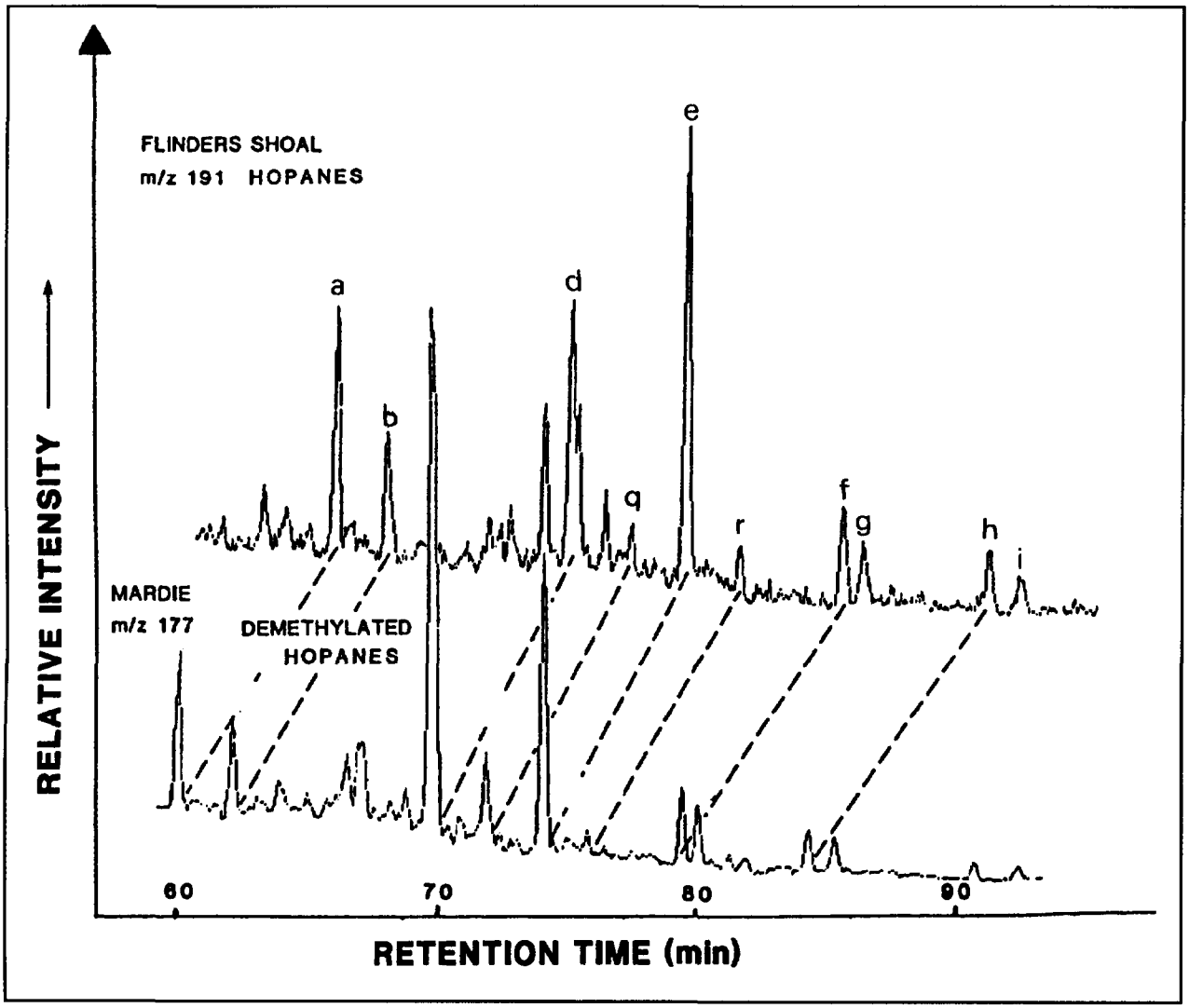


Figure 69—M/z 191 and 177 (triterpane) mass chromatograms comparing triterpanes in an extremely biodegraded oil (Mardie) with those in an unaltered oil (Flinders Shoal). The peaks in the m/z 191 mass chromatogram of the unaltered oil are mainly hopanes (see Table 3 for identifications). The dashed lines show the relationship between them and the corresponding demethylated hopanes (25-norhopanes, with one carbon atom fewer) resulting from biodegradation in the Mardie oil. The demethylated hopanes are shown as the m/z 177 mass chromatogram, because loss of the methyl group between rings A and B has decreased the size of the fragment ion. The change in ratio of the C_{29}/C_{30} hopane in the unaltered oil (about 0.7) to the altered oil (about 2.0 for the C_{28}/C_{29} demethylated hopanes) is the result of the fact that a given amount of C_{30} hopane yields twice as many m/z 191 ions as the C_{29} hopane does, whereas the C_{28} demethylated hopane yields twice as many m/z 177 ions as the C_{29} demethylated hopane does. From Alexander et al. (1983); reprinted with permission of the Australian Petroleum Exploration Association.

C_{29}. Williams et al. (1986) and Lin et al. (1989), in contrast, found that the smaller homologs were degraded faster.

Hopane alteration occurs after destruction of regular steranes, but before the diasteranes are attacked. (However, Peters and Moldowan (1991) have reported cases where homohopanes appear to have been attacked prior to regular steranes.) Tricyclic triterpanes are highly resistant, but under extreme conditions they can be attacked at about the same time as the diasteranes are altered (Connan, 1984; Lin et al., 1989). Gammacerane is thought to be the last of the steranes and triterpanes to be attacked (Zhang et al., 1988; Jiang et al., 1990). Fowler et al. (1988) reported biodegraded bitumens that had no recognizable sterane or triterpane biomarkers at all, although it is pos-

sible that some of the more resistant ones, such as gammacerane and oleanane, were never present.

The principle of sequential depletion of biomarkers in crude oils during biodegradation has been used to reconstruct the history of petroleum accumulation in reservoirs (Volkman et al., 1983b; Alexander et al., 1983; Philp, 1983; Sofer et al., 1986; Talukdar et al., 1986, 1988). In those studies, crude oils were observed to contain both a full range of n-alkanes (indicating no biodegradation) and a series of 25-norhopanes (indicating extreme biodegradation). To those authors, the best explanation in each case seemed to be that the severely degraded oil had been mixed with undegraded petroleum. Such scenarios indicate that either two distinct periods of migration were separated by a biodegradational event, or migration occurred into the reservoir along more than one pathway. However, Peter Grantham (personal communication, 1990) suggests that early biodegradation of a crude oil, followed by subsequent burial of the reservoir and then by thermal maturation, could produce crudes containing both 25-norhopanes and n-alkanes. The n-alkanes would form from cracking of NSO compounds and asphaltenes in the biodegraded oil.

Because biodegradation affects only oils, it creates no problems for analysis of source rocks. (In fact, any evidence of biodegraded material in a source-rock extract should be taken as an indicator of staining or contamination, since source rocks ordinarily do not have high enough permeabilities to allow meteoric waters to penetrate.) However, biodegradation may cause problems in maturity determination, organic-facies interpretation, and correlation. Each of these topics requires special consideration.

Biodegradation affects maturity determinations in crude oils in several ways. The effect that appears at the lowest level of sterane and triterpane biodegradation (Level 7) occurs as a result of alteration of the 20S/(20R+20S) ratio. There is no way to correct for this effect; the 20S/(20R+20S) ratios are simply worthless.

