CHAPTER 3: PRINCIPLES OF ORGANIC MATTER EVALUATION

Chapter 3

Principles of Organic Matter Evaluation

3.1 Quantity of Organic Material

Almost all measurements of the amount of organic matter present in a rock are expressed as TOC values in weight percent of the dry rock. Peters and Moldowan, (1993) showed that rocks containing less than 0.5% TOC are considered to have negligible hydrocarbon-source potential. The amount of hydrocarbons generated in such rocks is so small that expulsion simply cannot occur. Furthermore, the organic matter in such lean rocks is often highly oxidized and thus of low source potential. Rocks containing between 0.5% and 1.0% TOC are marginal. They will not function as highly effective source rocks, but they may expel small quantities of hydrocarbons and thus should not be discounted completely. Organic matter contains less than 1% TOC are commonly oxidized, and thus of limited source potential. Rocks containing more than 1% TOC often have good source potential. TOC values above 2% often indicate highly reducing environments with excellent source potential. Many rocks with high TOC values, however, have little oil-source potential, because the organic matter which they contain are woody or highly oxidized.

However, in this study TOC analysis was not preformed considering that all of the studied samples (i.e. coals and coaly sediments) are rich in organic matter.

3.2 Type of Organic Matter

Microscopic kerogen-type analysis describes the proportions of the various macerals present in a sample. These macerals are normally divided into oil-generative, gas-generative, and inert. The oil-generative macerals are those of Type I and Type II kerogens: alginite, exinite, resinite, cutinite, fluorescing amorphous kerogen, etc. Gas-generative kerogen is mainly vitrinite. Inertinite is considered by most workers to have no hydrocarbon-source capacity. Coal therefore has potential for oil generation depending on the type of macerals (Teichmuller, 1974; Stach, et al., 1984, Cook and Struckmeyer, 1986; Wan Hasiah, 1997a &b, 1999a, 2001).

3.2.1 Coal Macerals

A maceral is an elementary microscopic constituent of coal that can be recognized by its shape, morphology, and reflectance (Stopes, 1935). Broadly, the term is equivalent to mineral in rocks and synonymous with kerogen. Morphology is the main factor determining the classification of macerals.

There are three macerals groups: vitrinite, inertinite and exinite (liptinite). These are all subdivided into maceral subgroups and macerals.

The liptinite group is relatively enriched in hydrogen compared with the other two groups. Inertinites have greater carbon content and vitrinites have an intermediate chemistry. As rank increase the differences in the chemistry between the groups decreases (Stach, et al., 1982).

The vitrinite group generally represents the woody plant material (stems, trunks, roots and branches). Liptinite includes the more resistant parts of plants like spores, cuticles and resins. Inertinite originates from the same material as the vitrinite group

however, the oxidation endured before coalification has changed its optical properties and chemistry.

These coal macerals are distinguished by their optical characteristics of color, relief of the polished surface, morphology and reflectance and fluorescence (Tissot and Welte, 1984). Liptinite is identified by characteristic shape, high transmittance and intense fluorescence at lower levels of maturity and low reflectance compared to other maceral groups. Vitrinite is composed of angular to subangular particles, sometimes showing cell structure. Vitrinite is identified by moderate transmittance, intermediate reflectance, and usually absence of fluorescence. Inertinite is angular, high reflectance, often showing celluler outline or granuler texture. They show no fluorensce and are opaque in transmitted light.

3.2.2 Oil Generation and Macerals

Early opinion was that vitrinite was gas-prone, liptinite was oil-prone, and inertinite had little or no petroleum generation potential (Tissot and Welte, 1984). It is clearer that now not only liptinite, but also perhydrous vitrinites, have the potential to generate hydrocarbon liquids in the course of natural coalification (e. g. Khorasani, 1987). Some liptinites, especially alginite, cutinite, and suberinite contain a higher proportion of aliphatic fractions in their structure than other liptinites, such as sporinite and resinite, and are, therefore, more oil prone (Wilkins and George, 2002).

Littke and Leythaeuser (1993) have summarised observations that indicate there could have been important petroleum generation from coals:

- Coals may contain significant quantities of the hydrocarbon-rich and hydrocarbon-generating maceral group liptinite.
- When heated, coals produce petroleum-like pyrolysis products.

- Bituminous coals contain bitumen that can be easily released by extraction using common solvents.
- Coals are major source of methane.
- Some gas and oil accumulations occur in close proximity to coal seams.
- The maturation sequence of terrestrial organic matter through peat, bituminous coal and anthracite implies a significant loss of volatile products, including hydrocarbons.

Table 3.1 is summary of macerals in relation to kerogen type and hydrocarbon potential.

Maceral Group	Vitrinite Reflectance	Fluorescence	Kerogen type	Origin	Hydrocarbon potential
Liptinite	Low	Yellow or green	I II	Green algae and blue-green algae Waxy, lipid-rich and resinous of plants	High oil and gas producing
Vitrinite	Moderate	None or poor	III	Cell lumens, woody tissue of stems, bronches, leaves and roots of plants	Prone to gas generation
Inertinite	Very high	None		Bark, stems, leaves, roots	Not prone to oil and gas

Table 3.1: Summarized of macerals in relation to kerogen type and hydrocarbon potential (summarized after Hunt, 1995).

