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ORGANIC MATTER MATURATION AND PETROLEUM GENESIS:-GEOTHERMAL versus HYDROTHERMAL

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I. ABSTRACT

Sedimentary organic matter is derived from the catabolic and diagenetic residues of primary biological carbon fixation and in some cases also from recycled organic detritus of older geologic formations. This organic matter undergoes maturation following diagenesis and is easily converted to gas and petroleum under the catagenetic and metagenetic temperature regimes of increasing burial.

Organic matter in immature, recent sediments is comprised of minor amounts (based on total organic carbon content) of biogenic gas (CH_4 and CO_2, sometimes H_2S), significant lipid residues of terrigenous and/or marine origins and a major macromolecular fraction consisting of fulvic and humic acids and particulate detritus (eg. biopolymer fragments, cell membranes and miscellaneous carbonaceous matter) the pseudokerogen. The lipids and macromolecular material undergo diagenetic (including microbiological) alteration according to the environmental conditions during transport and in the depositional sinks, ie. oxidative degradation in high-energy, oxygenated environments and reductive in anaerobic environments.

Maturation of organic matter commences after cessation of diagenesis with increasing burial and concomitant rise in the geothermal gradient. This produces some low temperature cracking products from the kerogen, such as gas (CH_4-C_8+) and bitumen (C_8-C_{40+}), which are superimposed on the endogenous biogenic gas and lipid residues. Maturation of pseudokerogen occurs via molecular rearrangements and addition of geomonomers by copolymerization. Further thermal stress during catagenesis generates additional bitumen and gas, which far exceeds the original concentrations of endogenous lipids and gas, thus erasing their compositional signatures and resulting in the characteristic distributions of petroleum compounds. The spent kerogen remains as amorphous carbon. The late stages of catagenesis and the subsequent high-temperature phase called metagenesis (very deep burial) generate primarily methane from both bitumen and kerogen, and H_2S can also be formed, especially in carbonate sequences.

Hydrothermal processes can also act on sedimentary organic matter and result in "instantaneous" diagenesis and catagenesis of recent biogenic detritus and thus produce analogous petroleum products. Gas (CH_4-C_8+, CO_2 and H_2S) and bitumen (C_8-C_{40+}) are cracked from the pseudokerogen and superimposed on the endogenous gas and lipids. Additionally, products characteristic of elevated thermal processes (eg. olefins, PAH, stabilized molecular markers, etc.) are also found in the bitumen. The spent kerogen remains as amorphous "activated" carbon.

Pressure, temperature and time effects on the chemistry of the organic matter are all interrelated. Temperature and time primarily effect petroleum genesis and are coupled with mineralogical interactions and the elemental compositions of kerogens. Migration processes are understood least. In sedimentary basins migration appears to occur by diffusion and in solution (CH_4/CO_2/ H_2O solvent). In hydrothermal areas migration proceeds by the previous processes and also by thermally driven diffusion, advection and mass transport as oil and/or emulsions, although the overall result may be the same for both regimes.

II. INTRODUCTION

Organic matter of sedimentary sinks, usually marine and either of Recent or geologically old origin, is derived from the syngenetic residues of posthumus biogenic debris (Simoneit 1978a; 1982a). This detritus is composed of both autochthonous detritus and allochthonous residues derived from continental sources (Simoneit, 1982a). Aquatic sediments receive organic detritus primarily by river washin and eolian transport, with ice-rafting and sediment recycling as minor contributing processes (Simoneit, 1975; 1978a).

The preservation of organic matter in sediments depends on the initial diagenetic processes involving microbial degradation and chemical conversion, coupled with the environmental conditions of acidity and redox potential (eg., Didyk et al., 1978; Demaison and Moore, 1980). Then, during subsequent sediment maturation and lithification, the organic matter is modified by the effects of temperature, pressure and petrology (eg., Hunt, 1979; Simoneit, 1978a; Tissot and Welte, 1978; Tissot et al., 1971).

The analytical techniques of organic geochemistry are ideally suited to examine the character of such organic matter in terms of its structural and compositional makeup (Simoneit, 1978a). The sources, the diagenetic and catagenetic histories and the migration mechanisms of this organic matter can then be evaluated from such data. It should be noted that in the following discussion organic matter is comprised of gas, lipids (bitumen), humic substances (with fulvic substances, or asphaltenes) and kerogen (with "pseudokerogen") as outlined in Table 1, which summarizes the equivalent organic fractions in contemporary (Recent) versus ancient samples.

Various basic organic geochemical procedures with only minor modifications have been in routine use for recent times to fractionate organic matter prior to instrumental analyses. They are described in detail elsewhere (eg. Reed, 1977; Boon et al., 1978; Deroo et al., 1978; Simoneit et al., 1979; 1980; 1981; Simoneit, 1978a; 1981; 1982a,b; Stuermer and Simoneit, 1978; Stuermer et al., 1978; Philp et al., 1978; van de Meent et al., 1980).

TABLE 1. Organic Matter of Sediments and Petroleum

SEDIMENTS:

Contemporary and Recent (generally biogenic components):

Gas -	Lipids -	Humic and Fulvic substances -	Carbonaceous detritus (humin, pseudokerogen)-
(CH_4, CO_2, H_2S)	$(C_8-C_{40}+)$	(macromolecular	(macromolecular,
minor amount	minor amount	M.W. $\sim 10^3$ to $>10^6$)	>humates)
of total C_{org}	(max. $\sim 10\%$)	variable amount	major amount

Geologically Ancient (generally geogenic components):

Gas -	Bitumen -	Asphaltenes (sometimes humates) -	Kerogen -
(CH_4-C_8, CO_2, H_2S)	$(C_8-C_{40}+)$	(macromolecular,	(macromolecular,
minor amount	minor amount	M.W. $\sim 10^4$ to $>10^6$)	>alphaltenes)
of total C_{org}	(max. $\sim 10\%$)	variable amount	major amount

Table 1. (continued)

PETROLEUM:

Composition (liquid products from mature sedimentary organic matter):

Gas (and gasoline range) -	Bitumen -	Asphaltenes -	Kerogen -
$(CH_4-C_8+, CO_2, H_2S, N_2)$	$(C_8-C_{40}+)$	(macromolecular,	(absent)
significant amount of	major amount	M.W. $\sim 10^4$ to $> 10^6$)	spent kerogen
total C_{org}		major and variable	remained in
		amount	source rocks

III. NATURE OF ORGANIC MATTER IN IMMATURE SEDIMENTARY SINKS

Organic matter that accumulates in contemporary sediments represents the residues from primary biological carbon fixation and its degradation (remineralization).

Gas:
  Interstitial gas in recent sedimentary environments consists primarily of methane, carbon dioxide and sometimes hydrogen sulfide (Claypool and Kaplan, 1974). The biogenic hydrocarbon gases usually have $CH_4/(C_2H_6+C_3H_8)$ ratios greater than 1000, while those of a thermogenic origin have ratios less than 50 (Bernard et al., 1976). For example, the $C_1/(C_2+C_3)$ ratios for shallow sediment gases from Guaymas Basin, Gulf of California range from 41-150 and thus indicate a mixed origin of biogenic (CH_4) and thermogenic (C_2-C_8) hydrocarbons (Simoneit et al., 1979). The depth range where biogenic gas can be found is variable but shallow ($\sim$100 m) and depends on microbial production and environmental conditions in the sediments.

Lipids:
  The lipids extractable from recent sediments, especially the hydrocarbons, have been examined most extensively. The compound classes which are commonly found as lipid components and which are reasonably stable over geologic times are: hydrocarbons (normal, iso-, anteiso-, alkene, aromatic and isoprenoid), fatty acids (also normal, iso-, anteiso-, unsaturated and isoprenoid), fatty alcohols, ketones, wax esters, steroids, terpenoids (sesqui-, di-, sester-, tri-, and tetra-), and tetrapyrrole pigments (Simoneit, 1978a; 1982a; Cranwell, 1982; Mackenzie et al., 1982a). The following additional compound classes are analyzed in recent sediments only, since their geologic half-lives are short: amino acids and peptides, purines and pyrimidines, and carbohydrates (Simoneit, 1978a). The homolog distributions and molecular markers of the first category of compound classes will be briefly illustrated with some examples and further details can be found elsewhere (Simoneit, 1978a and Cranwell, 1982 and references cited therein).

  Some typical examples of homologous compound distributions in lipids of generally immature sediments are shown in Figure 1. DSDP sample 36-330-10-1, 95-102 cm, which is of Jurassic age from the South Atlantic, exhibits n-alkanes maximizing at $n-C_{17}$ and $n-C_{19}$ (Fig. 1A) and even carbon numbered n-fatty acids with a maximum at $n-C_{16}$ (Fig. 1E). Both these distributions are indicative of primary bacterial lipid residues of a marine origin and there are only traces of allochthonous
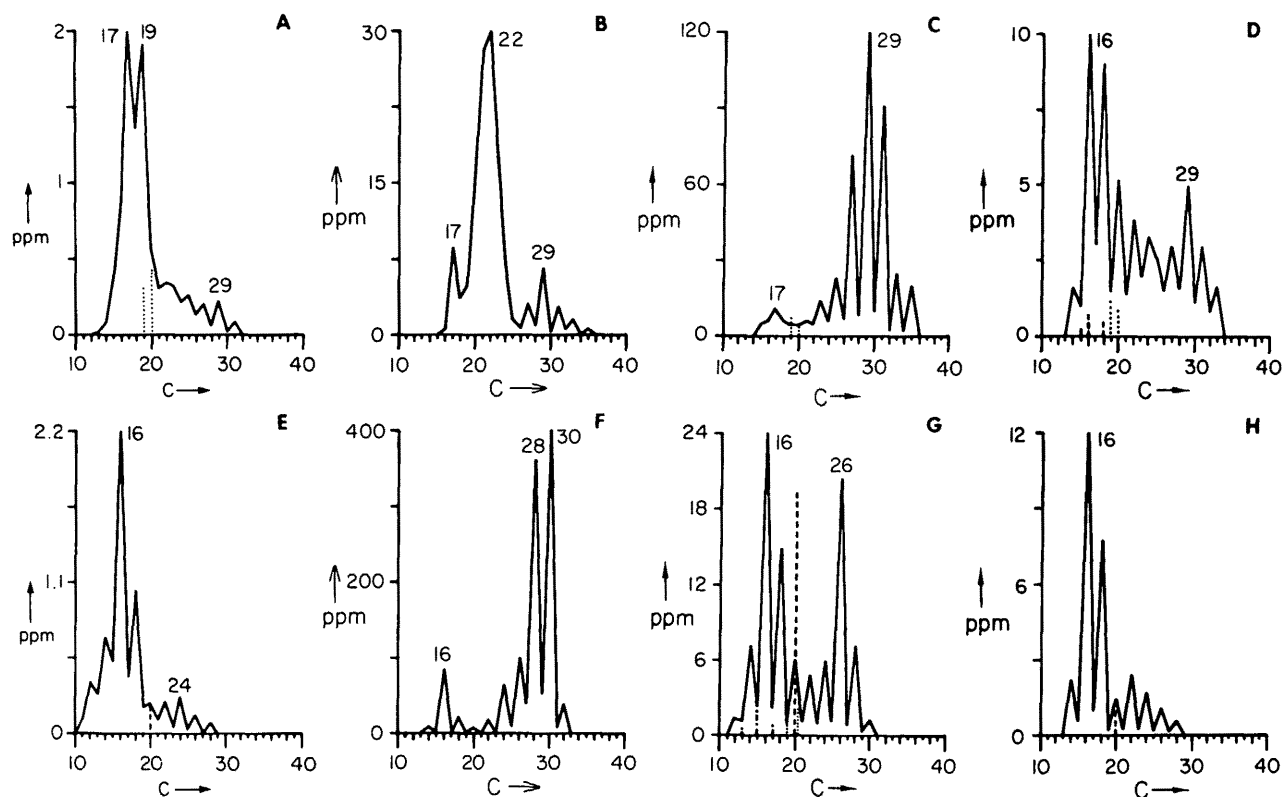
Fig. 1: Distribution diagrams (concentration versus carbon number) of n-alkanes (A-D) and n-fatty acids (E-H)(...isoprenoids,--- diterpenoids):