Level 8 or 9 biodegradation can also complicate maturity estimations using triterpanes, because the hopanes and moretanes are all converted to the 25-nor analogs. In principle, one might attempt to use the same ratios (Tm/Ts, 22S/(22R+22S), moretanes/hopanes, etc.) for the 25-nor series as for the undegraded oils, but no one has actually published such a study. Since nothing has been written on the fate of the oleananes during biodegradation, the utility of oleanane ratios for maturity estimation in extremely biodegraded oils is unknown. Finally, the tricyclic/pentacyclic ratio is likely to be badly distorted in heavily biodegraded oils. Thus, oils that have been biodegraded to Level 7 or higher may present some obstacles for maturity estimation using biomarkers.

Applications of biomarkers for organic-facies determinations are probably not as strongly affected by biodegradation as maturity determinations are. Where the 20R epimer has been preferentially degraded, the ratios of the ββ steranes obtained from the m/z 218 mass chromatogram (Figures 20 and 21) could be used to determine the proportions of C_{27}–C_{29} steranes. Possible preferential biodegradation of regular steranes compared with diasteranes should be considered, however.

If the hopanes have been demethylated to 25-norhopanes, the relative proportions of the members of the 25-nor homologous series should be interpretable in the same way that the hopanes and extended hopanes are. Further work on biodegradability of unusual triterpanes, such as the oleananes, is necessary in order to have full confidence in organic-facies interpetations of heavily biodegraded oils.

Correlations involving oils in which biodegradation has occurred require special consideration. These problems are discussed in the next chapter.

Finally, the reader should bear in mind that cases in which oils are biodegraded to Level 7 or beyond (i.e., where steranes and triterpanes have been affected) are not particularly common. They probably have been more strongly represented in the literature than their abundance alone would dictate because they provide interesting examples. In most biodegraded oils, the steranes and triterpanes have not been affected, and no special precautions are necessary in interpreting them.

Chapter 7

Correlations

PHILOSOPHY OF CORRELATIONS

Correlations involve the comparison of chemical and physical properties of two or more samples in order to determine whether there is a genetic relationship among the samples. If the samples are physically similar it is often quite easy to get a definite answer. However, when one attempts to correlate an oil with a rock extract, or a highly mature condensate with a normal oil, or a normal oil with a biodegraded oil, any genetic similarities can be heavily masked by chemical transformations or fractionations suffered during migration or in the reservoir. In such cases a definite answer to a correlation problem may not be possible.

In achieving a *positive correlation* we build as strong a case as possible for the similarity of the two samples. The more data we have, the stronger our case will be. The more unusual the characteristics of the samples in question, the more confident we are in any similarities that we do find. With a *negative correlation*, the problem often is simpler: we need only find one important difference, between the samples, that we cannot attribute to natural variation or transformation. For example, the lack of 28,30-bisnorhopane, 25,28,30-trisnorhopane, and C_{30} steranes in oil from the Beatrice Field (Moray Firth, U.K.) provided a definitive negative correlation between the oil and the Kimmeridge Clay as the oil's proposed source rock (Duncan and Hamilton, 1988; Peters et al., 1989). Jones and Philp (1990) present several examples of negative correlations in their study of Paleozoic oils from part of the Anadarko basin.

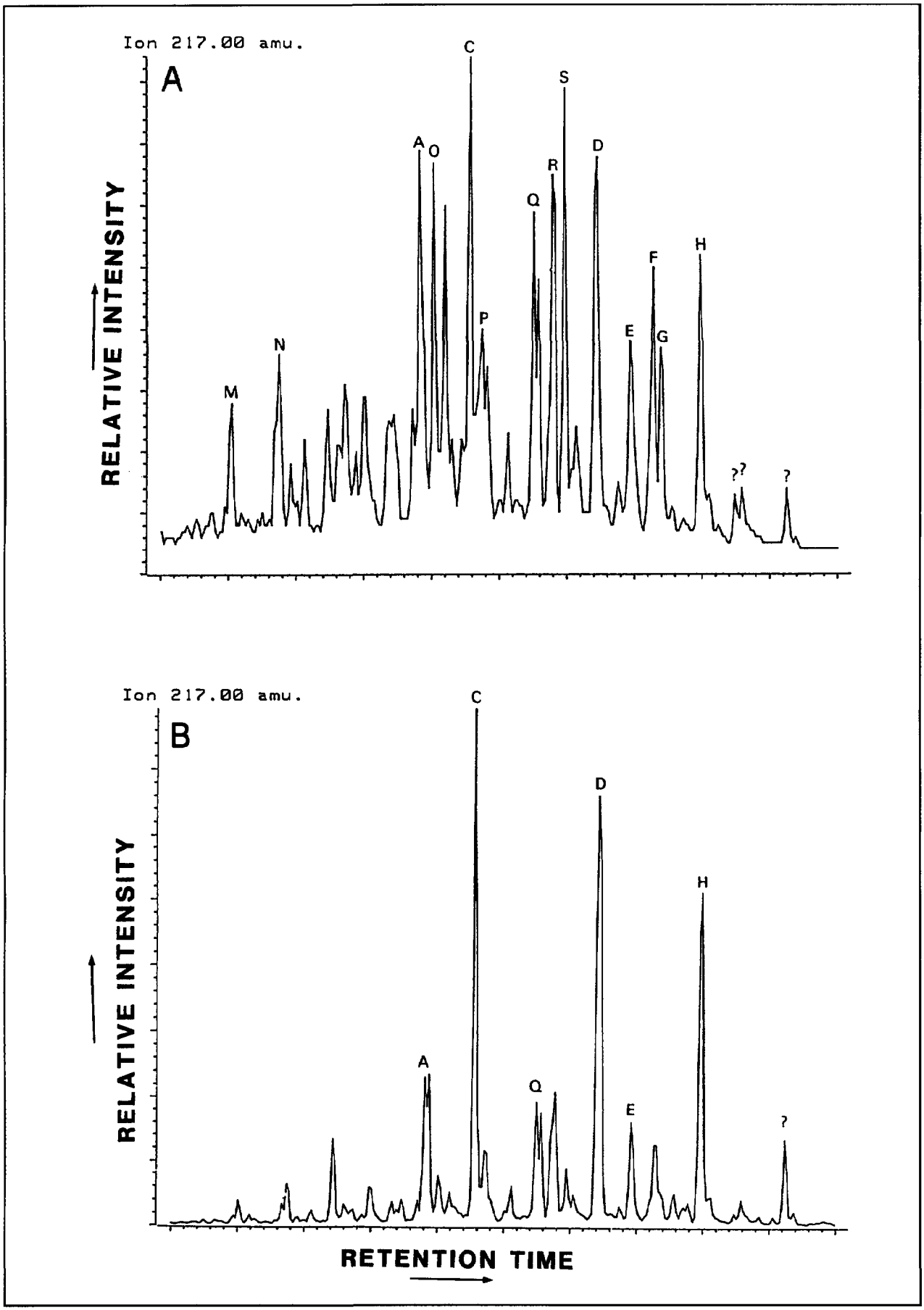
Commonly used correlation parameters include data from gas chromatograms (n-alkane distributions, pristane/phytane ratios, etc.), sulfur contents, API gravity, gross composition (e.g., percentages of saturated and aromatic hydrocarbons, nonhydrocarbons, and asphaltenes), carbon-isotope ratios, and various biomarkers (including steranes and triterpanes) obtained from gc-ms analysis. None of these parameters by itself is perfect, because they can be affected by transformation processes or by contamination, and because they are subject to natural variation. Taken together, however, they can be quite powerful, as illustrated by Jones and Philp (1990) in a study of oils and source rocks from the Anadarko basin.