3.3 Maturation of Organic Matter

Thermal maturity, a measure of the level of diagenetic alteration of organic matter in sedimentary rocks, provides a means of ascertaining the relative and, ideally, the absolute maximum temperatures to which sedimentary rocks have been exposed. Although various indicators of the level of thermal maturation (vitrinite reflectance, thermal-alteration index, conodont color alteration index, Rock-Eval pyrolysis) respond somewhat differently to time and temperature (Hood et. al., 1975; Héroux et. al., 1979), all appear to record the maximum temperature to which rocks have been exposed and are not susceptible to retrograde effects. In the absence of igneous heat sources, diagenetic temperatures are primarily a reflection of burial heating.

The most commonly used maturity parameters today are spore color (Thermal Alteration Index, or TAI), vitrinite reflectance, and pyrolysis temperature. Less commonly used are fluorescence and conodont color (CAI). A few of these parameters will briefly be discussed. Table 3.2 shows parameters used to estimate maturity (after Hunt, 1995).

Vitrinite Reflectance (VR) is the most commonly used organic maturation parameter. This is mainly because it is reasonably accurate, quick, non-destructive and inexpensive. Furthermore Vitrinite is a common constituent of coal and shales. Reflectance measurements must be made only on vitrinite group macerals, since the other macerals mature at different rates (Teichmuller, 1982).

As coal rank increases, and the chemical composition of vitrinite correspondingly changes, the vitrinite macerals become increasable reflective. Therefore, the percentage reflection of a beam of normal incident white light from the surface of polished vitrinite is a function of the rank (maturity) of the maceral. Vitrinite maturation is not affected significantly by pressure, only by temperature (Hunt, 1995).

Approximate $\%R_0$ values have been assigned to the beginning and end of oil generation ($\%R_0$ 0.50 – 1.30) (Hunt, 1995). However, kerogen types appears to be a major control on the relative range of the oil window. A source rock rich in type II and III kerogen dominated by suberinite, terpene resinite, and bituminite seem to have the top of the oil window at about $\%R_0$ 0.40 (Khorasani, 1987; Wan Hasiah, 1997 & 1999).

Biomarkers are transformed by thermal reactions, whose rates are controlled by subsurface temperatures and the length of time exposed to those temperatures. Biomarkers can therefore be used as indicators of the total thermal history of the organic matter, and hence as indicators of maturity. However, because they occur in the mobile bitumen fraction of rocks and sediments, biomarkers can be used as maturity indicators only if the bitumen is indigenous (Waples and Machihara, 1990).

Maturation rank				Microscopic parameters						Chemical parameters						
								Fluorescence			Pyrolysis					
Kero-gen	Coal	% Volatiles in coal (d.a.f.)*	Max. paleo Temp. °C	Vitrin refl. $\%R_0$	TAI	SCI	Conodant alteration index	Color of alginite	λ Max (nm)	CPI	T_{max}	P.I.	C wt%	H wt%	H/C wt%	Hydro-carbon products
Diagenesis	Peat			0.2	1 Yellow			Blue green		5			67	8	1.5	Bacterial gas
	Lignite	60		0.3		1	1 Yellow	Greenish yellow	500	3	400		70	8	1.4	Immature heavy oil
	Sub-bitumin C			0.4		2		Golden yellow								
	B			0.5		3			540	2	425	0.1	75	8	1.3	
	A	46	50	0.6	2 Orange	4				1.5	435					
Catagenesis	High volatile bituminous C			0.7								0.2	80	7	1.1	Wet gas and oil
	B			0.8				Dull yellow								
	A	33	80	0.9		5	2 Light brown		600	1.2						
	Medium volatile bitumin			1.0		6		Orange	640	1.0	450	0.3	85	6	0.85	
		25	120	1.3				Red				0.4				Condensate
				1.5	3 Brown	7			680		475		87	5	0.7	
	Low volatile bitumin		170	2.0		8	3 Brown									
	Semi-anthrac.	13		2.5	4 Brown/ black	9					500					Dry gas
Metagenesis			200	3.0			4 Dark brown	Nonfluorescent			550		90	4	0.5	
	Anthra-cite												94	3	0.38	
		4	250	4.0	5 Black	10	5 Black									
	Meta-anthrac.			5.0									96	2	0.25	

*Dry ash free

Table 3.2: Parameters of organic maturation, R_0 = reflectance with oil immersion; CPI = carbon preference index; PI = production index (Hunt, 1995).

3.4 Biomarkers

Biomarkers are structurally complex components of petroleum and rocks derived from biological molecular precursors, such as chlorophyll, sterols, and hopanoids (Peters and Moldowan, 1993). Mackenzie (1984) defined biomarkers as an organic compound detected in the geosphere whose basic skeleton provides an unambiguous link with a known natural precursor. They are transformed by thermal reactions, whose rates are controlled by subsurface temperature and length of time exposed to those temperatures.