(A,E) Sample 36-330-10-1, 95-102 cm, S. Atlantic (Simoneit, 1980)
(B,F) Sample ML71-2-23, 8.0 m, Mangrove Lake, Bermuda (Hatcher et al., 1982)
(C,G) Sample AII49-1462K, 5.0 m, Black Sea (Simoneit 1977b)
(D,H) Sample 18-175-2-2, 45-47 cm, N.E. Pacific (Simoneit, 1977a, 1978).

homologs > C_{21} (Simoneit, 1980). The n-alkanes are superimposed on a minor unresolved complex mixture (hump) which maximized in the GC retention region of C_{17}. Such humps have been found for bacterial residues in surface sediments at natural gas emanations in Chile (Simoneit and Didyk, 1978).

Sample ML71-2-23, 8.0m is from Mangrove Lake, Bermuda, of recent origin in a highly productive sapropelic environment (Hatcher et al., 1977; 1982). The n-alkanes (Fig. 1B) show maxima at n-C_{17} from primary algal synthesis, at n-C_{22} from microbial degradation of algal detritus and a minor one at n-C_{29}, with a strong odd carbon number predominance > C_{26}, derived from higher plant wax (eg. Simoneit, 1975; 1977a,b; 1978a). The maximum at n-C_{22} with no carbon number predominance is superimposed on an unresolved hump which also maximizes in that retention region. The n-fatty acids (Fig. 1F) exhibit a bimodal distribution where the predominant maximum at C_{28} and C_{30} is of a plant wax origin and the minor homologs < C_{20} of a marine derivation (Simoneit, 1977a,b; 1978a; 1982a).

The Black Sea is a sink for terrigenous lipids from plant waxes as is indicated by the example (Fig. 1C, G). The n-alkanes exhibit a maximum at n-C_{29} with a strong odd-to-even carbon number predominance, typical of higher plant wax (Simoneit, 1974; 1977b; 1978b). This is corroborated by the n-fatty acids with their maxima at n-C_{16} and n-C_{26} and strong even carbon number predominance, where the homologs > C_{20} are of an allochthonous terrigenous origin (Simoneit, 1977b; 1978b).

DSDP sample 18-175-2-2, 45-47 cm is an example of a hemipelagic reducing microenvironment in the Northwest Pacific, where the $\underline{n}$-alkanes (Fig. 1D) exhibit a strong even-to-odd carbon number predominance for the homologs < C_{24} and the distribution follows that of the n-fatty acids < C_{24} (Fig. 1H). These even $\underline{n}$-alkanes < C_{24} may be derived from reduction of fatty acids or of olefins from fatty alcohols (Simoneit 1977a; Tissot and Welte, 1978). The $\underline{n}$-alkanes > C_{24} with the odd carbon number predominance and maximum at $\underline{n}$-C_{29} are again derived from plant waxes.

Strong euxinic conditions of sedimentation are reflected in the saturated hydrocarbons by an excess of phytane (Ph) > pristane (Pr) as for example for DSDP sample 30-330-10-1 (Fig. 1A). A Pr/Ph ratio of less than unity, coupled with the presence of significant amounts of pigments and sulfur have been utilized as indicators for anoxic sedimentary conditions (Didyk et al., 1978).

The distribution patterns and the carbon preference index (CPI*) of homologous compounds in lipids can be used to make partial assessments of the genetic origins of those compounds. This approach can be further strengthened by coupling it with the analysis and interpretation of the molecular marker compounds in the lipids.

Molecular markers are indicator compounds which can be utilized in correlations of genetic sources (Simoneit, 1978a; 1981; 1982a). Such molecules have definitive chemical structures that can be related either directly or indirectly via a set of diagenetic changes to their source. Such sources can be biogenic, geologic or synthetic (Simoneit, 1978a). The terpenoids and steroids are the compound groups which have had the greatest utility as specific biomarkers in geological applications.

Sesquiterpenoids have been identified in the marine environment as primarily cadalene (I, all chemical structures are shown in Appendix I), with various tetrahydro analogs. They are of both a marine (algal) and terrigenous origin (Simoneit and Kaplan, 1980).

The diterpenoids that have been characterized fit into two classes, those derived from terrigenous sources (Simoneit, 1977a) and extended tricyclic terpanes of probably a marine origin. The terrigenous diterpenoids consist of a large number of compounds and the most abundant analogs are dehydroabietic acid (II), dehydroabietin (III), dehydroabietane (IV), simonellite (V) and retene (VI). The extended tricyclic terpanes (VII) were first identified in shale and petroleum (eg. Reed, 1977), where they are ubiquitous, and then in recent sediments.

The triterpenoids found in most marine sediments are of an autochthonous origin and are usually comprised of the hopane and to a lesser extent the moretane series. The homologs consist of trisnorhopane (VIII, R=H), norhopane (VIII, R=C_2H_5), hopane (VIII, R=C_3H_7) and extended hopanes ranging from C_{31} to C_{35} (IX) with minor amounts of the corresponding moretanes (X). The 17β(H) stereochemistry predominates in Recent, immature sediments (Dastillung and Albrecht, 1976) and various triterpenes (eg. diploptene, XI) are also present. Recent sediments from the Gulf of California (Fig. 2A) illustrate this point in that only 17β(H)hopanes and hopenes are present (Simoneit et al., 1979). The extended 17β(H)-hopanes occur as only the 22S diastereomer in Recent sediments as the direct markers of biosynthesis.

*CPI – Carbon Preference Index: for hydrocarbons it is expressed as a summation of the odd carbon number homologs over a range divided by a summation of the even carbon number homologs over the same range (Simoneit, 1978a; Cooper and Bray, 1963); for fatty acids and alcohols it is the same ratio only inverted to have even-to-odd homologs (Simoneit, 1978a; Kvenvolden, 1966).
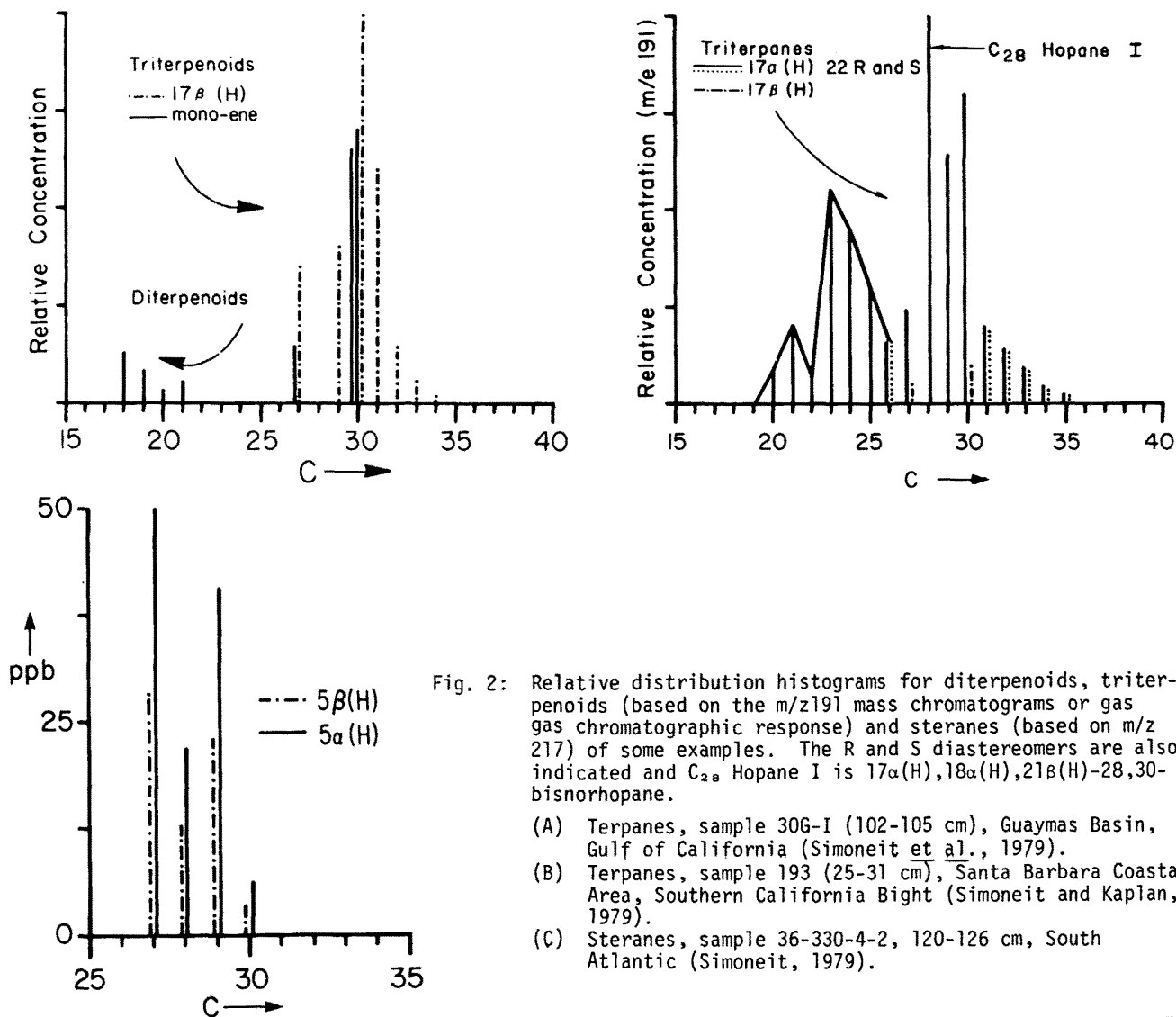
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Fig. 2: Relative distribution histograms for diterpenoids, triter-
penoids (based on the m/z191 mass chromatograms or gas
gas chromatographic response) and steranes (based on m/z
217) of some examples. The R and S diastereomers are also
indicated and C_{28} Hopane I is $17\alpha(H),18\alpha(H),21\beta(H)$-28,30-
bisnorhopane.