Sterane and triterpane biomarkers are now accepted as our single most powerful correlation tool. As Figure 50 demonstrates, oils and mature-rock extracts from their source rocks often contain nearly identical biomarker signatures. However, Figure 50 also indicates that immature-rock extracts may show important natural variations even within a genetically related group.

Figure 70 shows the sterane distribution in an oil from the Akita basin of Japan, together with the steranes from an immature sample of the Onnagawa Formation, a leading candidate as the source rock. The large maturity differences cause the mass chromatograms to look different, but comparison of the relative proportions of C_{27}-C_{29} regular steranes, the presence of the C_{30} steranes, and the minor proportions of diasteranes in both samples together suggest a positive correlation. The slightly higher diasterane content of the oil might be related to its greater maturity. Thus, it is preferable to base correlations on biomarker parameters that are independent of maturity. If this goal is not achievable, any variations due to maturity must be mentally factored out while making the correlations.

Not all mass chromatograms of biomarkers are of equal value for correlations. Although it is important that the common steranes and triterpanes be in agreement between the samples being correlated, simple agreement among the most common components is not conclusive enough to establish a strong positive correlation. Many unrelated samples can fortuitously contain the same distributions of common steranes and hopanes. In carrying out correlations, therefore, we pay particular attention to unusual steranes and triterpanes because they often are especially valuable for identifying genetically related samples. Examples of unusual triterpanes include gammacerane (Figure 54B, peak s), 28,30-bisnorhopane (Figures 32B, 52, and 55, peak c), oleananes (Figures 34, 51, 58, and 59), bisnorlupanes (Figure 53), bicadinanes (Figures 62 and 63), and hexacyclic hopanoids (Figure 65).

Biomarkers are of particular value in correlating biodegraded samples because they are among the last compounds to be attacked by bacteria. Thus at levels of biodegradation below Level 7 (Table 4), steranes and triterpanes should be unaffected. At higher levels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RETENTION TIME

Figure 70—M/z 217 (sterane) mass chromatograms for an oil from the Akita basin, Japan (A), and (B) an immature sample from the Onnagawa Formation (middle Miocene). Peaks at the right marked with (?) are 4-methylsteranes of unknown structure. Identities of other peaks are found in Table 2. See text for discussion.

of biodegradation, any correlations will have to consider possible changes in biomarkers. Particularly resistant biomarkers, such as 28,30-bisnorhopane and the diasteranes, can be of great value in such cases (Brooks et al., 1988).

Finally, we should be aware that although steranes and triterpanes are very powerful correlation tools because of the large amount of detailed information they carry, they are not infallible. Correlation Example 5 (later in this chapter) illustrates the problem of natural variation and facies changes between the real source rock for an oil and the rock samples actually analyzed in the laboratory. Bagge et al. (in press) discussed another example of problems caused by rapid facies changes in attempting to correlate nonmarine coals with oils sourced from them. Robinson and Kamal (1988) noted similar problems in various nonmarine facies in Sumatra. England (1990) has shown that in petroleum reservoirs, lateral and vertical inhomogeneities in oil composition are the rule rather than the exception; therefore, biomarkers may also be inhomogeneously distributed.

Furthermore, even when steranes and triterpanes are abundant, they only represent a tiny fraction of the total sample. They therefore are very susceptible to contamination or mixing. Figures 40 and 41 showed steranes and triterpanes that were not indigenous to the crude oils and condensate they were isolated from. Although these examples are extreme and probably unusual, they should make it clear that we cannot use biomarkers blindly. Furthermore, contamination is much more common in, and is likely to be more significant in, source rocks than in oils. Prior to initiating a correlation effort, one should always look for evidence of staining or other forms of nonindigenous material in any source-rock sample.

EXAMPLES OF CORRELATIONS

Example 1

The three oils in Figures 71 and 72 were all sourced from the same formation in two different parts of the same basin. Examples A and B in each figure, which have very similar distributions of both steranes and triterpanes, are from the same area. In addition to the close similarities between the hopanes, regular steranes, and diasteranes in both samples, there are several unusual peaks in the triterpane spectra (Figure 71)

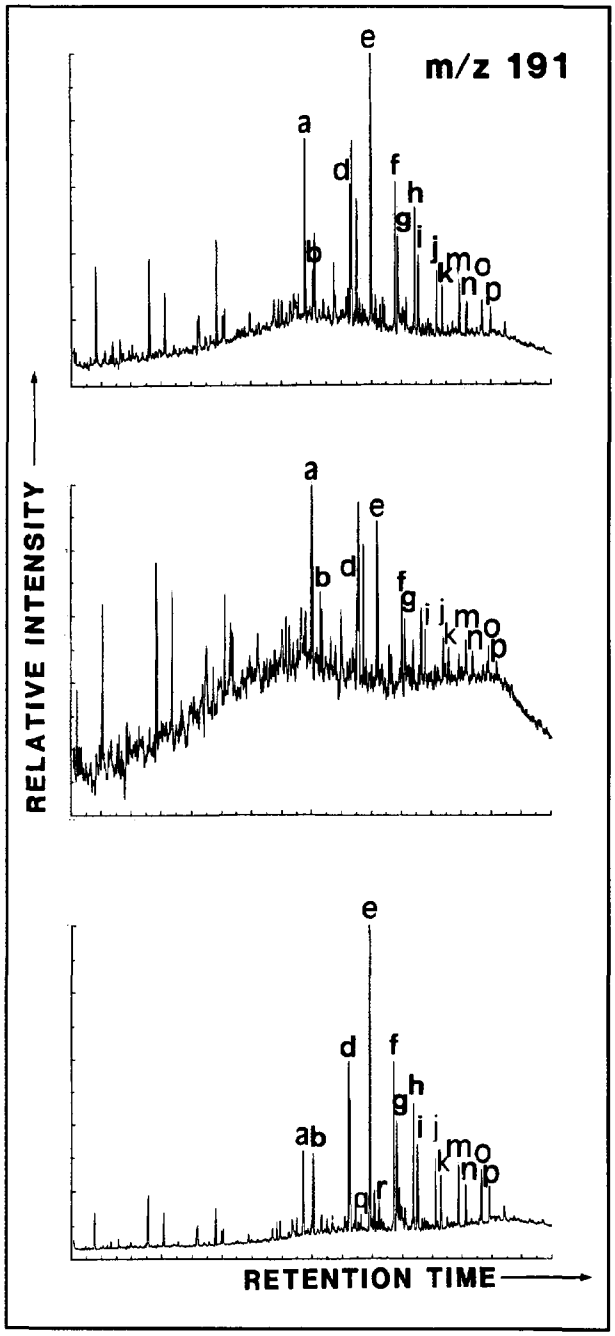

Figure 71—M/z 191 (triterpane) mass chromatograms for three oils sourced from the same formation in three different parts of the same basin. Identities of peaks are given in Table 3. M/z 217 mass chromatograms for these oils are shown in Figure 72. See text for discussion.

that further strengthen the positive correlation. These include the peak eluting immediately after the C_{29} 17α(H)-hopane, the peak midway between the C_{29} 17α(H)-hopane and the C_{29} moretane, and the peak immediately before T_m. In addition, the relative proportions of tricyclic triterpanes are quite similar.