The use of biomarkers in petroleum exploration has increased significantly due to development of gas chromatography-mass spectrometry (GC-MS), which is now used routinely for separating and identifying compounds is complex mixtures such as crude oils and rock extracts. Biomarker analyses can also aid in understanding and identifying the processes of transformation of organic matter after deposition (Philp, 1985).

The biomarker components of oils and rock extracts are used to assess the depositional environment, original type of organic matter, and thermal maturation level of source rocks. Biomarkers can also be used to recognize biodegradation and other alteration process in oils and sediments, and for oil-to-oil or oil-to source rock correlations (Eglinton and Calvin, 1967; Mackenzie, 1984; Philp, 1985; Peters and Moldowan, 1993). To be useful in oil exploration, biomarker structures must be sufficiently stable to survive the diagenetic and catagenetic processes in petroleum formation and must have an original precursor concentration high enough to be easily detectable in petroleum ultimately formed (Hunt, 1996).

Generally, biomarkers are used in petroleum exploration as an indicator: (1) of the depositional environment of source rocks (Didyk et al., 1978; Brassell and Eglinton, 1986; Fu Jiamo, et al., 1990), (2) of the type of organic matter from which oil is derived (Tissot and Welte, 1984), and (3) of the maturity of source rocks, crude oils, and

condensates (Eglinton and Calvin, 1967; Seifert and Moldowan, 1979; Mackenzie, 1984). The principal biomarker parameters used in paleoenvironment assessment and their implications are summarized in Table 3.3

The strength of biomarkers is in their ability to provide detailed information beyond what is available using only screening and microscopic parameters. However, biomarkers, screening, and microscopic techniques are best used together to provide the most reliable geological information on characterization of source rocks, thermal maturity, and biodegradation.

3.4.1 N-alkane

N-alkanes are the dominant natural hydrocarbon in organic materials and the most abundant in organisms. They have been isolated from bacteria, phyto-plankton, zooplankton, benthic and pelagic algae, and from higher level organisms of terrestrial and aquatic origin. The major alkanes found in organisms and sediments are normal alkanes and isoprenoids, which are structurally similar to biological acids and alcohols, and in many instances may be derived from these biological precursors. 0n the other hand, the relatively high concentration of alkanes in sedimentary deposits, as compared to those found in organisms, is at least partially due to their low chemical and catabolic activity which result in a preferential preservation and consequent relative enrichment of these compounds in deposits (Tissot and Welte, 1984)

3.4.2 Terpanes

A broad class of complex, branched, polycyclic alkane biomarkers commonly monitored using m/z 191 mass chromatograms. Many of the terpanes originate from bacterial membrane lipids (Ourisson et al., 1982).

Parameter	Description	Calculation	Indication	General explanation	Reference
Major peak carbon	The most abundant n-alkane	RIC or *m/z* 85	Organic input	– C_{17} main peak indicates algal input . Single peaks of C_{27} ,C_{29} or C_{31} imply higher plant input . Bimodal distribution is interpretated as mixing sources .	Brassell ,1978 Tissot *et al* , 1977 Caldicoff and Eglinton , 1973
C_{31}/C_{17}	$n-C_{31}/n-C_{17}$	*m/z* 85	Organic input ; values less than 0.5 indicate extensive algae input while values greater than 2 reflect higher plant input .	Generally , algae are rich in $n\text{-}C_{17}$ and higher plants contain abundant $n\text{-}C_{31}$.	Brassell *et al* , 1978 Gelpi *et al* ,1970 Eglinton *et al* ,1962
Pr/C_{17}	Pristane / $n\text{-}C_{17}$	RIC	Values greater than 1 imply algal source .But the value may be reduced with increasing degradation .	Pristane is thought to be of algal input,generally originated from chlorophyll and dehydro vitamin E .The parameter may be influenced by maturity and the rearrangement of hydrocarbons .	Blumer *et al* . 1971 Blumer and Snyder, 1965 Forsberg and Bjory, 1983 Mackenzie *et al*.1983 Leythauser and Schwarzkopt.1986
Ph/C_{18}	Phytane / $n\text{-}C_{18}$	RIC	Organic input ; values > 1 are regarded as to be of ancient bacteria source	High ratios are always indicative of strongly reducing environments .	Risatti *et al* ,1984 Didyk *et al* ,1978
Pr/Ph	Pristane / Phytane	RIC	Ratios less than 1 indicate ancient reducing environments .	The parameter is source-dependent .Pr and Ph may have been derived from aquatic organisms and bacteria in addition to chlorophyll .	Blumer and Snyder, 1965 Prahl *et al*.1985 Didyk *et al*.1978 Pratt *et al*.1986 Ten Haven *et al* .1985 Powell and Mckirdy , 1983
$iC_{25}+iC_{30}$	The percentage of C_{25} and C_{30} isoprenoids in relation to total isoprenoids	*m/z* 85	Organic input : the two compounds are thought to be methanogenic .	6 ,10 ,15 ,19-pentamethyl eicosane is methanogenic.	Brassell *et al*. 1981 Risatti *et al*. 1984 De Rose *et al*. 1983 Waples *et al* .1974
β/nC_{17}	β- carotane / nC_{17}	RIC	Environment	Abundant β-carotane is favored by reducing or hypersaline environments	Hall and Dauglas.1983 Jiang and Fowler.1986
C_{27} /T C_{28} /T C_{29} /T	$\Sigma C_{27}/\Sigma$ Sterane $\Sigma C_{28}/\Sigma$ Sterane $\Sigma C_{29}/\Sigma$ Sterane	*m/z* 217	Organic input ; algal input is indicated by large C_{27}/ T. C_{29}/ T ratio is a criterion of higher plant input or other algal species	Maturity dependent	Seifert *et al* , 1983 Williams and Dauglas, 1983 Huang and Meischein, 1979 Volkman , 1986

