



## CHAPTER V

### MARINE AND LACUSTRINE BIOMARKERS

The term "marine" and "lacustrine" are used to specify two depositional environmental types. It is not a simple matter to specify one unique characteristic biomarker for each types of sedimentary environment. For example, the marine environment includes intermingling coastal, shelf and open ocean settings with a mixing to various degrees of productivity and depositional environments. Similarly, the term lacustrine can both include freshwater or saline lakes of vastly differing area and ecologies. A scheme that summarized some different aspects comparing between marine and lacustrine environments is shown in Table 8. (KELTS, 1988). However, each of these environments will leave a different lipid signature in the sedimentary rock and the task of geochemical fossil for determining that which compound, or group of compounds can be characteristic their environment. A comparison of biological marker in all these different environments then can be established to test the validity or usefulness of petroleum palaeoenvironmental studies. A difference in the proportion of each type biomarkers may be useful to a palaeoenvironmental study also. This means not only a group of biomarkers can refer to type of depositional

environment, source, maturity and alteration processes of sediment and crude oil, but the relative amount of some specific biomarker can give more significant clue of the geologic history.

Basically, the principal sources of organic matter in sedimentary rock are bacteria, phytoplankton, zooplankton and higher plants. The biomass composition of these organic material depends upon what type of environment the organic matter was originally deposited. The environments can be associated either with open water (marine) and/or continental (non-marine) areas. The chemical constituents which play a dominant role in the formation of petroleum are the lipid and lipid like fractions (TISSOT and WELTE, 1978). Similarly, all organisms are composed of same groups of chemical constituents i.e., proteins, lipids, carbohydrate and lignin in higher plants, but considerable differences in chemical composition exist between certain kinds of organism that predominate in each type of environment. The most prominent marine plant, tiny unicellular planktonic algae, is quite different from the vast majority of terrestrial higher plants. For instance, the organic matter of marine plankton is composed mainly of protein (up to 50% or more), variable amounts of lipids (generally between 5 and 25%) and variable amounts of carbohydrates, whereas higher terrestrial plants including the majority of trees are composed largely of cellulose (30 to 50%) and lignin (15 to 25%) (TISSOT and

Table 8. The differing aspects of between lacustrine and marine environments of deposition (from KELTS, 1988).

Aspect	Lacustrine	Marine
Aqueous reservoir	Limited, variable	Immense, uniform
Chemistry	Highly variable, ion species function of drainage basin geology and climate	Uniform Na-Cl-
Salinity	Highly variable $10^1$ - $10^3$ mg TDS/l	35‰
pH	Variable 3.0-11.0	8.3 in surface waters 7.7 in bottom waters
Size	Highly variable, up to 80 000 km <sup>3</sup> today	Immense, but source-rock areas similar in size to lake basins
Deposits, thickness	Generally thin within continental clastics	Thin organic-rich zones
Sediment rates	0.1-2 m/ty rapid	0.001-0.35 m/ty modest
Tectonics	Event basins or sags or rifts + fault control	Sea floor spreading. Continental margin subsidence
Geodynamics	Includes altitude variations, drainage capture, sudden changes	Sea level, epirogeny; slower changes
Climate control	Zonal latitude dependent	
Climate change	Immediate, drastic response; level changes, composition tens of years	Long-term response; thousands of years
Residence time	1-500 yr	1000 yr +
Cycles	Annual, sun-spot, short-term climate	Long-term climate, palaeo-oceanography, Milankovitch
Tides	No tidal, seasonal level variation	Tidal dominated
Organic matter	Algae/bacteria; land plants. Type I common	Marine algae, or land plant. Type II & III
Productivity	Very high, high nutrient	Modest, upwelling zones
Preservation potential	High with high sed. rates. Anoxia, low sulphate, common	Requires high sed. rates, or anoxia
Bacteria/algae	Special adaptations. Photochemotroph, etc.	Marine
Palaeontology		
Silica microfossils	Diatoms dominant since Eocene, sponges	Diatoms since L. Cret., radiolaria
Calc. microfossils	No pelagic calcareous	Forams, Nannos dominant
Benthics	Ostracods. Local endemism	Forams. Worldwide index
Dinoflagellates	Abundant, but few cysts preserved	Cysts preserved
Vertebrates, etc.	Micromammals, reptiles, fish (kills), insects, chironomids	Vertebrates, insects rare
Littoral shelf	No corals, gastropods, stromatolites common, algal bioherms, charophyte chalks	Coral reefs, calc. algae, molluscs, strom. rare, subtidal, no marine charo.
Offshore	Macrofossils scarce	
Bioturbation	Worms, insects, vertebrates. Few burrowers	Numerous burrowers
Facies		
Evaporites	Derived, evaporitic concentration variable types, reworked, thin, fractionated basins	Marine, fixed sequence, giants, may be kms thick
Carbonates	No barrier reefs, no calcareous plankton oozes, mostly chemical, dolomite common	Mostly biogenic, calcite dominant
Oolites	Saline and brackish lakes	Turbulent upwelling
Silica	Abiotic chert common	Biogenic chert common
Basinal	Commonly anoxic sediments	Anoxia not common
Deltas	Short-term, rapid variance response to level changes	Long-term stability
Turbidites	Common in dilute waters	Rare events
Sands	Fan-delta complexes, flood plain, fluvial	Clastic shores, beach
Transgression/regression	Very short period	Long period phenomena
Stratigraphy	Often not by Walther's law, rapid supplantation	Walther's law, transitional
Life span	1 ma is old, up to 35 ma	1-100 ma
Kerogen	Variable Type I to III, common high wax, amorphous, low sulphur, high or low pour points	
Biomarkers	Botryococcane, bacterial common	