In contrast, sample in C in Figures 71 and 72, which is from a different part of the basin, is clearly not identical with the other two. It contains much more of the C_{27} and C_{29} regular steranes (Figure 72), and less of the unusual triterpanes noted above (Figure 71). On the basis of the biomarker data alone, a positive correlation is far from certain. In this case other data, including gas chromatography, carbon isotopes, and geologic information, were essential to complete the positive correlation. The differences were eventually ascribed to natural variation within this family of oils.

Example 2

Figure 73 shows steranes and triterpanes from an oil (A) and an extract from a cuttings sample (B) of immature, organic-rich (TOC = 3.7%), dark-colored carbonate. The cuttings sample had an anomalously high pyrolysis S_1 yield, extract/TOC ratio, and proportion of hydrocarbons in its extract. Staining was therefore suspected.

Triterpane distributions suggest that the samples are identical. Both contain extremely large amounts of gammacerane (peak s) and rather high concentrations of the C_{35} 17α(H)-extended hopanes (peaks o and p). The presence of these relatively unusual characteristics in both samples suggests a genetic relationship: either the rock is stained with the oil, or it is the source rock for the oil.

The sterane distributions tell another part of the story. Although the oil is clearly of rather low maturity (as indicated by the predominance of the 20R epimer of the 5α(H),14α(H),17α(H)-C_{29} sterane: peak H), the extract shows an even lower level of maturity. These data indicate that most of the steranes in the rock cannot be attributed to staining by this oil.

Although most of the steranes in the rock are indigenous, a significant proportion of the triterpanes appears to represent staining. We base this conclusion partly on the relative quantities of steranes and triterpanes in the two samples. The ratio of the intensity of the dominant triterpane (gammacerane, peak s) to that of the dominant sterane (peak C) in the extract is 190/147, or 1.3. The same ratio for the oil is about 4. The oil is therefore richer in triterpanes, whereas the extract is richer in steranes. The addition of minor quantities of oil to the rock would thus affect the triterpane distribution much more than it would affect the steranes, exactly as we see in the samples. This example underscores the need to use all available

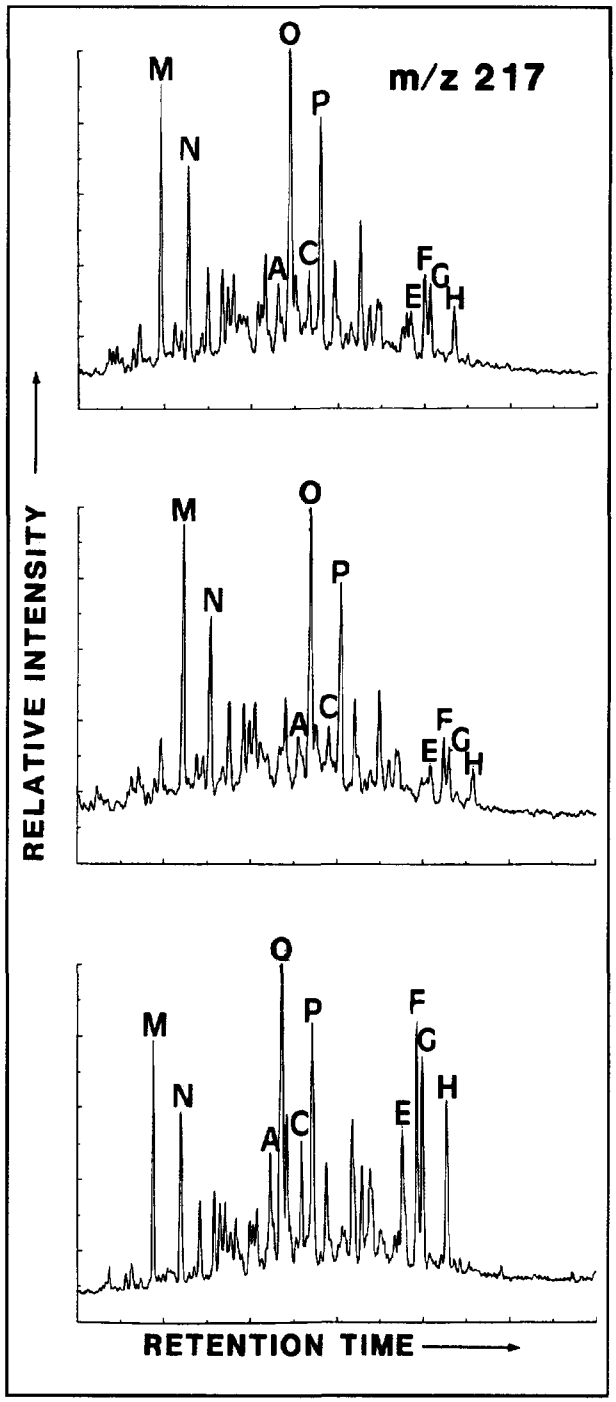

Figure 72—M/z 217 (sterane) mass chromatograms for the three oils shown in Figure 71. Identities of peaks are given in Table 2. See text for discussion.

information, and to realize that staining will affect some parameters more than others.

Our final conclusions are that the staining prevented a valid test of the possible relationship between source rock and oil. However, the difference in maturity noted in the steranes, and the differences in triter-