Table 3.3: Biomarkers: Calculation and explanation of their parameters (from Fu Jiamo et al., 1992)

Parameter	Description	Calculation	Indication	General explanation	Reference
20S%	$C_{29}\ \alpha\alpha\alpha\ \frac{20S}{20S+20R}$	*m/z* 217	Increasing with increasing maturity. Equilibrium value 55%	20S and $\alpha\ \beta\ \beta$ increase with increasing maturity	Mackenzie *et al.*1980
$\beta\beta$%	$\frac{C_{29}\ \alpha\ \beta\beta\ 20\ (S+R)}{\alpha\beta\beta+\alpha\alpha\alpha\ 20\ (S+R)}$	*m/z* 217			
4-me- index	ΣC_{30}-4-methyl / C_{29} (20S+20R) sterane	*m/z* 231 / *m/z* 217	Organic input; 4-me-sterane is contributed by methanogenic algae.	4-me-steranes are diagenetic products of 4-me-sterol concentrated in methanogenic algae.	Robinson *et al.*1984 Wolft *et al.* 1986a Woltt *et al.* 1986b Boon *et al.* 1979
Rearranged sterane index	20R+20SC_{27} rearranged sterane 20R+20S$C_{29\alpha\alpha\alpha}$ sterane	*m/z* 217	Under diagenetic conditions high ratios may be indicative of an environment of abundant clay, or, otherwise, carbonate environment.	Clay may have acted as a catalyzer for the rearrangement of steranes to form rearranged steranes. Also maturity-dependent.	Machkenzie *et al.*, 1982 Rubinstein *et al.*, 1975 Rullkotter, 1983
Hopane / Sterane	$C_{29\alpha\beta}$ hopae / ΣC_{29} sterane	*m/z* 191 / *m/z* 217 /	High ratios (>10) indicate abundant terrestrial inputs.	The ratio is sensitive to the relative proportion of algae and terrestrial organisms. It may also be affected by bacterial reworking.	Hoffman *et al.*1984 Mackenzie *et al.*1982 Cassani and Eglinton. 1986 Moldowan *et al.* 1985
$\beta\alpha/\alpha\beta$	$\beta\ \alpha$ moretane / $\alpha\ \beta$ hopane	*m/z* 191	Maturity	May also be affected by source matefial.	Ensminger *et al.*1977 Seifert and Moldwan. 1980
22S%	$C_{32\alpha\beta}$22S/22S+22R	*m/z* 191	Maturity; variation range: 0−60	The 22R biological structure would be changed into the more stable 22S structure with increasing maturity.	Mackenzie *et al.*1980 Ensminger *et al.*1977
Gammacerane index	Gammacerane / $\alpha\beta C_{30}$ hopane	*m/z* 191	A source indicator	Recognizable in all environments but high abundances are found in brackish and subbrackish basins.	Hills *et al.*. 1966 Brassell and Eglinton. 1983 Shi *et al.*1982 Fu *et al.*1986. 1982
Homohopane index	C_{35} (22S+22R) homohopane / C_{32} (22S+22R) homohopane	*m/z* 191	High ratios are associated with hypersaline sediments.	The distribution of C_{35}> C_{34}>C_{33} is commonly noticed in hypersaline environments.	Ten Haven *et al.* 1985.1988 Fu *et al.*1986.1988 Brassell *et al.*.1988 Mello *et al.*1988

Table 3.3: Continued

The bacterial terpanes include homologous series such as bi-, tri-, and tetra- and pentacyclic terpanes. These compounds can be used for characterization of depositional environments, source of organic matter and thermal maturity.

The pentacyclic triterpanes commonly contain 27- 35 carbon atoms in a naphthenic structure. They are often divided into hopanoids and nonhopanoids. Hopanoids include both the 17α (H), 21β (H) hopanes and 17β (H), 21α (H)hopanes (moretanes).

A pair of C_{27} hopanes, 17α (H)-22, 29, 30-trisnorhopane (Tm) and 18α (H)-22, 29, 30-trisnorhopane (Ts), are widely used. Tm is believed to represent the biologically produced structure; Ts is generated from it by either diagenetic or thermal processes or both (Peters and Moldwan, 1993). All these biomarkers originate from microorganism (Waples and Mahihara, 1990).