(A) Terpanes, sample 30G-I (102-105 cm), Guaymas Basin,
Gulf of California (Simoneit et al., 1979).
(B) Terpanes, sample 193 (25-31 cm), Santa Barbara Coastal
Area, Southern California Bight (Simoneit and Kaplan,
1979).
(C) Steranes, sample 36-330-4-2, 120-126 cm, South
Atlantic (Simoneit, 1979).

Steroidal compounds are widespread in sediments and they undergo complex diagenetic reactions
yielding various series of hydrocarbons, alcohols and ketones (XII) (Mackenzie et al., 1982a,b; Lee
et al., 1977, 1979; Huang and Meinschein, 1979). The saturated hydrocarbons are comprised of the
steranes [XIII, eg., cholestane, $5\alpha(H)$ vs. coprostane, $5\beta(H)$], diasteranes (XIV) and traces of
other isomers. An example of a sterane distribution is shown in Fig. 2C for a Cretaceous sample
from the South Atlantic. The 5α stereomers are predominant over the 5β (Simoneit, 1980). Steroid
residues in Recent sediments are unsaturated hydrocarbons, found mainly as ster-2-enes, ster-4enes,
diasterenes and monoaromatic diasteranes, and functionalized analogs found as stan-3-ols and stan-
3-ones (Simoneit, 1978a; Cranwell, 1982; Mackenzie et al., 1982a,b).

Other minor components that can be utilized as molecular markers are tetraterpenoids (Watts
and Maxwell, 1977), iso- and anteiso- alkanes or fatty acids, hydroxy fatty acids (Boon et al.,
1977), wax esters (Boon and deLeeuw, 1979), tetrapyrrole pigments and aromatic hydrocarbons
(Windsor and Hites, 1979). Tetrapyrrole pigments (chlorins) have been extensively studied and they
are excellent molecular markers (Baker and Smith, 1974).

Pseudokerogen, detritus, humic and fulvic substances:

Both humic and fulvic substances (solubles in aqueous base) are mixtures of complex macromole-
cules, and the latter are of lower molecular weights and thus soluble in dilute HCl. Little is

known about the detailed structures of the compounds concerned and the analytical data consist of their various bulk properties (eg., Schnitzer and Khan, 1972; Stuermer, 1975; Stuermer et al., 1978; Huc, 1973, 1978; Huc and Durand, 1977; Harvey et al., 1983). It has been shown that humic and fulvic substances decrease in concentration with depth of burial or geologic age and are probably incorporated into the kerogenous material (eg., Nissenbaum and Kaplan, 1972; Huc and Durand, 1977; Stuermer and Simoneit, 1978).

Kerogens are also complex mixtures of high molecular weight moieties of various, essentially unknown structures. The end members of kerogen sources are coals for terrigenous and alginites for marine origins, but most kerogens of sediments are admixtures of all input sources (eg., Tissot et al., 1974; van de Meent et al., 1980). Kerogen is an invaluable endogenous paleoenvironmental marker for the origin of the bulk of the sedimentary organic matter. Recent sediments (eg., algal mats) yield a "pseudokerogen" which is a lipoid macromolecular material, constitutionally less complex than ancient kerogen, but related to it (Philp and Calvin, 1976, 1977). In addition, recent sediments can receive terrigenous influx of plant detritus (eg. lignin, pollen, etc.), which then constitute the more oxygenated pseudokerogen components (Hedges and Parker, 1976; Hedges and Mann, 1979). Recycled detritus as for example charcoal can also be incorporated into Recent sediments (Griffin and Goldberg, 1975; 1983).

Diagenesis:

The microbiological, chemical and physical transformations of organic matter in sedimentary systems are termed diagenesis. These processes tend to approach equilibrium under mild conditions and shallow depths of burial, thus affecting primarily the lipids, humic/fulvic substances and the pseudokerogen. This degradation and alteration results in the polycondensation of some of the lower molecular weight organic residues, which upon further reaction with macromolecular detritus are insolubilized to generate the geopolymers (kerogen). Labile lipid components are also incorporated in part into the kerogen fraction and fulvic and humic substances condense further by elimination of H_2O, NH_3, etc. yielding moieties with even higher molecular weight ranges.

IV. NATURE OF ORGANIC MATTER IN MATURING BASINS

The processes of maturation, ie. catagenesis and metagenesis, will be examined in this section and how these affect sedimentary organic matter after diagenesis. Basically, the nature of the organic matter determines the resulting products in terms of gas versus oil provinces.

Gas:

Natural gas forms by a variety of processes and thus occurs with many different composition ranges. Methane (CH_4) is always a major constituent and higher homologs (wet gas), with carbon dioxide, hydrogen sulfide, nitrogen, hydrogen and noble gases may also be found in varying amounts. The origin of these constituents can be from organic matter and from atmospheric, volcanic and geothermal sources.

Organic matter derived from marine or lacustrine paleoenvironments (type I or II kerogen, Tissot et al., 1974) will ultimately yield wet gas associated with petroleum in the late catagenetic stage. More terrestrial and oxidized organic matter (type III kerogen) will generate dry gas (CH_4, CO_2 and N_2) during the cata- and metagenetic stages. The stable carbon isotope compositions of CH_4 in natural gases range from $\delta^{13}C = -60°/oo$ (immature, low temperature

genesis) to > -30°/oo (late metagenetic stage) (Galimov, 1975; Frank et al., 1974; Galimov and Simoneit, 1982a,b; Simoneit and Galimov, 1983). Thermogenic natural gases reflect their varied hydrocarbon composition in a range of $C_1/C_2 + C_3$ ratios usually < 50 (Bernard et al., 1974). Intermediate values of $C_1/C_2 + C_3$ ratios are usually interpreted as admixtures of thermogenic and biogenic gas (eg. Simoneit et al., 1979).

Bitumen:

The principal stage of oil formation proceeds under the catagenetic regime, as the geothermal stress increases with greater burial. Hydrocarbons are cracked from the kerogen and are superimposed on the original bitumen of the source rock. Most of these new hydrocarbons have a medium ($<C_{20}$) to low molecular weight range and thus skew the n-alkane distribution to low carbon numbers (eg. Fig. 3). The CPI approaches unity and a major envelope of unresolvable branched and cyclic hydrocarbons (N,S,O compounds, naphthenes, or hump) is also generated (Vassoevich et al., 1974). This petroleum genesis also yields significant amounts of gas. The oil genesis window has been estimated to commence at temperatures in the range of 50 to 120°C (Tissot et al., 1975).
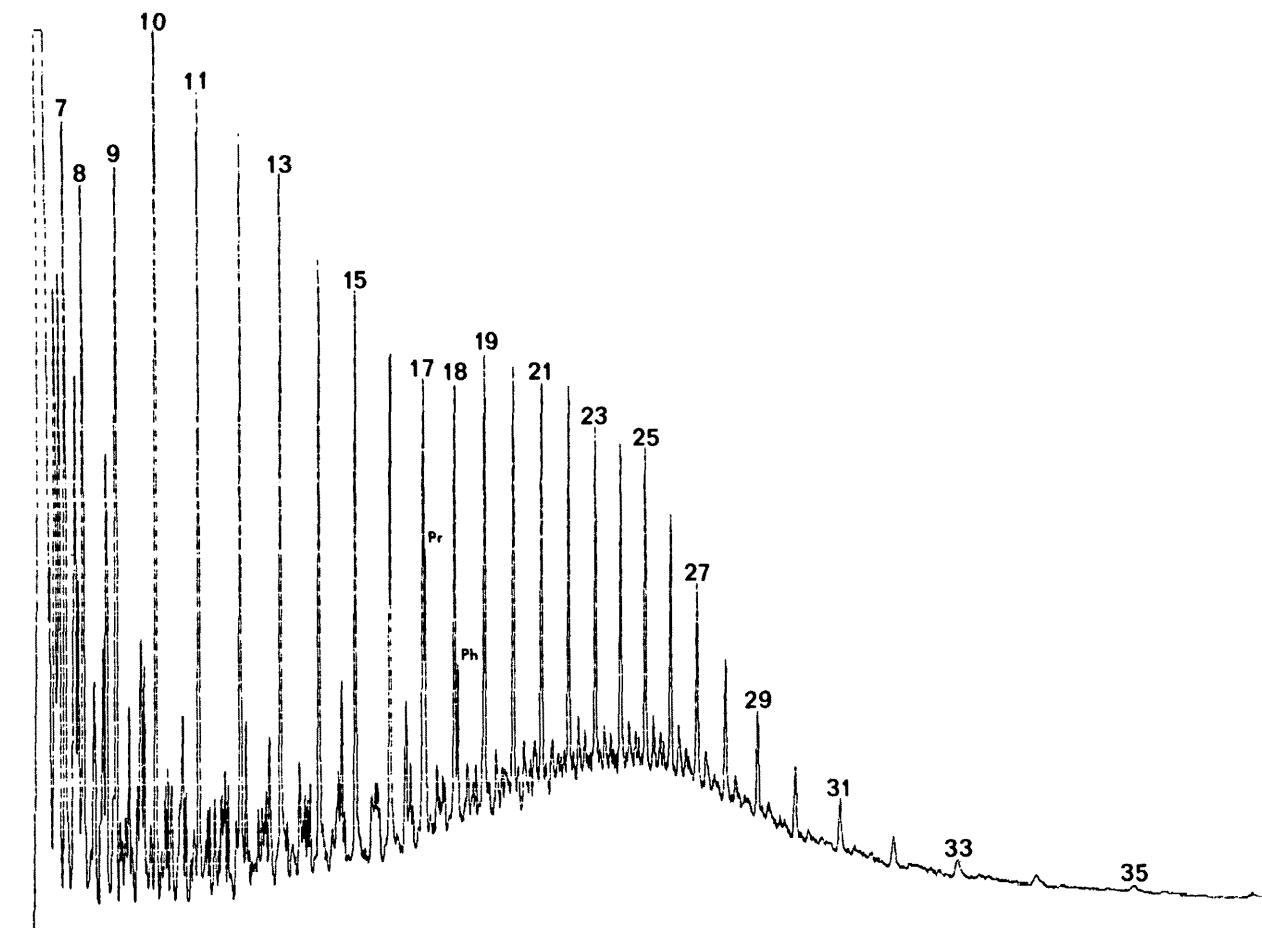

Fig. 3: Capillary gas chromatographic trace of an example of a petroleum (Bradford crude oil, Pennsylvania). The carbon numbers of the n-alkanes are indicated and Pr = pristane and Ph = phytane.