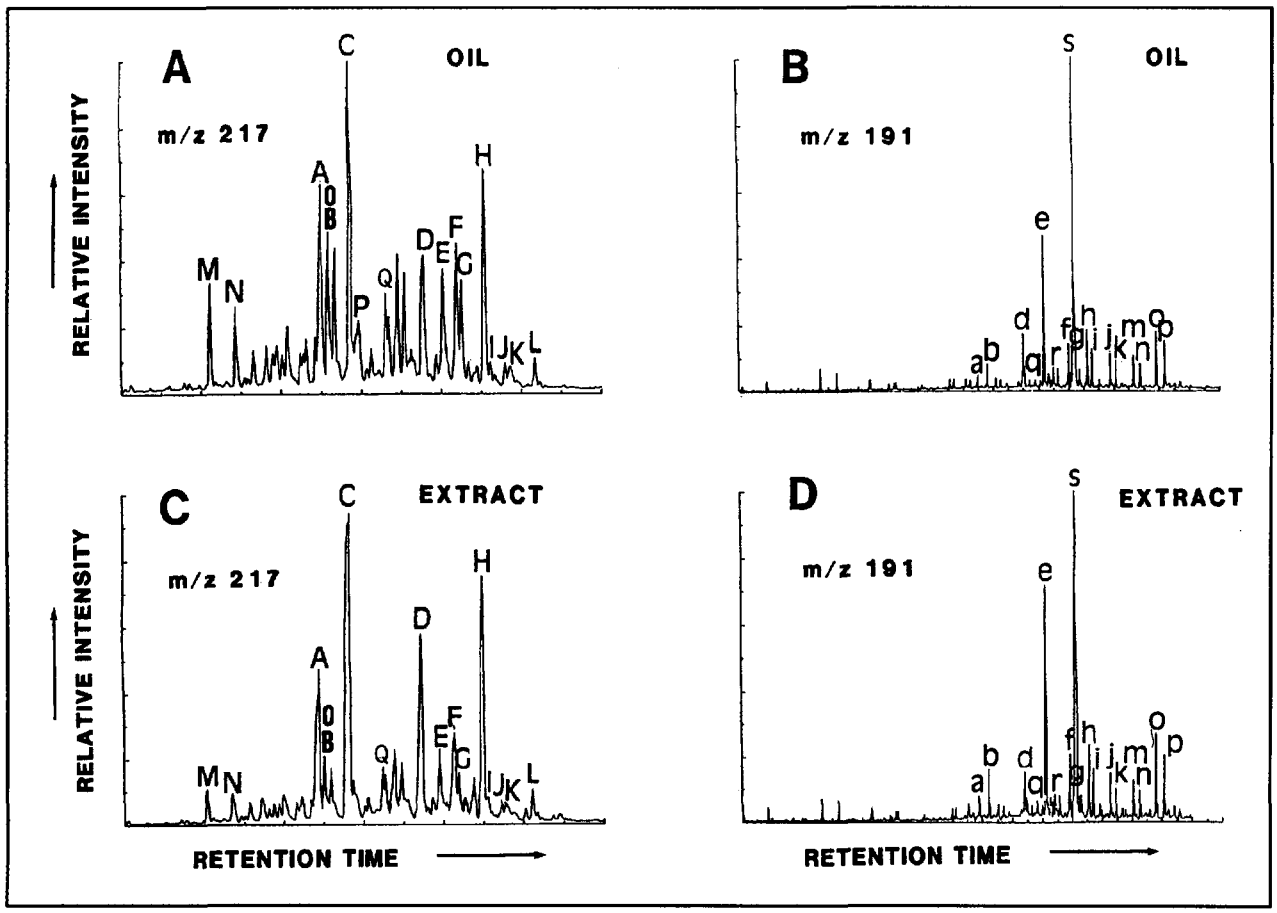

Figure 73—M/z 217 (sterane: left) and 191 (triterpane: right) mass chromatograms for an oil (A and B) and an extract from a cuttings sample (C and D). Identities of peaks are given in Tables 2 and 3. See text for discussion. From Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology*.

pane/sterane ratios, suggest that this rock sample is not from the effective source rock.

Example 3

Sofer (1988) was faced with the problem of correlating a group of extremely mature oils from the Gulf of Mexico. As a result of this high maturity, virtually all the steranes and triterpanes in the oils had been destroyed; m/z 191 and 217 mass chromatograms showed only a baseline with no obvious peaks. However, he noted that the shapes of the m/z 191 baselines in his sample suite fell into two families (Figure 74), and used this information as a tentative beginning for his correlation work. He was also able to use the tricyclic triterpanes to group some of the less-mature oils because those compounds, less sensitive to maturation effects, still remained in some abundance.

Establishing a correlation on baseline shape alone is obviously foolhardy. In this case, however, the baseline shapes were used only to start the grouping process, which was completed (and probably modified) by other geochemical and geological data. The biomarkers in this example thus served as a source of ideas rather than of data.

Example 4

Grantham (1986a) and Grantham et al. (1988) divided Oman oils of definite or suspected Precambrian origin into two groups using sterane and triterpane distributions in conjunction with other geochemical and geological data. In the type "A" oils (called the Huqf oils in Grantham et al., 1988) there is very strong dominance of the C_{29} steranes over C_{27}, and a virtual absence of diasteranes (Figure 75A). In the type "B" oils (called "Q" crudes in Grantham et al., 1988), in contrast, the C_{27} steranes are dominant, with a modest proportion of diasteranes (Figure 76A). These differences in carbon-number distributions are summarized in Figure 77.

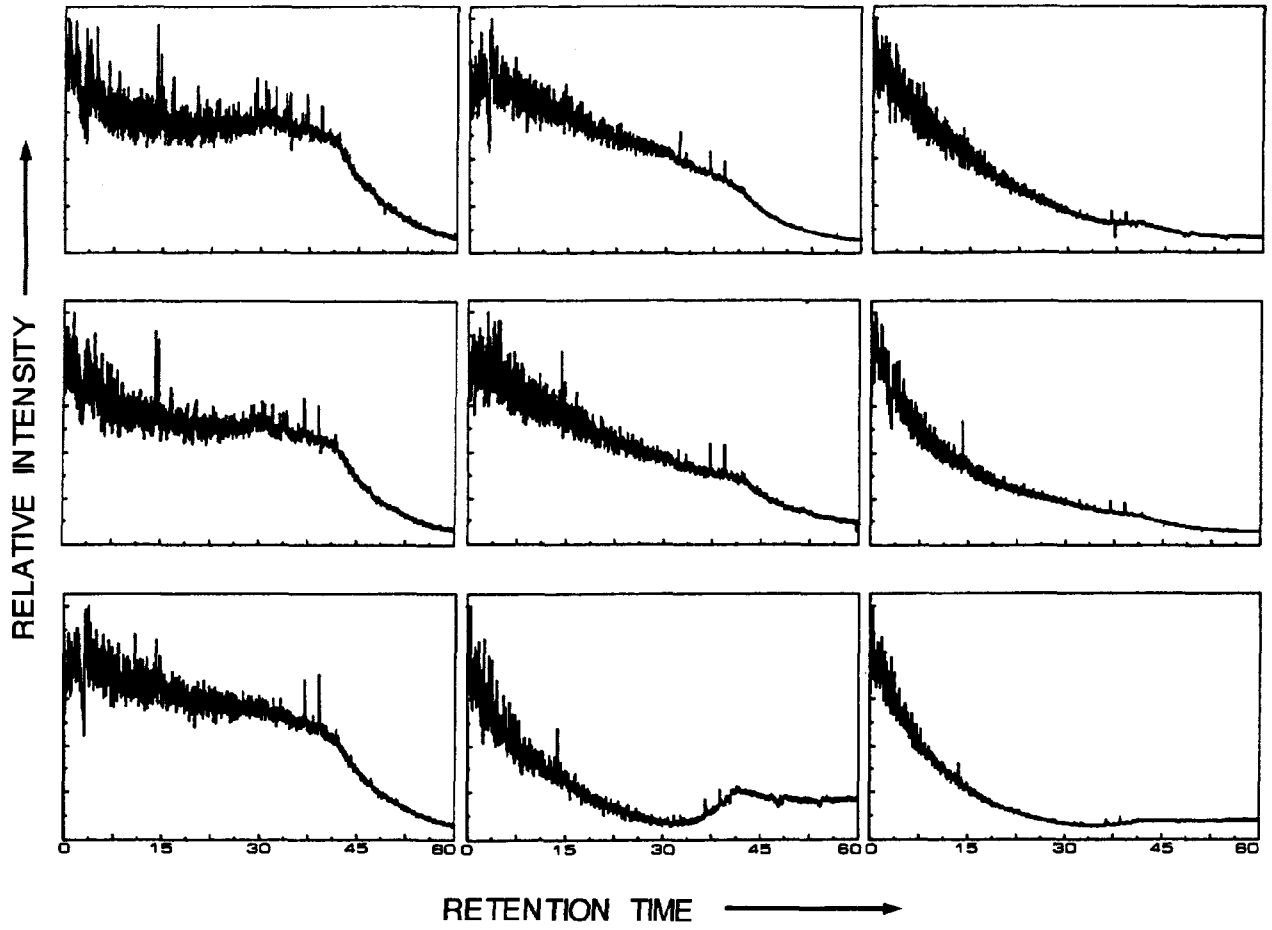

Figure 74—M/z 191 (triterpane) mass chromatograms of nine highly mature oils from the U.S. Gulf Coast that have no individually identifiable triterpanes. In this case, the different shapes of the baselines were used to begin a grouping into families, although the causes for these differences were not understood. From Sofer (1988); reprinted with permission of Pergamon Press PLC.