Common group of non-hopanoid are the oleananes. These pentacyclics occur in Cretaceous or younger rock and oils, and are thought to originate from terrestrial angiosperms (Ekweozor and Udo, 1987).

Tricyclic and tetracylic triterpanes do not appear to be degraded pentacyclics, but rather members of separate genetic families. They are probably either generated in smaller quantities by the same bacteria that produced the pentacyclics, or by other species of microorganisms that synthesize them instead of pentacyclics (Waples and Mahihara, 1990). Figure 3.1 shows structures and names for typical triterpanes.

3.4.3 Steranes

Steranes are derived from the sterols commonly found in higher plants and algae but which are rare or absent in prokaryotic organisms (Volkman, 1988). Sterol precursors containing 27, 28, 29, and 30 carbon atoms have been identified that give rise to four different "regular" steranes during diagenesis (Figure 3.2).

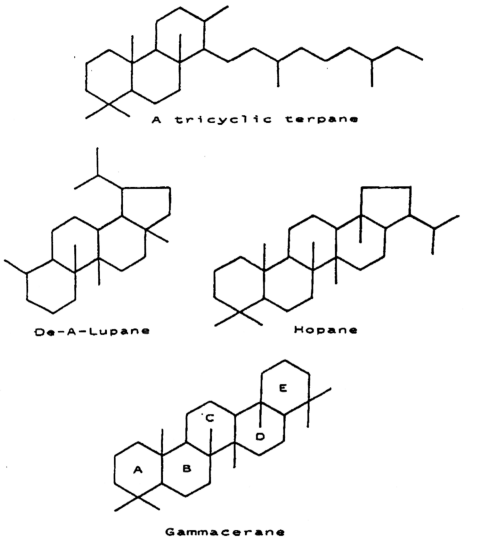


Figure 3.1: Chemical structures and names for typical triterpanes. Rings are identified by letters. (Waples and Machihara, 1990)

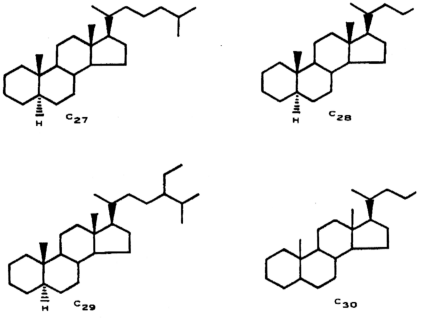


Figure 3.2: Structures of $C_{27} - C_{30}$ steranes.

These four steranes are members of a homologous series because they only differ by the addition of a sequence of -CH2- units at a certain place in the molecule. The term "regular" indicates that the carbon skeletons are the same as in the biological precursors.

The C_{27}-C_{29} steranes are sometimes referred to as cholestane, ergostane, and sitostane, respectively. They can also be named as derivatives of cholestane: cholestane, 24methylcholestane, and 24-ethylcholestane.

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 are generally very similar. In particular, all newly formed steranes are believed to exist only as the ααα-20R epimer (Figure 3.8), because only that form is produced biologically.

Other studies, however, suggest that stereochemical changes can occur at C-14 and C-17 during diagenesis. The sterol molecules have hydrogen atoms in the α configurations at both these positions. This form is designated "5α (H), l4α (H), 17α (H)" or "14α (H), 17α (H)", or more simply "ααα" or "αα". Although most diagenetically produced steranes will also be of the αα: form, the 5α (H), 14β (H), 17β (H) form (αββ or ββ) may also be produced during diagenesis, especially under hypersaline conditions (ten Haven *et al.,* 1986; Peakman and Maxwell, 1988; Rullkötter and Marzi, 1988; Peakman *et al.,* 1989). ββ steranes are also "regular" steranes.

3.5 Biomarker Parameters

Biomarker indicators differ from the other organic parameters because they represent single molecules found in both the liquid and solid phase of OM. They are found in oils, asphalts, asphaltenes, and pyrobitumens as well as in kerogen and coal. Their complex structure provides more information about their source material, depositional environment, thermal maturity and, in some cases, geological age than do any other geochemical parameters. Biomarker, and other maturation parameters, can be used to calibrate models of generation of oil and gas versus the time of trap and fault formation, so that one can predict the volume of petroleum available for migration to reservoir accumulation. Biomarkers can be used to estimate relative contribution of marine, lacustrine, and terresterial OM as well as to evaluate redox conditions of deposition.

3.5.1 N-alkane Isoprenoids Parameters

3.5.1.1 CPI Value

The relative abundance of odd versus even carbon-numbered n-alkanes can be used to obtain a crude estimate of thermal maturity of rocks and petroleum. This measurement is called the carbon preference index (CPI; Bray and Evans, 1961).

$$CPI= \{[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/ (C_{24}+C_{26}+C_{28}+C_{30}+C_{32})] +$$

$$[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/ (C_{26}+C_{28}+C_{30}+C_{32}+C_{34})]\}/2$$

CPI values considered as qualitative indicators of maturity and should be used in association with other independent indices. High CPI values (above 1.5) always indicate relatively immature samples. Low CPI values, however, don't necessarily mean higher maturity; they can also mean a lack of higher n-alkanes stemming from terrestrial input. Finally, it should be mentioned that an even predominance (CPI values

of 0.8 or less) may be observed in carbonate-evaporate sediments or sometimes has to be interpreted also as a sign of immaturity (Tissot and Welte, 1984).