Molecular marker geochemistry has been extensively applied to assess maturity and for oil-source rock and oil-oil correlations (eg. Welte et al., 1975; Seifert, 1978; Seifert and Moldowan, 1978; 1980; Seifert et al., 1979). In ancient sediments or crude oils, the hopanes (VIII, C_{27}, C_{29} and C_{30}), occur as the $17\alpha(H)$ stereomers and the extended $17\alpha(H)$-hopanes (IX, C_{31}-C_{35}) are found as 22R and 22S diastereomeric pairs, where full maturity is indicated by an S/R ratio of about one (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980). For example, a seep oil from the Southern California Bight off Santa Barbara shows the typical triterpane distribution of petroleum consisting of mainly the $17\alpha(H)$-hopane series (eg. Fig. 2b). Also, $17\alpha(H),18\alpha(H),21\beta(H)$-28,30-bisnorhopane, a $C_{28}H_{48}$ triterpane is a major analog in this sample (Seifert et al., 1978; Simoneit and Kaplan, 1980). Extended tricyclic terpanes (VII) are present in this sample and they are usually coupled with the occurrence of the $17\alpha(H)$-hopane series of triterpanes (Simoneit and Kaplan, 1980). These extended tricyclic terpanes range from $C_{19}H_{34}$ to $C_{26}H_{48}$ and sometimes to $C_{29}H_{54}$, with very similar distributions and maximum at $C_{23}H_{42}$ (Fig. 2b). Steroidal hydrocarbons are widespread in mature source rocks and in petroleum. The steranes (XIII), usually with the $5\alpha(H) > 5\beta(H)$ stereochemistry, and diasteranes (XIV) are commonly present (Seifert and Moldowan, 1979; Ensminger et al., 1978). An example of a sterane distribution in a Cretaceous shale is shown in Fig. 2c (Simoneit, 1980). Monoaromatic steranes, common as minor constituents, have also been utilized as maturation temperature indicators (eg. Mackenzie et al., 1982b).

Other minor components that can be utilized as molecular markers are tetraterpenoids, iso- and anteiso- alkanes, tetrapyrrole pigments and alkylated aromatic hydrocarbons. The tetrapyrrole pigments (porphyrins) have been extensively studied and they are excellent molecular markers as well as geothermal sensors (Baker and Smith, 1974; Mackenzie et al., 1980).

Kerogen:

Kerogen is an invaluable endogenous paleoenvironmental marker for the origin of the bulk of the organic matter and for the thermal effects during maturation. This can be enhanced by characterizing its bulk structure, and thus its genetic origin. The elemental composition and atomic H/C and O/C ratios of kerogen can be correlated using van Krevelen (1961) diagrams to assess the magnitude of the allochthonous influx and the extents of diagenesis and catagenesis (eg., Deroo et al., 1978). Using stable carbon isotope ratios in a correlation versus H/C (eg., Figure 4) of kerogens of Recent to Cretaceous age reveals a clustering which reflects the genetic origin, i.e., terrigenous, marine or a mixture of both.

Kerogen is sensitive to thermal stress from either the normal gradient due to depth of burial (eg., Tissot et al., 1971; Tissot and Welte, 1978) or from transients such as intrusions or hydrothermal activity (Simoneit et al., 1978; 1981; Simoneit and Philp, 1982). This catagenesis results in the generation of bitumen (petroleum) from the kerogen, and this kerogen thus becomes more aromatic or remains as spent amorphous carbon (Simoneit, 1982b). This is illustrated in Figure 5, where an igneous sill intrusion into Cretaceous shale resulted in the loss of volatiles and a decrease in the H/C in the sill proximity (Simoneit et al., 1978; 1981). Additional parameters and techniques that can be utilized in kerogen evaluation are vitrinite reflectance, Rock-Eval pyrolysis, pyrolysis GC and pyrolysis GC-MS and maceral analysis by microscopy. Thus, the bulk parameters of kerogen can be good indicators of the thermal history of the source rock and its organic matter.

V. NATURE OF ORGANIC MATTER IN HYDROTHERMAL SYSTEMS

The effects of hydrothermal activity on sedimentary organic matter will be illustrated here with the extensively studied case of the Guaymas Basin in the Gulf of California. This is an example
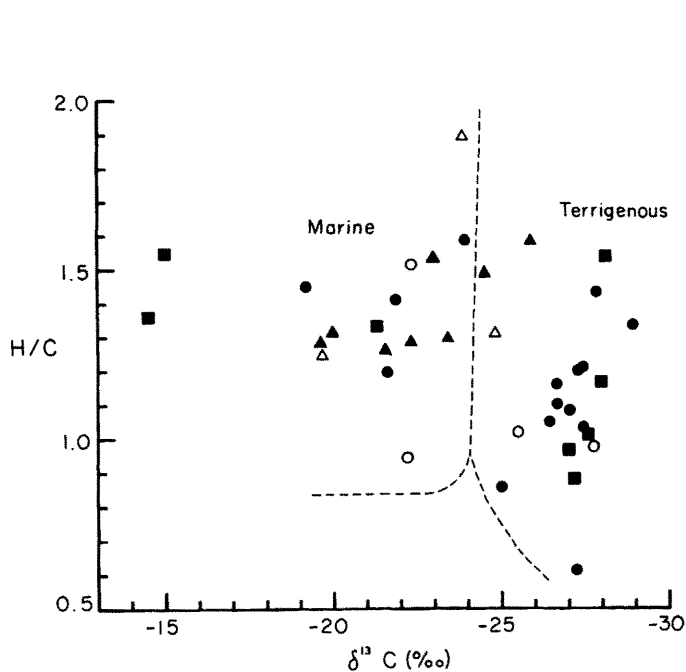
Fig. 4. Correlation diagram of H/C versus $\delta^{13}C$ for some kerogens and humates (▲ Recent kerogen; ● Cretaceous kerogen; ■ Recent kerogen from work of Stuermer et al., 1978; △ Recent and o Cretaceous humates.
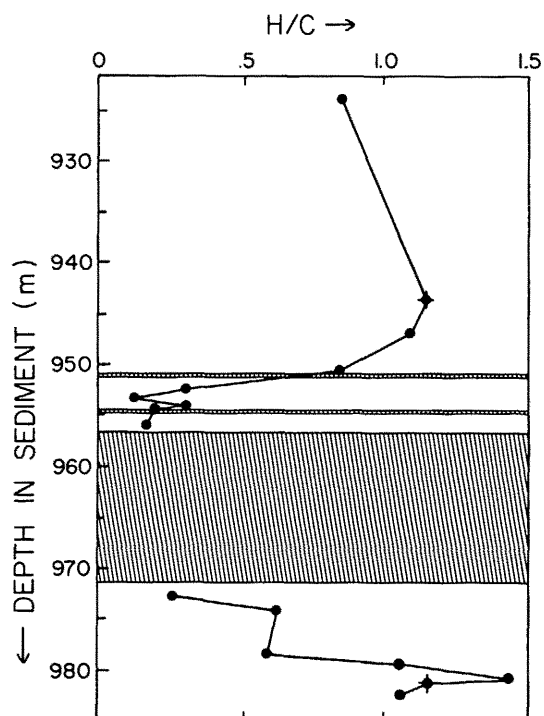
Fig. 5: Plot of the atomic H/C of the kerogens at DSDP site 41-368 versus depth in the sediment (Simoneit et al., 1978; 1981). The intrusions are indicated by the hatched areas.

of a ridge-crest hydrothermal system with a sediment cover (maximum water temperature measured = 315°C at ∿200 atmospheres) and it differs from hydrothermal systems depositing more of the noble metals (Barnes, 1979). However, it is ideal in terms of petroleum genesis.

Geologic Setting:

Guaymas Basin (Fig. 6) is an actively-spreading oceanic basin, which is part of the system of spreading axes and transform faults that extend from the East Pacific Rise to the San Andreas fault (Curray et al., 1979, 1982). The processes of ocean plate accretion result in high conductive heat flow (locally exceeding 1.2 Wm^{-2}) and dike and sill intrusions into the unconsolidated sediments (Williams et al., 1979; Einsele et al., 1980; Curray et al., 1982). Sediments accumulate at a rate of more than 1 m/1000 yrs. and have covered the rift floors to a depth of up to 400 m (Curray et al., 1979; 1982).

Organic matter of these Recent hemipelagic sediments is comprised of various operational fractions as defined by the analytical procedures. The fractions that have been analyzed here are interstitial gas, lipids, fulvic and humic substances and detrital carbon (pseudokerogen). All of these carbonaceous fractions are very sensitive to thermal stress, as for example from an intrusion or a deep-seated heat source and are thus easily pyrolized, as is the case here, especially in the southern rift (Fig. 6).

Experimental:

The samples described in this summary are derived from gravity coring (30G, Simoneit et al., 1979), Deep Sea Drilling Project, Leg 64 coring (Curray et al., 1979, 1982; Simoneit et al., 1982), dredging operations (7D, Simoneit and Lonsdale, 1982), piston coring (LaPaz 9P, 13P and 15P) and sampling with the submersible Alvin (Fig. 6). The salient analytical results for all samples are collected in Table 2.
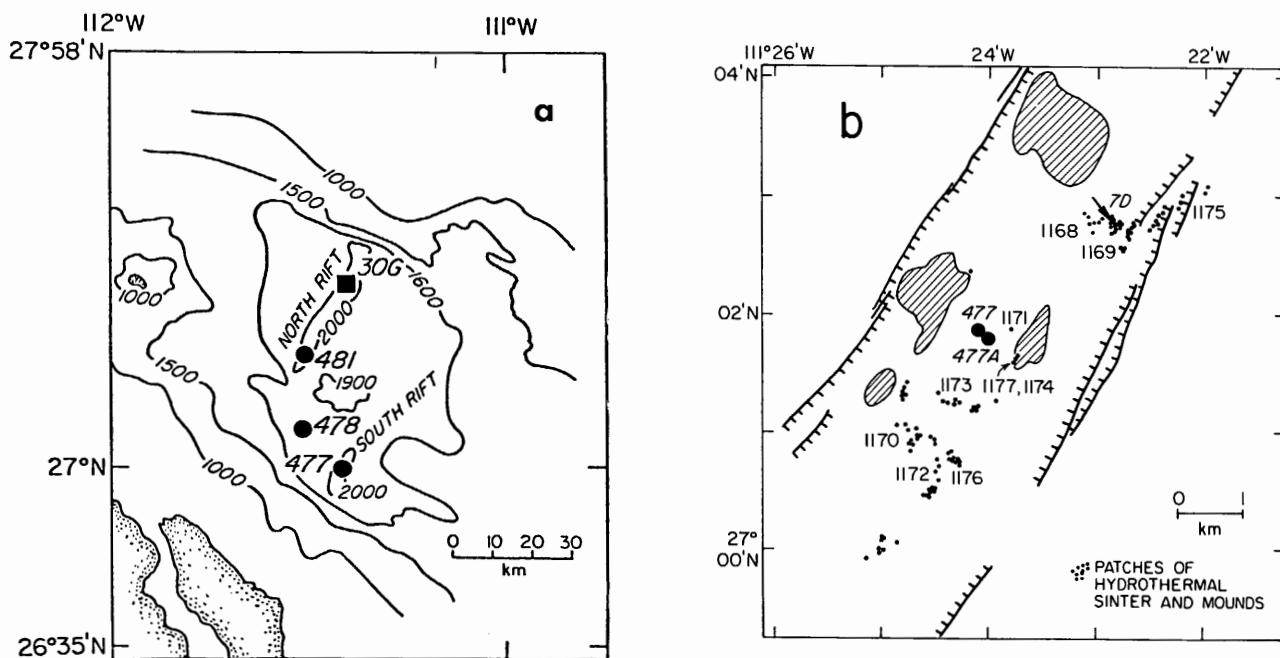
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Fig. 6: Location maps of the Guaymas Basin area in the Central Gulf of California, showing the sampling locations. (a) Overall basin with DSDP sites, and (b) portion of Southern Trough showing locations of DSDP Site 477, dredge 7D and the mound patches visited by DSRV Alvin.