WELTE, 1978). Therefore, understanding the basic information of chemical composition of relevant classes of organism is useful in distinguishing biomarkers which represent the geological evolution of organic source materials in such depositional environments. Presently, geochemical evidence and biological marker distribution are both used for the characterization and differentiation of ancient marine and non-marine petroleum source rocks (MACKENZIE et al., 1984; MOLDOVAN et al., 1985; MCKIRDY et al., 1986; PETER et al., 1986). Many recent evidences show that such features provide diagnostic criteria for the distinction of oils derived from source rocks deposited in different environments, such as lacustrine freshwaters and hypersaline waters in China (POWELL 1986; BRASSEL et al., 1988), marine carbonate in Venezuela, Australia and Florida (TALUKDAR et al., 1986; MCKIRDY et al., 1984; PALACUS et al., 1984) and lacustrine freshwater in Australia (MCKIRDY et al., 1986; PHILP and GILBERT, 1986). It is evident that the components of particular sediment extract or oil reflect the precursor compounds. The molecular properties which are useful for palaeoenvironmental assesment should ideally be diagnostic of specific types of organisms with ubiquitous and documented occurrence in recent and ancient depositional environments (BRASSEL and EGLINTON, 1986). In addition, such biomarker molecular features can be affected by diagenetic processes and may therefore reflect evolutionary change in the source of sedimentary

organic matter as previously mentioned.

### MARINE DEPOSITIONAL ENVIRONMENTS

Marine source rocks or oils derived from marine organic sources are those that accumulate under marine conditions but in general, they can contain both marine and terrigenous organic matter. The accumulation and preservation of such organic matter in sediments is a crucial process in the formation of hydrocarbon source rock in addition to the characteristic type of original sedimentary deposition. For marine depositional environments, three different depositional regimes can be distinguished: namely, marine evaporitic, marine carbonate and marine deltaic. The characteristic of such biomarkers will be described below.