However, the CPI values close to 1 indicate complete maturation (Simoneit, 1978). Environment of deposition may also influence the odd carbon predominance. In oxic or sub-oxic environments, alcohols and acids synthesized by living organisms, as even numbered carbon chain lengths can be decarboxylated (loss of CO_2) resulting in the even number acid or alcohol being reduced to an odd carbon numbered hydrocarbon. In strongly reducing environment, the oxygen of the acid or alcohol is removed as H_2O with no loss of carbon atom resulting in the formation of an even chain length.

3.5.1.2 Pr/Ph Ratio

Pristane and Phytane are regular isoprenoids that are present in relatively high concentrations in oils and coals and are easily detectable by using GC alone (Philp, 1985). They are thought to originate from the phytol side chain of chlorophyll (Brooks et al., 1969; Peters and Moldowan, 1993) (Figure 3.3), although pristane and phytane are also known to have other sources beside chlorophyll e.i. from zooplankton (Blumer et al., 1963). Under reducing conditions, phytane will form by dehydration and hydrogenation of the phytol, and pristane by decarboylation of phytane acid or by reduction of the phytol structure. Conversely, under oxidizing conditions, pristane forms by oxidation and decarboxylation of the phytol structure. Hence, the ratios of pristane to phytane reflect variations in the degree of oxidation during the early stages of chlorophyll degradation and can be used to distinguish types of environment (Powell and Mckirdy, 1973). Brooks et al., 1969 suggested that pristane forms in terrestrial or more oxidizing environments and phytane forms in more reducing or marine environments.

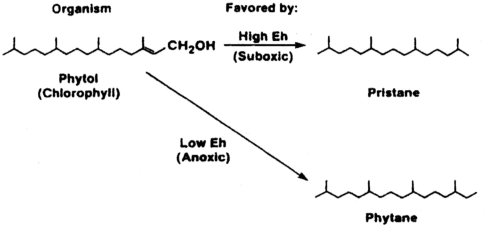


Figure 3.3: Diagenetic origin of pristane and phytane from phytol (derived from side chain of chlorophyll-a). Other source of acyclic isoprenoids having 20 carbon atoms or less includes chlorophyll-b, bacteriochlorophyll-a, α- and β-tocopherols, carotenoid pigments, and archaebacterial membrane components. The pristane/phytane ratio of petroleum provides information on the redox potential of the depositional environment for the source rock, but must be taken with caution. (Peters and Moldowan, 1993)

A high Pr/Ph ratio (>1), therefore, infers an oxidizing environment or a high content of terrestrial organic matter, whereas a low Pr/Ph (<1) suggests marine organic matter deposited in anoxic environments.

Volkman and Maxwell (1986) discussed how an oxic condition, results in Pr/Ph ratios greater than 1 and a ratio lower than 0.6 is related to anoxic conditions. Thermal maturity decreases the relative intensity of this ratio.

3.5.1.3 C_{31}/C_{17} Ratio

The dominant normal-alkanes in aquatic organisms (algae) are C_{15} to C_{19}. On the other hand, the terrestrial organisms are rich in normal-alkane C_{27} to C_{31}. This difference between land plants and aquatic organisms is summarized in (Figure 3.4). Waxes in the high-molecular-weight range, C_{27} through C_{31}, end up in coal and petroleum that is formed from land-derived organic matter. The C_{15}-through-C_{19} hydrocarbons are found in petroleum whose sources is largely aquatic organisms (Hunt, 1996). Therefore, C_{31}/C_{17} ratio can be used to show type of organic matter input. It should be noted to that lacustrine samples and lacutrine oils can be very waxy-these waxes come from freshwater algae.

3.5.1.4 Isoprenoid/N-alkane Ratios

Pristane/n-C_{17} and Phytane/n-C_{18} are sometimes used in petroleum correlation studies. Didyk et al. (1978) suggested that high Pr/n-C_{17} ratio (>1) for a petroleum was evidence that terrigenous plants played a major role in the origin of the petroleum and high ratios of Ph/n-C_{18} are always indicative of strongly reducing environments.

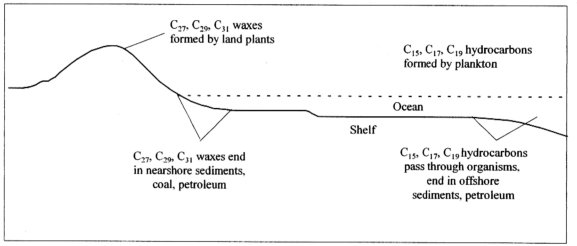


Figure 3.4: The contributions of odd-chain-length n-alkane molecules to sediments by land and marine organisms (Hunt, 1995)

Lijmbach (1975) indicated that oils derived from sediments deposited in open marine conditions are characterized by Pr/*n*-C_{17} ratios lower than 0.5, whereas those from inland peat- swamp environments show ratios higher than 1. Intermediate ratios in the 0.5 –1.0 range suggest depositional environments with alternating swamp and more open-water conditions.