TABLE 2. Summary of analytical results for sedimentary bitumen and hydrothermal petroleum from Guaymas Basin, Gulf of California.

Samples	Total Organic Carbon (%)	Total Extract Yield (µg/g dry weight of sample)[1]	Total Hydrocarbon Yield (µg/g dry sample)[2]	CPI[3]	Reference
30G (~3 m)	1.7-2.5	n.d.	1-24 (60-1000)	1.4-6.0	Simoneit et al. (1979)
64-477-5-1	2.6	2160 (83,000)	78 (3000)	1.9	Simoneit and Philp (1982)
64-477-17-3	0.8	1230 (153,750)	430 (53,700)	1.03	Simoneit and Philp (1982)
64-477A-9-1	0.4	2380 (600,000)	14 (3500)	1.02	Simoneit and Philp (1982
7D-2B	n.a.	1075	27	1.03	Simoneit and Lonsdale (1982)
7D-4A,B	n.a.	70,400	4850	1.2	Simoneit and Lonsdale (1982)
9P (12.9-14.4 m)	n.d.	2110	41	1.05	Simoneit (1983)
13P (10.5-12.4 m)	n.d.	3040	17	1.7	Simoneit (1983)
15P (11.2-11.9 m)	n.d.	5000	16	1.2	Simoneit (1983)
1172-2 (DSRV Alvin)	n.a.	76,300	n.d.	1.0	Simoneit (1983)
1172-4 (DSRV Alvin)	n.a.	552,000	n.d.	n.d.	Simoneit (1983)
1177-3 (DSRV Alvin)	n.a.	55,000	n.d.	0.88	Simoneit (1983)

[1] Values include entrapped bitumen liberated after mineral removal with HF; values in parentheses are µg/g C_{org}.

[2] Values in parentheses are hydrocarbon yield in µg/g C_{org}.

[3] Carbon Preference Index (Simoneit, 1978a).

n.d. - not determined

n.a. - not applicable

Analyses for gasoline range (C_4-C_9) hydrocarbons were carried out on canned or bagged samples by the methods described (Simoneit et al., 1979; Whelan and Hunt, 1982). Interstitial gases in vacutainers were analyzed for composition and stable isotope contents (Simoneit, 1982b; Galimov and Simoneit, 1982a,b). The extractable bitumen and protokerogen analyses were carried out by the well defined organic geochemical practice (Simoneit and Philp, 1982; Jenden et al., 1982) and the petroleum was analyzed by the same methods after extractive separation from the minerals (Simoneit and Lonsdale, 1982; Simoneit, 1983).

The various organic fractions were analyzed by capillary gas chromatography (GC) and computerized gas chromatography/mass spectrometry (GC/MS)(Simoneit and Philp, 1982; Simoneit, 1983). The pseudokerogen from sediments was separated and then analyzed by Curie point pyrolysis, electron spin resonance spectrometry (ESR), and for stable isotope and elemental compositions (Simoneit and Philp, 1982; Jenden et al., 1982).

Hydrothermal Petroleum:

The first indication that thermogenic products were diffusing to the seabed from depth in Guaymas Basin was found in a gravity core taken at Site 30G in the north rift (Fig. 6a)(Simoneit et al., 1979). The bulk of the organic matter was of an autochthonous marine origin, but the lower sections of the core contained significant concentrations of gasoline range hydrocarbons. Similar migration of hydrocarbons was observed in other shallow (9P,13P and 15P, cf. Table 2) cores from this rift (Simoneit, 1983).

Leg 64 of the Deep Sea Drilling Project encountered intrusives and hydrothermal alteration at depth at Sites 477, 478 and 481 (Fig. 6a) (Curray et al., 1982). Thermogenic gas and H_2S and CO_2 were identified for all sites based on composition and stable carbon isotope data (Simoneit, 1982b; Galimov and Simoneit, 1982a,b). At shallow depths, the data indicated a typically biogenic pattern (Sites 481 and 478, and also 30G, cf. Simoneit et al., 1979), however, with increasing depth, the $\delta^{13}C$ values became heavier indicating the removal (by diffusion and/or distillation) of the lighter $^{12}CH_4$ due to the thermal stress from intrusive and conductive heat sources. The CH_4 at Site 477 was heaviest, reflecting the highest temperature effects, and the data for Site 481 between the sills indicated various thermal stresses.

The total hydrocarbon fractions of the lipids were evaluated to compare these effects and two examples are shown in Fig. 7, one of unaltered biogenic lipids and one of thermogenic petroliferous bitumen. The unaltered sample exhibits n-alkanes ranging from C_{14}-C_{35}, with a strong odd carbon number predominance, especially >C_{23} (terrestrial plant wax, eg., Simoneit, 1978a), and subordinate amounts of C_{20} and C_{25} natural cyclic olefins and triterpenes. The thermally altered sample exhibits n-alkanes with essentially no carbon number predominance and a range from C_{15}-C_{31}. Primary olefins and elemental sulfur are also dominant components.

The lipids in the sediments from shallow depths of Sites 477, 478 and 481 are primarily of an autochthonous marine origin, with a minor influx of terrestrial plant wax (Simoneit and Philp, 1982). The paleoenvironmental conditions of sedimentation were partially euxinic, probably as a result of the high deposition rates. Lipids are thermally altered close to and below the sills (Simoneit and Philp, 1982), which is indicated by the loss of the carbon number predominance of the n-alkanes, the appearance of a broad hump of unresolvable complex material, the thermodynamic equilibration of certain stereoisomers of the hopane molecular markers, and the presence of large
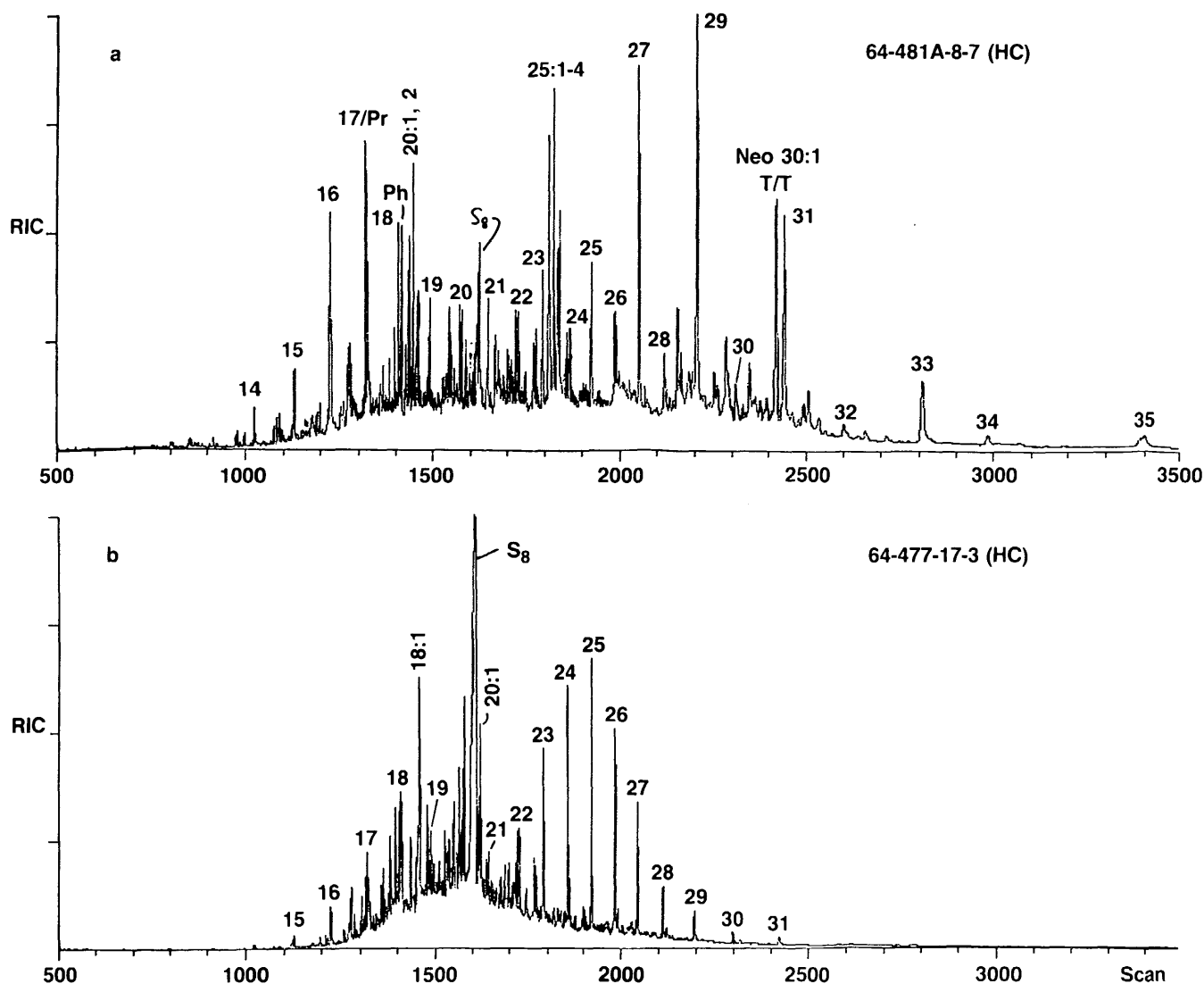
Fig. 7: GC-MS total ion current traces for total hydrocarbon fractions from (a) an unaltered, immature
sample and (b) a thermally altered sample (a: DSDP 64-481A-8-7; b: 64-477-17-3; numbers
indicate n-alkanes).

amounts of primary olefins and elemental sulfur. This thermal alteration of organic matter is most
severe at Site 477 and intermediate at Sites 478 and 481 (Simoneit et al., 1982).