#### Marine Evaporitic

Marine evaporitic depositional environments of source rock generated oil have been widely studied. Biomarkers characterized this marine type environment have also mentioned in those studies. Low molecular weight n-alkanes with a slight even/odd preference and the predominance of phytane over pristane are all consistent with the hypersaline environment of deposition (FU JIAMO et al., 1986; ten HAVEN et al., 1985, 1988; CONNAN et al., 1986; ALBAIGES et al., 1986). The origin of an even n-alkane dominance has been suggested as the result of the reduction of precursor lipid (fatty acids



and alcohols), under anoxic conditions (GRIMALT et al., 1985; CONNAN et al., 1986) being always linked with a low pristane/phytane ratio. This ratio is directly related to the salinity of depositional environment. Low ratios ( $< 1$ ) appear to be associated with hypersaline conditions. The abundant presence of long chain isoprenoids mainly the regular  $i\text{-C}_{25}$  and  $i\text{-C}_{30}$  (squalane) components, is also a consistent feature of hypersaline environments (WAPLES et al., 1974; PALACAS et al., 1984). The  $\text{C}_{25}$  (regular) and  $\text{C}_{30}$  isoprenoids have been suggested to increase in abundance with an increase in salinity and to maximize in oils derived from an evaporitic environment (MELLO et al., 1988). High abundance of  $\beta$ -carotane also appears to be associated with highly anoxic saline environments (HALL and DOUGLAS, 1983).

$\text{C}_{27}\text{-C}_{29}$  steranes and  $\text{C}_{28}\text{-C}_{30}$  4-methyl steranes are present in high concentrations in samples from this type of environment (MELLO et al., 1988). A relatively high abundance of these compounds is commonly observed in oils from hypersaline origins (RULLKOTTER et al., 1984; ten HAVEN et al., 1985; FU JIAMO et al., 1986; CONNAN et al., 1986). Source input and mineral matrix effects as well as maturity may play an important role in the distribution pattern of the sterane isomers i.e.  $20\text{S}$  and  $20\text{R } 5\alpha(\text{H}), 14\beta(\text{H}), 17\beta(\text{H})$  and  $20\text{S}$  and  $20\text{R } 5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$ . An abundance of the  $\text{C}_{30}$  steranes is also possible because it is indicative of a marine source contribution (MOLDOWAN et al., 1985). Even though

the precise origin for the C<sub>30</sub> steranes has not been established, it is thought to be derived from C<sub>30</sub> sterol constituents in marine algae (DJERASSI, 1981). The presence of abundant C<sub>21</sub> and C<sub>22</sub> steranes and 4-methylsteranes is in keeping with a hypersaline environment. The presence of diasteranes may be explained in terms of availability of acidic clay minerals present hypersaline environments, which catalyse the sterane rearrangement process (RUBINSTEIN et al., 1975) and also be observed in sediments and oils from both evaporitic and carbonate environments (MCKIRDY et al., 1984; FU JIAMO et al., 1986).

In general, hypersaline conditions lead to an increase in the bacterial contribution to sediments as demonstrated by relatively high concentrations of bacterially derived hopanes. It is also possible that bacteria produce the precursor for the tricyclic terpanes although CONNAN et al. (1986) reported a low abundance of tricyclic terpanes in rock samples from Guatemalan hypersaline environments.

Another biomarker that may be a good indicator for hypersaline environment is gammacerane which may appear in high concentrations in more saline environments (FU JIAMO et al., 1986; MOLDOWAN et al., 1985). Ts/Tm ratios are dependent on the maturity, organic source input and/or mineral matrix effects of the sediments whereas 17 $\alpha$ (H), 21 $\beta$ (H) 28,30-bisnorhopane and 25,28,30-trisnorhopane can be present in a high abundance because

they are presumably originated from anaerobic bacteria in highly anoxic depositional environments (RULLKOTTER and WENDISCH, 1982). Also, the concentration of the C<sub>35</sub> extended hopanes is relatively high abundance compared to the C<sub>34</sub> homologues and this is a significant characterize of samples from both marine carbonate and hypersaline environments (ten HAVEN et al., 1985, 1988; Brassell et al., 1988; FU JIAMO et al., 1986; ALBAIGES et al., 1986).