As with the Pr/Ph ratio, thermal maturity diminishes the relative intensity of Pr/*n*-C_{17}.

However, Alexander et al. (1981) suggested the use of the ratios (Pr + n-C_{17})/ (Ph + n-C_{18}) because it is less affected by variations in thermal maturity than Pr/n-C_{17} or Ph/n-C_{18}. These ratios are also readily affected by secondary processes such as biodegradation. In which the n-alkanes are generally attacked by aerobic bacteria prior to the isoprenoids (Peters and Moldowan, 1993).

3.5.2 Triterpane Parameters

3.5.2.1 Homohopane Isomeration

Hopane isomerisation for C_{31} –C_{33} at C-22 (22S / (22S+22R)) are probably the most widely applied biomarker maturity parameters, and record the relative abundance of the more thermally stable 22S isomer (e.g. Peters and Moldowan, 1993; kolaczkowska et al., 1990) compared to the biologically-derived 22R stereochemistry (Figure 3.5).

The parameter is usually measured using the C_{31} homohopanes, although the C_{32} homologues are also commonly used due to the possible coelution of gammacerane with the former (Farrimond et al., 1998).

During maturation, the ratio rises from 0 to about 0.60; Seifert and Moldowan (1986) consider samples showing ratios in the range 0.50 to 0.60 as having barely entered oil generation while ratios in the range of 0.57 to 0.62 indicate that the main

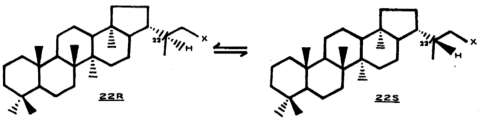


Figure 3.5: Structures of two diastereomeric 17(H)-extended hopanes (designated 22S and 22R), which are interconverted in a reversible reaction (from Waples and Machihira)

phase of generation has been reached or surpassed. After reaching equilibrium of 0.57-0.60 at the early generative stage, no further information is available because 22S/ (22S+22R) remains constant.

However, the inflection point in a plot of 22S/ (22S+22R) versus vitrinite reflectance or other maturity parameters can be used to calibrate these parameters to the onset of oil generation for a given source rock in a basin (Peters and Moldowan, 1993). It should be borne in mind; however, that isomeration is probably not the only process controlling the ratio of S+R isomers. Others controlling processing include the relative rates of destruction of both isomers and the relative rates of release of the isomers during hydrocarbon generation from kerogen.

3.5.2.2 Moretane/Hopane Ratios

The biological 17β (H), 21β (H)-hopane in organisms is very unstable and is not found in crude oils (unless contaminated by immature sedimentary organic matter).

The ββ-hopanes readily convert to 17β (H), 21α (H)-hopane (moretane) and 17α (H), 21β (H)-hopane. Both moretanes and hopanes are formed during diagenesis and the more labile moretanes decrease more rapidly during catagenesis compared to αβ-hopanes (Peters and Moldwan, 1993). As mentioned above, moretanes are much less stable than hopanes, and thus decrease in concentration more rapidly with increasing maturity. All or most of the moretane loss occurs at very low maturities. However, moretane are not present in living organism but form from hopanes at higher levels of maturity (Hunt, 1996). Moretanes/hopane ratios, like 22S/ (22S+22R) ratios for extended hopanes are mainly useful as a qualitative indicator of maturity (Grantham, 1986). This ratio is variable from about 0.8 in immature bitumens to values of less than 0.15 in mature source rocks and oils to minimum of 0.05 (Mackenzie et al., 1980; Seirfert and Moldowan, 1980)

3.5.2.3 Oleanane Index

The pentacyclic triterpenoid oleanane is frequently encountered in sediments younger than Late Cretaceous (Ekweozor and Udo, 1988) which contain organic matter derived from terrestrial higher plants, and in petroleum generated from such source rocks (Moldowan et al. 1994).

Oleananes are formed in sediments though diagenetic and catgenetic alteration of various 3β-funcionalized angiosperm triterpenoids (Figure 3.6) (ten Haven and Rullkotter, 1988).

Oleanane has two isomers: 18α (H)-oleanane and 18β (H)-oleanane. The α configuration is the most stable, thermodynamically; therefore, it is the predominant configuration in mature crude oils and rocks (Riva et al., 1988). So, the use of the oleanane index (oleanane/C_{30} hopane) when comparing samples showing major differences in maturity can be complicated by the presence of 18β (H)-oleanane in immature bitumens (Peters and Moldowan, 1993).

Oleanane Index is the ratio of oleanane (an angiosperm marker) to C_{30} 17α (H) hopane (a bacterial marker)

However, at high levels of maturity, the oleanane index tends to increase due to relative destruction of hopanes. High maturity oils could show a higher oleanane index than the original organic matter in the immature or low-maturity-level source rocks (Alberdi and Lopez, 2000).