Numerous hydrothermal mounds rising 20-30 m above the basin floor (water depth about 2000 m)
have been mapped in the Southern Trough and some have active hydrothermal plumes (Lonsdale, 1980).
A dredge haul (7D, Fig. 6b) across a 50 m-wide patch of sinter deposits (forming a mound) recovered
claystones, massive sulfides, barite, talc and other hydrothermal minerals, together with tube-worm
specimens. Many of the fragments in the dredge were stained with a petroleum-like oil and had a
strong odor similar to diesel fuel.

Gasoline range hydrocarbons (C_5-C_{10}) were analyzed in two dredge samples (Simoneit and
Lonsdale, 1982). The relative distributions of all hydrocarbons in this range were very similar
for both samples, and the large concentrations with the associated structural diversity confirmed
their origin by thermal generation from the sedimentary organic matter (Whelan and Hunt, 1982).

The total bitumen (lipid) extract of sample 7D-2B is light amber in color and black for sample 7D-4A,B; both extracts of the samples exhibit blue fluorescence in solution typical for petroleum condensates. These two bitumens are clearly different (Simoneit and Lonsdale, 1982). The aliphatic fraction (F1) is lowest for both samples and most of the bitumen is comprised of asphaltic (F3) and then aromatic/naphthenic (F2) material. The aromatic to aliphatic ratio for sample 7D-2B is 9.3 and it is 4.7 for sample 7D-4A,B, typical for many crude oils (Hunt, 1979).

The GC traces of the aliphatic hydrocarbons (Fig. 8) are dramatically different. Sample 7D-2B exhibits a pattern typical of petroleum, where the dominant $\underline{n}$-alkanes range from C_{12}-C_{33} with no carbon number predominance (CPI_{12-33}= 1.03) and a maximum at $\underline{n}$-C_{21}. Pristane and phytane are about equal (Pr/Ph = 1.06). The mixture of branched and cyclic hydrocarbons (i.e., hump) ranges from C_{11} to C_{31}, also typical of petroleum. On the other hand, sample 7D-4A,B exhibits a much narrower GC profile, skewed to lower carbon numbers. The dominant resolved peaks are various mono- and diolefins ranging from C_{12} to C_{19} and the hump ranges from C_9 to about C_{21}. This is very much unlike typical petroleum, as olefins are not found in mature crudes (Hunt, 1979; Tissot and Welte, 1978).
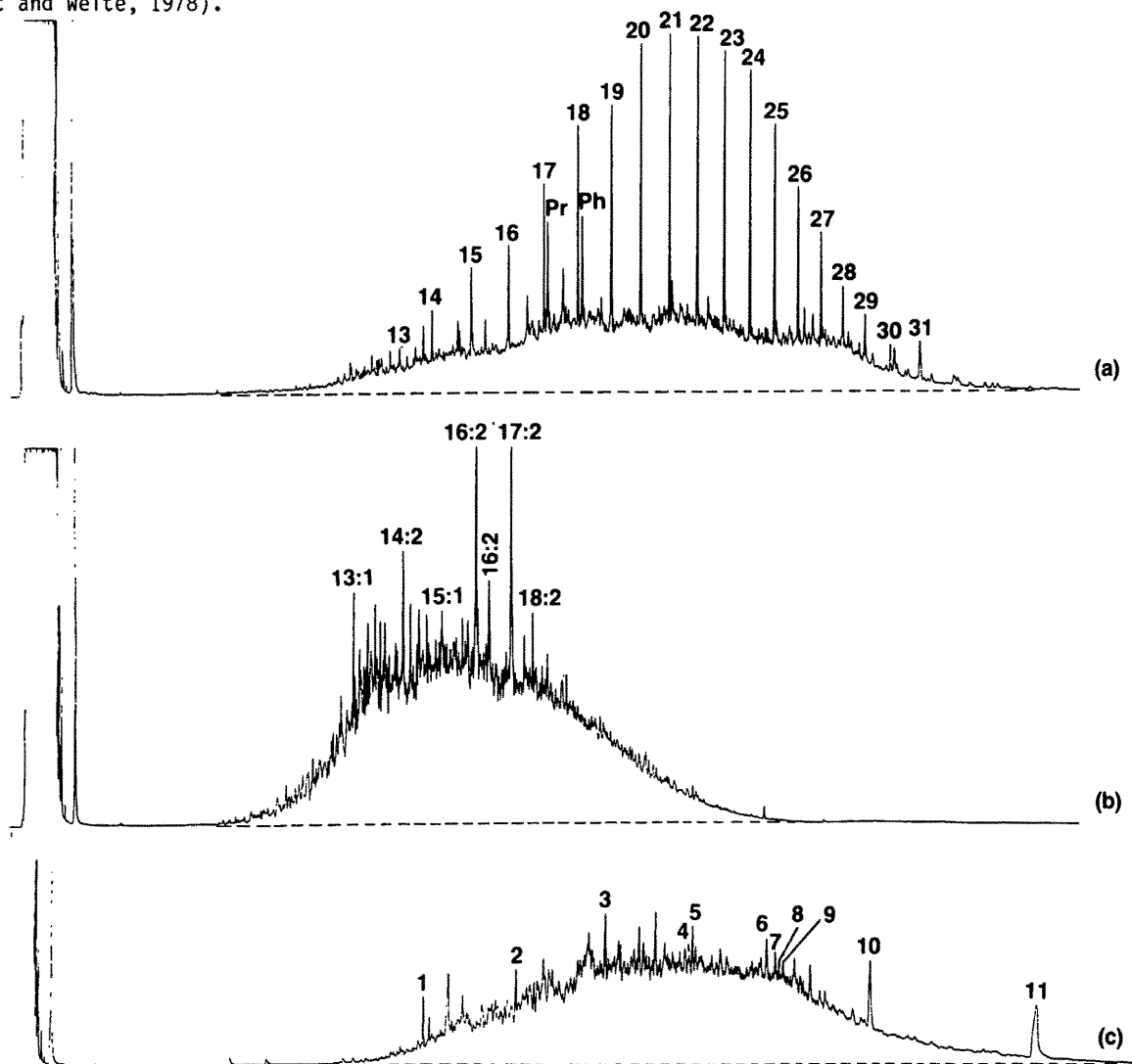

Fig. 8: Capillary gas chromatograms of aliphatic (F1) and aromatic (F2) hydrocarbon fractions for dredge samples (a and c) 7D-2B and (b) 7D-4A,B (Simoneit and Lonsdale, 1982): (a) sample 7D-2B, F1 (the carbon chain length of the $\underline{n}$-alkanes is indicated by the arabic numerals, Pr = pristane, Ph = phytane); (b) sample 7D-4A,B, F1 (olefins are indicated by chain length: double bond equivalent); (c) sample 7D-2B, F2 (1 = tetramethylbenzene, 2 = phenanthrene, 3 = pyrene, 4 = benz(a)anthracene, 5 = chrysene, 6 = benzofluoranthenes, 7 = benzo(e)pyrene, 8 = benzo(a)-pyrene, 9 = perylene, 10 = benzoperylene, 11 = coronene).

The $\underline{n}$-alkanes of sample 7D-4A,B were determined by GC/MS analysis to be present as minor components, ranging from C_{10} to C_{23}, with a minor odd carbon number predominance (CPI_{10-23} = 1.20) and a maximum at C_{15}. Pristane is more abundant than phytane (Pr/Ph = 1.6). The GC/MS data for both samples confirmed the presence of mono- and diolefins ranging from C_{12} to C_{19}. These compounds are not terminal olefins as were identified near the sills of DSDP Site 481A (Simoneit and Philp, 1982). They are slightly more stable "in-chain" olefins with methyl branching, similar to those in Bradford crude oil (cf. Fig. 3) (Hoering, 1977).

The major diagnostic molecular markers in the hydrocarbon fraction (7D-2B,F1) consist of triterpenoids, extended tricyclic terpanes and steranes with their rearranged analogs (diasteranes) (Simoneit and Lonsdale, 1982). The extended tricyclic terpanes range from C_{20} to C_{29} in a similar distribution pattern as observed for other mature petroleum samples (Simoneit and Kaplan, 1980). They are, however, not present in the unaltered surface sediments. The triterpenoids (Fig. 9) are essentially "mature"; they are for the most part in their thermodynamically more stable form, completely different from those in unaltered lipids of surface sediments (Simoneit and Philp, 1982; Simoneit $\underline{et}$ $\underline{al}$., 1979). The triterpenoids are comprised primarily of the $17\alpha(H),21\beta(H)$hopane series ranging from C_{27} (no C_{28}) to C_{35} and the homologs from $C_{31}-C_{35}$ are present as 22-S and R diastereomeric pairs in a ratio of about unity (Fig. 9). This series constitutes the stable mature form of these compounds (Dastillung and Albrecht, 1976; Ensminger $\underline{et}$ $\underline{al}$., 1974) and appears to have been generated by the hydrothermal activity. The compounds are not found in the unaltered sediments, where the biogenic markers with the $17\beta(H),21\beta(H)$ stereochemistry and various triterpenes predominate. Minor amounts of $17\beta(H),21\alpha(H)$moretanes(C_{29}, C_{30} and C_{31}), $17\beta(H)$, $21\beta(H)$-hopanes (C_{27} and C_{30}), $\underline{iso}$-hop-13(18)-ene and $17\beta(H)$-moret-22(29)-ene are also present in sample 7D-2B. These are precursor relics and intermediates from the thermal conversion process.
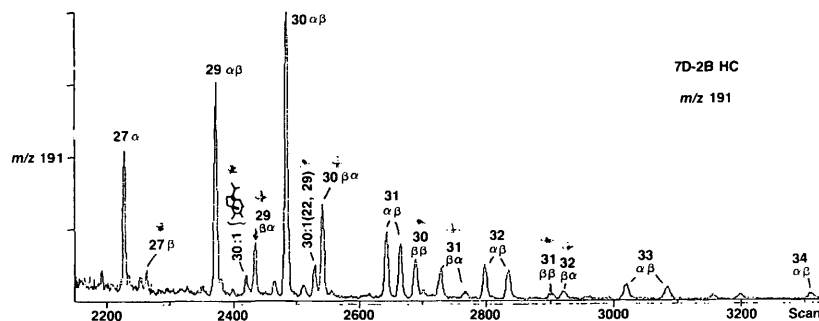

Fig. 9: Mass chromatogram (GC-MS, m/z 191) showing the triterpenoid distribution of dredge sample 7D-2B (Simoneit and Lonsdale, 1982). The predominant $17\alpha(H)$-hopanes are indicated by the arabic numerals followed by α, moretanes by $\beta\alpha$, $17\beta(H)$-hopanes by β and olefins by 30:1 (*indicates $\underline{not}$ present in mature crude oils, + not common in mature crude oils).