In addition, the diagenesis of oils derived from source rocks deposited in a hypersaline (marine evaporitic) environments can be characterized by other particular sets of bulk, elemental and molecular features. The biota in such an environment are expected to be largely restricted to a few species of salinity tolerlant aquatic organism. The effect of these phenomena on the biological marker distributions would be expected to be dramatic and lead to the dominance of specific compounds.

#### Marine Carbonate

In general, the biomarker distribution of oils derived from marine carbonate sources are supposed to be similar to those derived from marine evaporitic depositional environment. They might show low or medium content of saturated hydrocarbons and a dominance of phytane over pristane and have a slight even/odd predominance of n-alkanes. The enhanced salinities in the environment during carbonate deposition would affect



the distribution of the C<sub>25</sub> and C<sub>30</sub> isoprenoid components and the  $\beta$ -carotane concentrations. The sterane concentrations may also be affected by the salinity of this type of environment. Short chain steranes may be present in a high concentrations and diasteranes are commonly present in low abundance (MCKIRDY et al., 1984; CASSANI 1986; CONNAN et al., 1983), whereas C<sub>30</sub> steranes suppose to be found in most types of marine oils.

In contrast to the steranes, the precursors of tricyclic terpanes may be suppressed by the hypersalinity in carbonate deposition. This may lead to a different biomarker patterns from oils generally derived from hypersaline environment (CASSANI 1986; PALACAS et al., 1984). Significant concentrations of 28,30-bisnorhopane 25,28,30-trisnorhopane and gammacerane are typical for such oils which are similar to those derived from evaporitic marine environments. These similarities presumably reflect the similar salinity and chemical characteristics of both environments. In summary, there are some biomarker characteristics that are both shared between oils derived from marine carbonate and marine evaporitic environments.

#### Marine Deltaic

Source rocks and oils derived from marine deltaic depositional environment have a predominance of medium to high molecular weight n-alkanes from an input

of terrestrial higher plants. Pristane/phytane ratios are always close to/or  $< 1$ , and linked to a slight even/odd n-alkanes. Other features are a predominance of  $C_{35}$  over  $C_{34}$  hopanes, and the presence of relatively high concentration of low molecular weight steranes. Diasterane concentrations in these samples depend on the level of maturity and amount of clay minerals in their deposition consistent with high terrestrial organic input. The presence of  $C_{30}$  steranes can still be seen which indicates the marine contribution to the depositional environment.

The main distinguishable biomarkers for samples derived from this type of marine environment are the terpene distributions. These include biomarkers diagnostic of higher plant inputs. An abundance of  $18\alpha(H)$ -oleanane has been suggested to originate from precursors in higher plants present in the angiosperm. Presently,  $18\beta(H)$ -oleanane has been reportedly linked to a terrestrial input in predominantly Tertiary basins, mainly of deltaic nature (GRANTHAM et al., 1983; PHILIP and GILBERT, 1986; BROOKS, 1986). The occurrence of high abundance of the  $C_{24}$ -tetracyclic terpene relative to the tricyclic terpene may appear to be an indicator of a significant input of higher plant material (TRENDEL et al., 1982). Hence, the presence of a high abundance of  $18\alpha(H)$ -oleanane and the  $C_{24}$ -tetracyclic terpenes plus an abundance of high molecular weight alkanes can be used to specifically indicate the deltaic origin in this type of

marine deposition. Examples of oils derived from deltaic environments have been reported that those originated from the Mahakam delta in Indonesia (SCHOELL et al., 1983; GRANTHAM et al., 1983; HOFFMANN et al., 1984) and the Beaufort-Mackenzie delta in Canada (BROOKS, 1986).