The triterpanes in the type "A" oils consist mainly of hopanes. Unusual characteristics include a dominance of the C_{29} hopane (peak d) and high C_{35} extended hopanes (peaks o and p: Figure 75B). In contrast, the type "B" oils have much larger proportions of tricyclics and very few hopanes (although the hopane distributions do appear to be similar to those in the type "A" oils).

According to Grantham, there is good geologic evidence that the type "A" oils in south Oman are from a Precambrian (and thus algal or bacterial) source, in spite of their dominance by the C_{29} steranes. Other characteristics (high C_{35} extended hopanes, high C_{29} hopane, lack of diasteranes) suggest the source rock was a carbonate.

A specific source rock for the type "B" oils was not proposed, but Grantham et al. (1988) suggested they are probably also of Precambrian origin. In our view, the higher diasterane contents might suggest a more clay-rich facies; the distinct distribution of regular steranes indicate a much different algal source; and the dominance of tricyclics points to a much different bacterial population. However, these tentative interpretations on our part assume that there are no major maturity differences between the two groups of oils.

No direct information on oil maturities was given by Grantham (1986a). However, the C_{29} sterane diastereomer ratios (peak E/[peak H + peak E]) in Figures 75 and 76 suggest that type "B" oils are more mature than those of type "A." Furthermore, Grantham et al. (1988) indicated that the type "A" oils are heavy and rich in sulfur (suggesting low maturity), while the type "B" oils are light and mature. Thus the tricyclic/hopane ratio and diasterane contents may have increased in the type "B" oils as a result of maturity, and these particular differences should not necessarily be ascribed to a facies change.

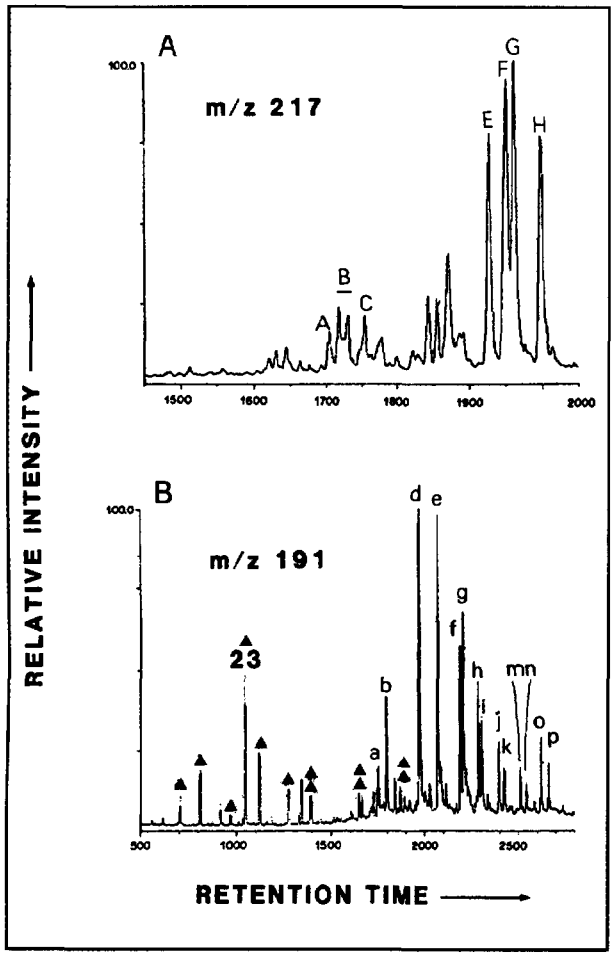

Figure 75—M/z 217 (sterane: A) and 191 (triterpane: B) mass chromatograms from a typical member of the type "A" oils from Oman. Compare with chromatograms of type "B" oils in Figure 76. Triterpanes marked with solid triangles are tricyclics. The C_{23} tricyclic is numbered. The triangle on the far left marks the C_{20} member. Double triangles indicate the existence of R and S epimers. The leftmost of the double triangles represents the C_{26} pair. C_{27} and C_{29} species are absent. Identities of other peaks are given in Tables 2 and 3. See text for discussion. From Grantham (1986a); reprinted with permission of Pergamon Press PLC.

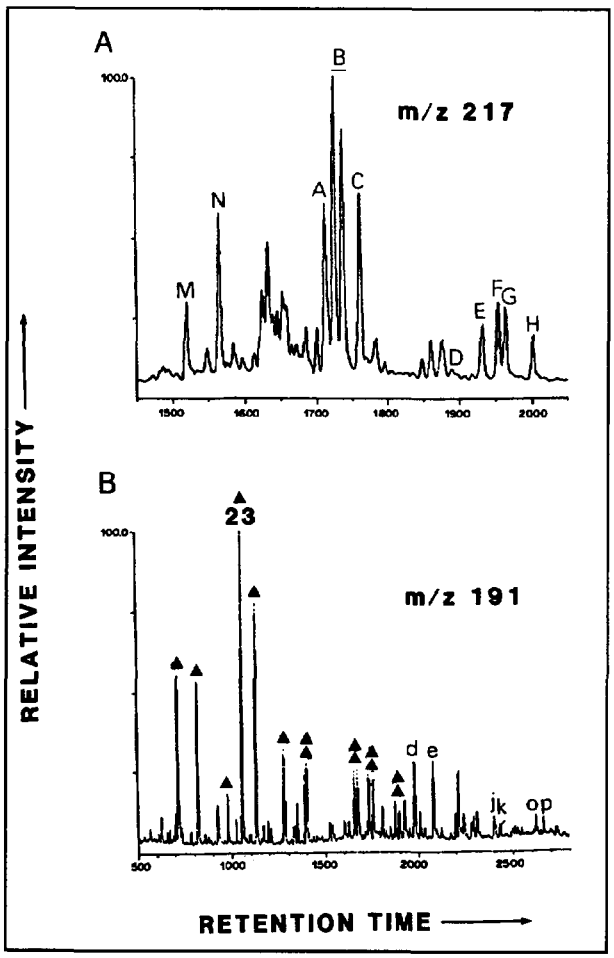

Figure 76—M/z 217 (sterane: A) and 191 (triterpane: B) mass chromatograms from a typical member of the type "B" oils from Oman. Compare with chromatograms of type "A" oils in Figure 75. Compounds marked with solid triangles are tricyclic triterpanes. Identities of other peaks are given in Tables 2 and 3, and in the capiton for Figure 75. C_{29} tricyclics are present here. See text for discussion. From Grantham (1986a); reprinted with permission of Pergamon Press PLC.

Example 5

Figure 78 plots on a single diagram the relative proportions of the C_{27}-C_{29} regular steranes for extracts from four formations in a single well in the Niigata basin of Japan. (Examples of the sterane mass chromatograms themselves were shown in Figure 25.) Differences among the four formations are rather minor, with the sterane distributions forming a continuous band across the triangular diagram.