The steroidal markers consist of primarily $5\alpha(H),14\alpha(H),17\alpha(H)$-steranes (20 R), with lesser amounts of $5\beta(H),14\alpha(H),17\alpha(H)$steranes (20 R) and diasteranes [mainly the $13\beta(H),17\alpha(H)$-20 R or S series]. The steranes ranged from C_{26} to C_{30}, with cholestane as the major homolog. The distribution pattern indicates a marine autochthonous origin and fits best with similar data for DSDP Site 477 (Simoneit and Philp, 1982). The large $5\alpha(H)$-sterane concentration is a result of the elevated thermal stress which probably converted other steroidal compounds to these hydrocarbons.

An example of a GC trace of the aromatic/naphthenic fraction (F2) of sample 7D-2B is shown in Fig. 8c. The GC/MS data indicate that the major resolved peaks are polynuclear aromatic hydrocarbons (PAH), another group of compounds uncommon in petroleums but ubiquitous in higher temperature

pyrolysis residues (Geissman et al., 1967; Hunt, 1979; Blumer, 1975; LaFlamme and Hites, 1978; Ishiwatari and Fukushima, 1979). The dominant analogs for both samples are the pericondensed aromatic series as for example pyrene, benzopyrenes, perylene, benzoperylene and coronene. A further indication for a pyrolytic origin is the presence of five-membered alicyclic rings (eg., acenaphthene, fluorene, fluoranthene, etc.), which are found in all pyrolysates from organic matter, since once formed they do not easily revert to pericondensed aromatic hydrocarbons (Blumer, 1975, 1976; Scott, 1982). It should also be noted that this fraction contains significant amounts of toxic PAH. The benzopyrenes are major components and the highly toxic benzo(a)pyrene is present in the two samples at levels of 25 and 16 ng/g of total bitumen, respectively. Perylene is present in these fractions and it is the predominant PAH in the unaltered sedimentary lipids of samples deposited in the Gulf from oxygen-minimum environments (Simoneit and Philp, 1982; Simoneit, 1982b). Thus, the chemical composition of this fraction indicates a source from pyrolysis with rapid quenching by hydrothermal removal and subsequent condensation at the seabed.

This process of pyrogenesis, hydrothermal removal and transport to the seabed appears to be operative at most of the mounds explored by subsequent diving with the deep submersible R.V. Alvin during January, 1982 (Fig. 6b). Most of the areas with lower temperature regimes that were sampled at the mounds consisted of hydrothermal minerals cemented by solid petroleum. This material liquified upon warming on deck, thus liberating the characteristic volatile and odorous components. The data indicate that hydrothermal petroleum has become incorporated into seven of the nine areas sampled by the D.S.R.V. Alvin and one vent was discharging a water-oil emulsion. The boiling ranges and compositions of the various oil samples are quite variable (eg., Fig. 10), but reflect
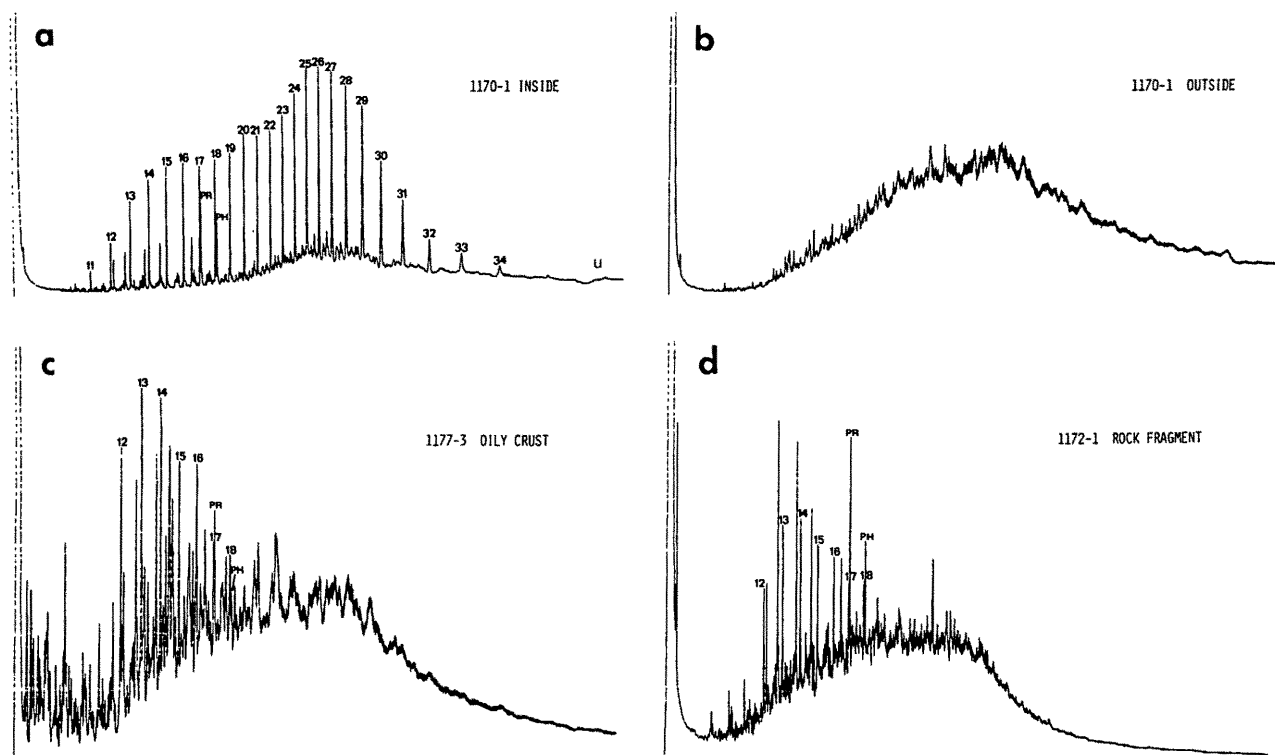

Fig. 10: Capillary gas chromatographic traces of total solvent extracts from samples recovered by D.S.R.V. Alvin in Guaymas Basin (normal alkanes are indicated by the arabic numerals, Pr = pristane, Ph = phytane): (a) sample 1170-1 (interior); (b) sample 1170-1 (exterior, exposed); (c) sample 1177-3 (oily crust); (d) sample 1172-1 (rock fragment).

their rapid hydrothermal genesis and similarity with the samples described from the dredging operations. The oil on exterior surfaces of the mounds and in unconsolidated shallow sediments is weathered, leached and/or biodegraded, whereas interior samples are relatively unaltered.

Pseudokerogen-amorphous carbon:

Kerogen, the isoluble, detrital organic matter is an excellent in situ indicator of the effects of "instantaneous" thermal stress. For example, the organic nitrogen content at Site 477, expressed as the carbon to nitrogen ratio in Fig. 11 can be used as an illustration. A C/N value of 11-14 is typical for immature, marine organic matter (Simoneit, 1982b). At depths exceeding 150 m, the C/N ratio increases to infinity, indicating all organic nitrogen has been removed by pyrolysis (under laboratory simulation this requires temperatures in excess of 500°C). An increase in the C/N is also observed above and below the upper sill, confirming that it is an intrusion and not a flow, i.e., the organic matter was thermally stressed on both sides of the sill.

Pyrolysis-GC and pyrolysis-GC/MS has been utilized to characterize kerogens (van de Meent et al., 1980) and the DSDP samples were analyzed by these same techniques to assess both their composition and degree of thermal catagenesis (Simoneit and Philp, 1982). Examples of pyrograms for unaltered and thermally altered kerogen from Site 477 are given in Fig. 12. The shallow sample exhibits a pyrogram that is virtually identical to those of surface samples from all the other sites and is representative of typical unaltered marine organic matter (Simoneit and Philp, 1982). The other (deepest) sample reflects a pattern of essentially complete expulsion of pyrolysate. The in situ appearance of the kerogen in the zones of high thermal stress (at depth of Sites 477 and 478) resembles activated amorphous carbon (Simoneit, 1982b) and is representative of the spent kerogen.
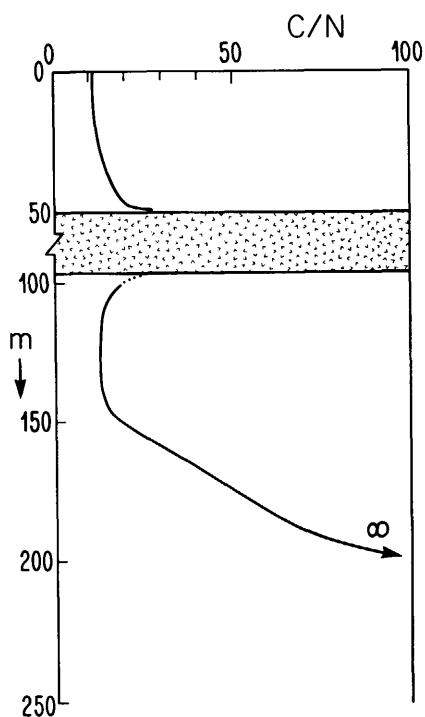

Fig. 11: Atomic ratios of organic carbon to nitrogen versus depth at DSDP Site 477 (includes data for 477A)(Simoneit, 1982a).
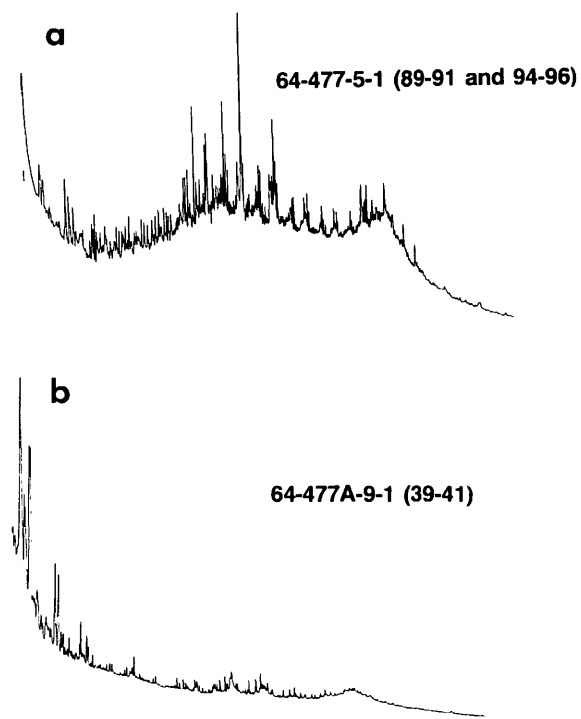
Fig. 12: Examples of Curie point pyrolysis - GC traces for kerogen concentrates from Site 477 (sub-bottom depths are given in parentheses) (Simoneit and Philp, 1982):
a) 64-477-5-1 (unaltered, 30 m)
b) 64-477A-9-1 (strong hydrothermal alteration, 240 m).