#### LACUSTRINE DEPOSITIONAL ENVIRONMENTS

A lacustrine depositional environment may be defined as an inland body of standing water occupying a depression in the Earth's crust (KELTS, 1988). As such, lakes can exhibit a wide range of possible settings, sizes, chemistries, concentration of mineral salts and morphologies. Lacustrine deposition has been generally applied to limnic or freshwater environments and brackish to hypersaline ecosystems. They are dynamic systems with rates of change greater than marine environments (VOLKMAN, 1988) and may be archived by the geochemical signals in organic matter and lacustrine carbonates, as well as changes in biota. The importance to understanding lacustrine deposition environments is to discern which type, or types of lakes are likely to contain important petroleum reserves. Differences between lacustrine and marine environments are due to the environmental sensitivity of lake to their regional setting and the accompanying biological diversity. Therefore, the major differences lie in the variable geochemical signature, carbonate mechanism and biota. Biological markers which characterize original organic

source precursors and reveal the typical characteristics of both types of lacustrine environments therefore will be discussed following.

#### Lacustrine Freshwater

Simple biomarkers characterize samples derived from this type of environment are an odd/even n-alkane dominance in n-alkanes distribution plus the bias towards high molecular weight n-alkanes ( $>C_{23}$ ). This bias indicates a major contribution of long chain lipids from higher plant algae (DIDYK et al., 1978; MCKIRDY et al., 1986). The high pristane/phytane ratios will reflect the relationship between their precursors and the chemistry of the environment (ten HAVEN et al., 1987), e.g. low salinity rather than simply the anoxic/oxic condition of sedimentation (DIDYK et al., 1978). Pristane has been reported as originating from phytol (DIDYK et al., 1978) and/or tocopherols (GOOSSENS et al., 1984) of photosynthetic organisms whereas phytane may arise in part from phytol or more likely from archaeobacterial lipids in organisms such as methanogens and halophiles (KAPLAN and BAEDECKER, 1970; RISATTI et al., 1984; ten HAVEN et al., 1985). In a freshwater environment, photosynthetic organisms containing phytol and tocopherols would be expected to be abundant. Thus, the more saline the environment, the greater the potential for an increase in the concentration of phytane precursors. This can be an explanation of the high

predominance of pristane in freshwater environments compared with dominance of phytane in hypersaline environments (ten HAVEN et al., 1985, 1987).

The characteristic features of other biomarker distributions can be based on the occurrence or absence of such a specific compound. The comparatively low relative abundances of C<sub>25</sub> and C<sub>30</sub> isoprenoids are consistent with a freshwater origin, since their biological source are held to be archaebacteria which might to be expected to be relatively more abundant in marine or more saline waters. (WAPLES et al., 1974; ALBAIGES, 1980; BRASSELL and EGLINTON, 1986). In general, source rocks or oils derived from lacustrine freshwater environments usually have low concentrations of steranes and an absence of C<sub>30</sub> steranes which can be held to be diagnostic of marine environments (MOLDOWAN et al., 1985; MCKIRDY et al., 1986). A predominance of C<sub>29</sub> steranes will indicate a major concentration of higher plant material in non-marine environments. But the interpretation of C<sub>29</sub> sterane predominance as an indication of higher plant input or as characteristic of a non-marine environments must be made with caution since C<sub>27</sub> steranes which dominate in oils from the Brazilian lacustrine freshwater environments have been reported by MELLO et al. (1988). The presence bacteria, which contain documented as precursors for the hopanes and tricyclic terpanes (OURISSON et al., 1979, 1982) will effect the abundance and distribution pattern of those



biomarkers. Gammacerane may be found in a low concentrations. A diagnosis of this biomarker was first specified to be a biomarker of lacustrine environment (SEIFERT and MOLDOWAN, 1981). Recently, it has been reportedly found in source rock and oil derived from marine carbonate and hypersaline environments (MELLO et al., 1984; MCKIRDY et al., 1986; FU JIAMO et al., 1986). It has been stated by MOLDOWAN et al. (1985) that gammacerane can not be used to distinguish between marine and non-marine samples even though the only biological-occurring compound with a gammacerane type structure is tetrahymanol, a constituent of protozoa (BRASSELL and EGLINTON, 1986). Such evidence suggests the possibility of a bacterial origin for gammacerane, given its widespread occurrence in time and space. Hence, the potential quantitative value of gammacerane is strongly suggested as an environmental indicator owing to its relative abundance and concentration rather than its mere presence.