According to Murray et al., 1997 the occurrence of oleanane in a mature sediments and oil is enhanced by contact of plant matter with seawater during early diagenesis.

3.5.2.4 Ts/Tm or Ts/ (Ts+Tm) Ratio

During Catagenesis, C_{27} 17α (H)-trisnorhopane (Tm or 17α (H)-22, 29, 30-trisnorhopane) shows a lower relative stability than C_{27} 18α (H)-trisnorhopane (Ts or 18

(H)-22, 29, 30-trisnorneohopane) (Figure 3.7). Therefore, the Ts/Tm ratio (sometimes reported as Ts/ (Ts+Tm) is commonly used for maturity assessment, although its variation with organic matter input is well understood (Seifert and Moldowan, 1978).

Farrimond, et al (1996) consider to the increase in Ts/Tm ratio to be caused by the relatively greater degradation of Tm. Therefore, the Ts/Tm or Ts/ (Ts+Tm) ratio should be used with caution.

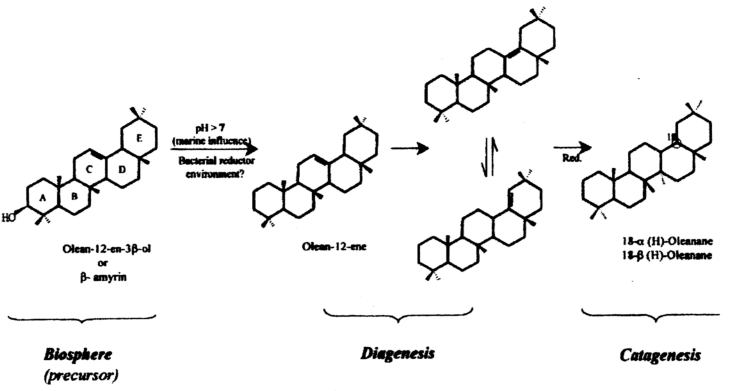
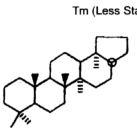


Figure 3.6: Scheme of diagenesis and early catagenesis of oleanane. Relationship precursor-oleanane (from Tan Haven et al., 1988)



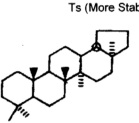


Figure 3.7: Structures of 17α (H)-22, 29, 30-Trisnorhopane (Tm) and 18α (H)-22, 29, 30-Trisnorneohopane (Ts). Ts is more stable to thermal maturation than Tm. (Peters and Moldowan, 1993).

3.5.2.5 C_{29}/C_{30} Hopane

Hopanes are a class of pentacyclic triterpane biomarker derived primarily from hopanoids in bacteria (Ourisson et al., 1984; Prince, 1987). The C_{29} and C_{30} 17α (H)-hopanes, the most common triterpanes in most samples, are used as environmental indicators. Oils and extracts from organic-rich carbonates (Zumberge,1984; Connan et al., 1986; Price et al., 1987) and evaporates (Connan et. al., 1986) may have unusually high concentration of C_{29} 17α(H)-hopane.

3.5.3 Sterane Parameters

3.5.3.1 20S/ (20S + 20R) Epimer Ratios

The most widely used biomarker maturity parameter is the proportion of two epimer forms (20R and 20S) of the αα steranes. This proportion has been expressed in a number of ways, including 20S/ (20S + 20R), %20S, and 20S/20R. The biologically produced form is exclusively ααα-20R, but with increasing maturity the proportion of 20S increases at the expense of 20R (Figure 3.8). Eventually equilibrium between the two forms is reached, comprising approximately 55% 20S and 45% 20R. Once equilibrium is reached, no further changes in maturity can be recorded (Waples and Machihara, 1990).

3.5.3.2 ββ/αα Ratios

ββ steranes are formed from αα steranes (Figure 3.8). The ββ/αα ratio for regular steranes has frequently been used as a maturity parameter (especially when cross plotted against 20S/20/R ratios), but these ratios can be as affected by diagenetic condition as by maturity (tan Haven et al., 1986; Peakman and Maxwell, 1988; Rullkötter and Marzi, 1988; Peakman et al., 1989; Waples and Machihara, 1990).

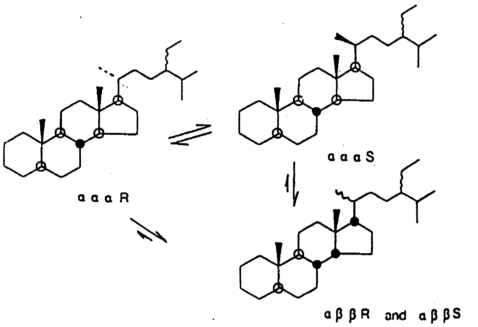


Figure 3.8: Reversible Intercoversion of 20R and 20S steranes (empires) and ααα and αββ steranes (diastereomers). The wavy line in the αββ structure at C-20 indicates that the stereochemistry at that Site is unspecified. (Mackenzie, 1984)