The similarity of the sterane distributions from the four formations indicates that the relative proportions of C_{27}-C_{29} steranes cannot be used as a decisive correlation parameter. However, upon closer inspection of Figure 78, we see that even though the differences in sterane distributions among the formations are small, they are consistent for the numerous samples analyzed. For example, the samples from the Nishiyama and Shiiya formations all plot on the right-hand side of the trend, whereas those from the Nanatani and Teradomari formations are all found on the left-hand side. The consistency of these trends indicates that we can, with some confidence, distinguish these two

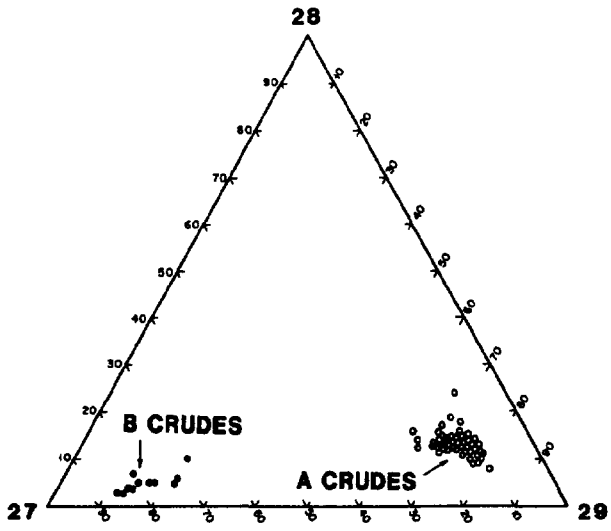

Figure 77—Triangular diagram showing clear distinction between type "A" and type "B" oils in Oman on the basis of regular-sterane distributions. From Grantham (1986a); reprinted with permission of Pergamon Press PLC.

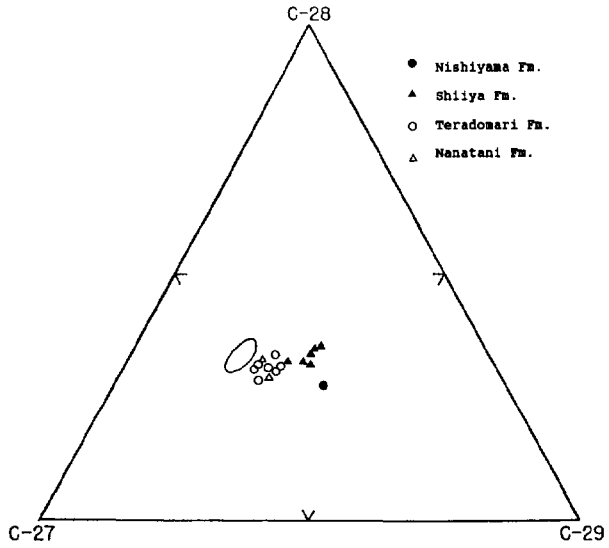

Figure 78—Triangular diagram showing C_{27}-C_{29} regular-sterane distributions for extracts from rocks of four formations in the Higashi Niigata NS-6 well, Niigata basin, Japan. Formation names and ages are: Nishiyama (Pliocene-Pleistocene); Shiiya (late Miocene-Pliocene); Teradomari (middle-late Miocene); and Nanatani (early-middle Miocene). Elliptical outline shows the range of compositions in four oils from various formations in the area. See text for further discussion.

groups of rocks, although we cannot make further distinctions within the two groups.

The ellipse in Figure 78 shows the range of sterane distributions of four oils from this area. They were recovered from the Shiiya, Nishiyama, and Teradomari formations, but all show very similar characteristics. The sterane distributions are much more like those of extracts from the Nanatani and Teradomari formations. These and other data lead to the conclusion that the deeper formations are probably the sources. A definitive correlation is hampered by lack of drilling and sampling of mature source facies (many of the source-rock samples are rather immature), and by rapid lateral changes in organic facies.

Example 6

A final example shows two oils and an extract from the Devonian of the Williston Basin of the northern US. The extract came from black, tarry material recovered from a salt crystal. Because it did not appear to be indigenous to the salt, a correlation with the oils was attempted.

Steranes (Figure 79A and B) and triterpanes (Figure 80A and B) for the two oils are very similar. The sterane distributions are not precisely identical, but both have dominant diasteranes and show no C_{30} steranes. The triterpane distributions, however, are quite unusual but similar to each other: both are dominated by three peaks (two of them unidentified), with the 17α(H)-hopanes and moretanes nearly absent. The oils therefore were concluded to be of the same unusual origin. The positive correlation was confirmed by other geochemical data, including gas chromatograms and carbon isotopes.

The black material (Figures 79C and 80C), in contrast, is quite different from the oils. It contains a full complement of 17α(H)-hopanes and moretanes, and the peaks that dominated in the oils are minor. Sterane distributions are also slightly different. C_{27} regular steranes (peaks A, B, and C) in particular are more abundant than in the oils, and there is a small amount of what appear to be C_{30} steranes. We therefore conclude that the extract is not genetically related to the oils.

SUMMARY

Steranes and triterpanes play important roles in modern correlations. The following guidelines are useful in applying biomarker technology correctly to correlation problems.

1. Any differences due to migration, biodegradation, or maturity must be factored out before executing correlations. Whenever possible, one should emphasize those correlation parameters that are least affected by maturity.

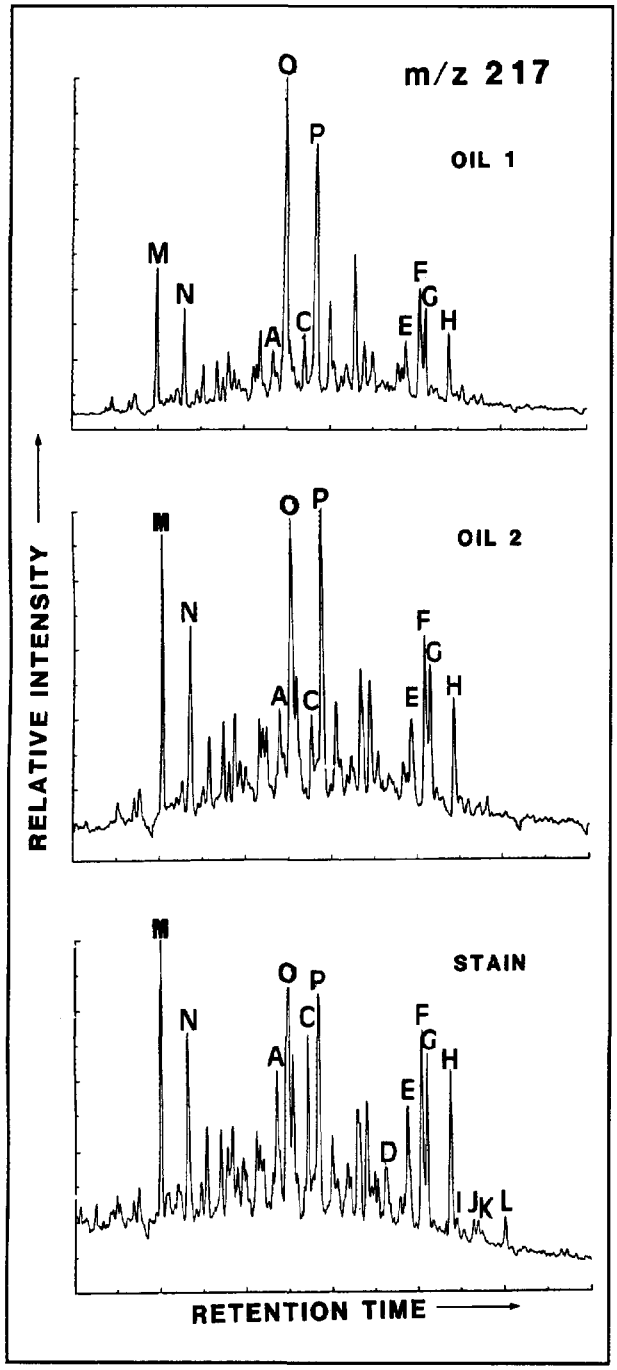

Figure 79—M/z 217 (sterane) mass chromatograms for two oils and the extract from a black stain. Identities of peaks are given in Table 2. See text for discussion, and Figure 80 for m/z 191 mass chromatograms. From Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology.*