#### Lacustrine Saline Water

The increased salinity of this type of lacustrine environment compared to lacustrine freshwater environment will effect the character of the deposition and sedimentation of organic matter. Plants from saline environments preferentially utilize carbonate complexes as their carbon source for photosynthesis. As a sequence, oils derived from this type of environment may

be isotopically heavy than those from lacustrine freshwater environments. The predominance of pristane over phytane and the odd/even n-alkane preference is somewhat unexpected since oils derived from saline lakes generally show opposite characteristics (ten HAVEN et al., 1988; MOLDOWAN et al., 1985; FU JIAMO et al., 1986). Such a difference may reflect the establishment of a lacustrine environment with a moderate salinity rather than hypersaline conditions. A more saline environment might increase the abundance of phytane precursors (archaeobacteria) over pristane precursors. Alternatively, the difference could simply reflect the added input from higher plants, since the wax content and bimodal n-alkane distribution (maxima at C<sub>16</sub> and C<sub>28</sub>) clearly indicates the importance of such contributions. Higher concentrations and relative abundance of the regular C<sub>25</sub> isoprenoids and i-C<sub>30</sub> (squalane) compared to lacustrine freshwater conditions are expected to be found. The abundance of these biomarkers may reflect an increase in salinity of the depositional environment (BRASSELL et al., 1988). The presence of  $\beta$ -carotane albeit in small amount concentrations, can also characterize its occurrence.  $\beta$ -Carotane was first identified in saline sediments by MURPHY et al. (1967) and more recently, HALL and DOUGLAS (1983) suggested that its presence might be related to a lacustrine saline environment. MOLDOWAN et al. (1985) regarded  $\beta$ -carotane as a terrestrial marker because it has not been reported

from source of marine origin. Its abundance in samples from lacustrine saline and hypersaline environments (SHI JI-YANG et al., 1982; JIANG and FOWLER, 1986) is supported by the suggestion that salinity is the controlling characteristic of  $\beta$ -carotane concentration.

Steranes can be detected in a low concentrations and the C<sub>30</sub> steranes would be absent. These features have been considered characteristic of non-marine oils (MCKIRDY et al., 1986; MOLDOWAN et al., 1985). A significant feature of these oils is the presence of higher concentrations of low molecular weight C<sub>21</sub> and C<sub>22</sub> steranes and 4-methylsteranes than in the oils derived from freshwater lacustrine environments. These compounds have been associated with carbonate and hypersaline environments (ten HAVEN et al., 1985; CONNAN et al., 1986; FU JIAMO et al., 1986). The predominance of C<sub>29</sub> steranes over C<sub>27</sub> steranes can be used to designate non-marine environments. The concentration of the bacterially-derived hopane might be extremely high, reflecting the importance of bacteria lipids in saline lakes. In addition, the prominence of tricyclic components ranging from C<sub>20</sub>-C<sub>35</sub> can be a result of the specific saline condition of each lake. Tricyclic terpanes have been recognized in oils from various origins and may arise from bacterial precursors, perhaps specific membrane lipids (OURISSON et al., 1982). The Ts/Tm ratios depend on a specific source input or mineral matrix in the depositional environment.

The pentacyclic triterpane distribution is always seen in general. The  $17\alpha(H), 21\beta(H)$  28,30-bisnorhopane and 25,28,30-trisnorhopane have been recognized in many oils (GRANTHAM et al., 1980; VOLKMAN et al., 1983). It has been suggested that they originate from a similar natural precursor, perhaps in anaerobic to strongly anoxic conditions. (GRANTHAM et al., 1980; ROLLKOTTER et al., 1982). Recent evidence indicates that these triterpanes occur as free hydrocarbons rather than being released from kerogen (NOBLE et al., 1984). The presence of these compounds then may indicate that the salinity at the time of sediment deposition (and consequent increase in anoxicity) plays a role in its occurrence. Similarly, the variable, but significant, concentrations of gammacerane are also a quantitative measure of the salinity of the environment of deposition (ten HAVEN et al., 1985; FU JIAMO et al., 1986).