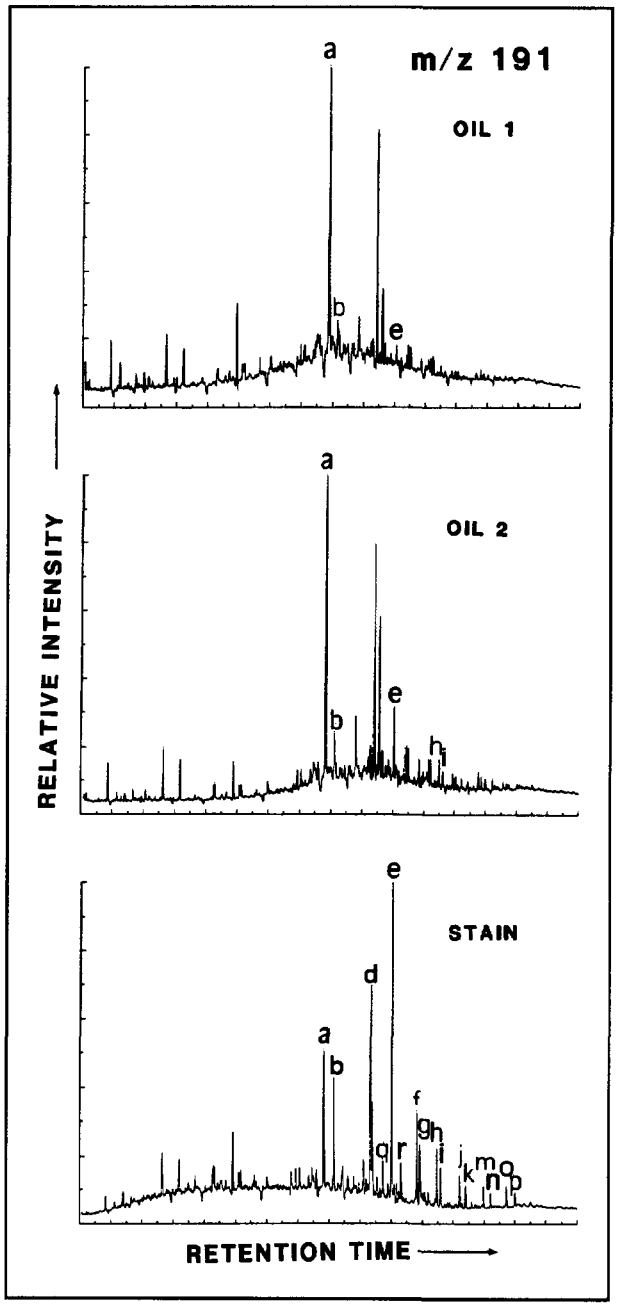

Figure 80—M/z 191 (triterpane) mass chromatograms for the oils and extract in Figure 79. Identities of peaks are given in Table 3. See text for discussion. From Waples and Machihara (1990); reprinted with permission from the *Bulletin of Canadian Petroleum Geology.*

2. Distributions of C_{27}–C_{30} regular steranes and C_{27} and C_{29} diasteranes are important for correlations.

3. Distributions of the extended hopanes are sometimes of value, especially when they do not show a regular decrease from C_{31} to C_{35}.

4. Unusual triterpanes such as gammacerane, 28,30-bisnorhopane, 25,28,30-trisnorhopane, "compound X," the various oleananes, the bisnorlupanes, and hexacyclic hopanes are particularly valuable for correlations when they are present.

5. All the cautions expressed about using biomarkers for organic-facies analysis apply to correlations as well. In addition, one should remember that oils themselves will probably represent mixtures of material from various facies that differ to varying degrees. Furthermore, rapid facies variations, especially in carbonate environments (see Example 5 above and Clark and Philp, 1989, for examples), can make it difficult to sample the true source rock for a given oil. Therefore, it is unlikely that one will find a single source rock that perfectly matches any oil.

6. All correlations should use other geochemical and geological data in addition to sterane and triterpane biomarkers (e.g., Jones and Philp, 1990). Although biomarkers are excellent correlation tools in many cases, in other situations they are not definitive. The added weight of other corroborating evidence—such as isotope ratios, gas chromatograms, and the like—is therefore very important. Furthermore, the final interpretation should draw as consistent a picture as possible from all available geochemical and geological data.

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Chapter 8

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Table 2. Identities of common steranes in the m/z 217 mass chromatograms in most of the illustrations in this book.

Designation	Number of Carbon Atoms	Ring Stereochemistry*	Side-chain Stereochemistry
		Regular Steranes	
A	27	αα	20S
B	27	ββ	20R + 20S
C	27	αα	20R
Q	28	αα	20S
R	28	ββ	20R
S	28	ββ	20S
D	28	αα	20R
E	29	αα	20S
F	29	ββ	20R
G	29	ββ	20S
H	29	αα	20R
I	30	αα	20S
J	30	ββ	20R
K	30	ββ	20S
L	30	αα	20R
		Diasteranes	
M	27	βα	20S
N	27	βα	20R
O	29	βα	20S
P	29	βα	20R

*Stereochemistry of hydrogen atoms at positions 14 and 17 for regular steranes and 13 and 17 for diasteranes.

Table 3. Identities of triterpanes in the m/z 191 mass chromatograms in most of the illustrations in this book.

Designation	Identity	Number of Carbon Atoms
	Hopanes	
y	25,28,30-trisnorhopane	27
a	Ts	27
b	Tm	27
c	28,30-bisnorhopane	28
d	C_{29} 17α(H)-hopane (norhopane)	29
e	C_{30} 17α(H)-hopane (hopane)	30
f	22S C_{31} 17α(H)-hopane	31
g	22R C_{31} 17α(H)-hopane	31
h	22S C_{32} 17α(H)-hopane	32
i	22R C_{32} 17α(H)-hopane	32
j	22S C_{33} 17α(H)-hopane	33
k	22R C_{33} 17α(H)-hopane	33
m	22S C_{34} 17α(H)-hopane	34
n	22R C_{34} 17α(H)-hopane	34
o	22S C_{35} 17α(H)-hopane	35
p	22R C_{35} 17α(H)-hopane	35
	Moretanes	
q	normoretane	29
r	moretane	30
	Other	
s	gammacerane	30
t	18α(H)-oleanane	30
u	18β(H)-oleanane	30
x	C_{30}-pentacyclic (compound X)	30