VI. EFFECTS OF PRESSURE, TEMPERATURE AND TIME ON CHEMISTRY OF ORGANIC MATTER

Pressure, temperature and time all affect the nature of sedimentary organic matter. The end results of these processes yield various grades of petroleums and cause its migration and inter-actions with the inorganic surroundings.

Petroleum genesis:

The principal zone of petroleum formation in sedimentary sequences under normal geothermal gradients commences at about 1 km to as low as 3 km (eg. Tissot and Welte, 1978; Hunt 1979). This corresponds to a temperature range of 50°-120°C and is dependent on the geologic age of the sediments (duration of heating). The effect of pressure on this process is significant, but less important and needs more supportive data (Tissot and Welte, 1978). The cracking of organic matter to natural gas is believed to take place at elevated temperatures of 150°-250°C (eg. Hunt, 1979; Vassoevich et al., 1974; Kartsev et al., 1971). These proposed temperature regimes for the oil and gas "windows" need some adjustment in consideration of more recent data.

The "instantaneous" petroleum genesis in Guaymas Basin occurs at temperatures approaching a maximum of 315°C. In this case, the lack of extensive organic matter destruction can be inter-preted by the rapid removal of the thermogenic products from the hot zone. The formation of this hydrothermal petroleum appears to commence in low temperature areas, first generating products from weaker bonds (eg. ether, sulfide, carbonyl, tertiary carbon linkages), and later as the temperature regime rises, products from more refractory and even "resynthesized" (eg. PAH) organic matter.

The organic matter associated with deeper hydrothermal systems (eg. epithermal ores in volcan-ic terranes) is usually more asphaltic with a high PAH content. Such organic matter is widely distributed and for example has been studied from the California mercury deposits (idrialite, Blumer, 1975; Geissman et al., 1967) and other hydrothermal sulfide deposits (Germanov and Banni-kova, 1972). The advent of deep well drilling (>7000 m) has yielded core materials (Cretaceous shales) which were at in situ temperatures of about 260°-300°C (eg. Price, 1982; Price et al., 1981). These samples had high concentrations of bitumen components and the kerogens still had a significant hydrocarbon generation potential. This indicates that in situ petroleum is stable at much higher temperatures as discussed above and over long geologic time periods. Metagenesis also appears to require much higher temperature conditions than normally believed.

Migration Processes:

Migration of petroleum in sedimentary sequences proceeds in solution and in the gas phase (supercritical?) from the source rocks to the traps (Hunt, 1979). The aqueous solubility of petro-leums and various hydrocarbon fractions has been determined experimentally (Price, 1976). It was found that the petroleum solubility increased exponentially above 100°C to 180°C and these solubilities were high enough to account for the formation of petroleum reservoirs by the primary migration mechanism of molecular solution. Salinities of 150°/oo NaCl caused drastic exsolution of the petroleum and at 350°/oo essentially total "salt-out" was observed (Price, 1976). This finding supports the requirement for the exsolution of the petroleum from the migration solution in the salty waters of reservoir sands. In addition, it has been demonstrated that methane in the presence of water is an even better carrier for petroleum than each alone (Price et al., 1983). Both increases in pressure (to about 1800 atmospheres) and temperature (to 250°C) raised the

solubility of petroleum. Cosolubility was found at rather mild conditions (eg. $100^{\circ}C$ at 1000 atm., $200^{\circ}C$ at 500 atm.). The addition of other gases (eg. CO_2, ethane) to this mixture also has a positive effect. Thus, primary migration appears to proceed by gaseous and aqueous solution.

In the case of the Guaymas Basin hydrothermal system the petroleum products have migrated by advection, diffusion, distillation and hydrothermal circulation away from the heat sources, also in gaseous but mainly in aqueous solution upward to the seabed. There the petroleum condenses according to the ambient temperatures in the conduits and vugs of the hydrothermal mineral mounds. PAH and sulfur condense in the hot vents; waxes crystallize in intermediate temperature regions ($\sim20-80^{\circ}C$); and the volatile petroleum partially collects in cold areas ($0^{\circ}C$) and emanates into the ambient sea water (Simoneit, 1983).

Inorganic Interactions:

Processes involving organic matter contribute to the formation of a variety of ore deposits (Saxby, 1976). The deposition of metal carbonates and phosphates is a process with a definite biogenic origin, whereas the deposition of sulfides represents a mineralization at the oxidative expense of organic matter. Metal-organic complexing has been invoked to concentrate metals and such entities can be derived from biogenic precursors (eg. porphyrins) or be generated de novo.

During mineral diagenesis and metamorphism under non-oxidizing conditions the organic matter composition changes progressively to more aromatic and asphaltic residues by the expulsion of volatile components (eg. CO_2, CH_4, H_2O, etc.). The inferred residuum is graphite and in the Guaymas Basin hydrothermal system the spent kerogen remaining in the altered sediments (at about $300^{\circ}C$) consisted of amorphous, activated carbon (Simoneit, 1982b). This higher temperature aromatic and asphaltic organic matter is often associated with heavy metal enrichments as for example uranium (eg. Schidlowski, 1981) or Carlin-type gold and silver ores (eg. Radtke and Scheiner, 1970). Heavy aromatic hydrocarbons (PAH) are a product of high temperature alteration and thus may be good indicators for such processes in the periphery of sulfide ore bodies (Germanov and Bannikova, 1972).

VII. SUMMARY AND CONCLUSIONS

The sequences of organic matter transformations in the lithosphere have been described briefly. Organic matter occurs as gaseous (volatile), liquid and solid components (Table 1) and is usually analyzed in these categories (Table 3). Recent immature sediments are the receptables of posthumus biogenic detritus, which upon deposition undergoes diagenetic and additional microbial alteration.

Increasing burial in sedimentary basins results in the onset of organic matter maturation, which generates some volatile products from the kerogen (easily cracked moieties) that become superimposed on the endogenous lipid residues. This is the beginning of petroleum formation. As the depth of burial (ie. temperature) keeps increasing catagenesis commences and here major petroleum generation takes place. At still greater depths of burial the metagenetic stage is envisaged, where extensive cracking, disproportionation and reforming of the organic matter, both petroleum and kerogen residues, occur to yield primarily gases and amorphous carbon (with heavy tars).

In the case of hydrothermal systems the previous processes are compressed into an "instantaneous" geological time frame. Hydrothermal systems operative below a sediment blanket (eg. Guaymas Basin) generate petroleum from that sedimentary organic matter, which migrates upward and leaves behind a spent carbonaceous residue. This same process of organic matter pyrolysis and movement appears to have occurred in hydrothermal regions where ore deposits formed and the organic matter content of the country rocks is low. Organic matter associated with such minerals reflects the temperature of their formation.

Migration of petroleum is aided by the presence of gases (CH_4, CO_2, etc.) and water, with elevated temperature and pressure regimes. High salinities result in essentially complete salting-out of dissolved petroleum. Heavy aromatics and asphalts can migrate during mineral metamorphism under non-oxidizing conditions and they can thus be associated with heavy metal enrichments.

In conclusion, gases, lipids (bitumen) and kerogens are ideal carbonaceous fractions that complement each other in providing information about the sources and thermal history of sedimentary organic matter (Table 3). Kerogen is a sensitive in situ indicator for thermal stress, and bitumen (petroleum-asphalt) represents the product mixture of that stress - products that may have remained in situ or migrated.

TABLE 3. Overview for the Analysis and Data Interpretation of Sedimentary Organic Matter.

I.   INTERSTITIAL GAS:
- Analog identification and quantitation by gas chromatography (FID, TCD), GC-MS
- Range   a) C_1-C_7 hydrocarbons and other gases (CO_2, H_2S, etc).
          b) Gasoline range hydrocarbons (C_4-C_{15})
- Other methods (eg. stable isotope compositions, $\delta D, \delta^{13}C...$)
- Results
  - Evaluation of biogenic versus thermogenic gas
  - Commercial exploration and drilling safety

II. BITUMEN (LIPID) ANALYSIS:
- Chemical separations (into functional group or compound class fractions, sometimes with derivatization)
  - Liquid chromatography (column)
  - Thin layer chromatography
  - High pressure LC
- Instrumental analysis
  - Gas chromatography - homologies, quantitation, hump
  - GC-MS - homologies, hump, molecular markers
  - High resolution MS - absolute compositions
  - Stable isotope MS - element isotope fractionation
- Ancillary techniques
  - NMR - for individually isolated compounds
  - IR and UV - functional and structural determination
  - ORD - asymmetry
- Results
  - Compositional survey (concentration of homologs and analogs in lipids)
  - Source and degradation correlations

Table 3. (continued)

                    - Molecular markers - product/precursor relationships
                                        - stereochemistry - thermal stress
                                        - identity - sources and transport

III. KEROGEN ANALYSIS (Asphaltenes, fulvic and humic acids, and humin):
    ● Bulk properties
        - Elemental composition (C,H,O,N,S)
        - Stable isotopes ($\delta^{13}C$, $\delta^{15}N$, δD, $\delta^{34}S$)
        - ESR, NMR
    ● Results
        - Parameter correlations
        - Indicative of sources (autochthonous vs. allochthonous)
    ● Specific analyses
        - Vitrinite reflectance
        - Petroleum generating potential
        - Pyrolysis GC and py-GC-MS
    ● Results
        - Evaluations of maturity
        - Thermal history
        - Resource potential
        - Oil versus gas
    ● Other methods
        - Microscopy (visual classification and identification)
        - Chemical degradation (some indications of molecular origin)

VIII. ACKNOWLEDGEMENTS

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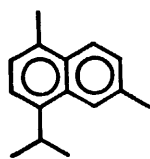
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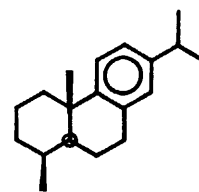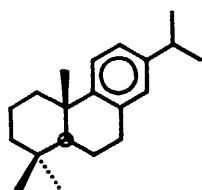
Appendix I -
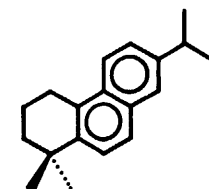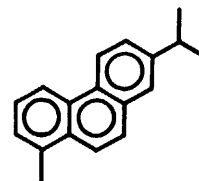Chemical Structures Cited

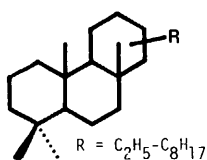I. Cadalene
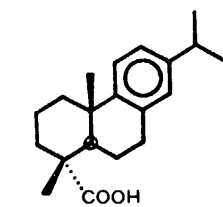
II. Dehydroabietic acid

III. Dehydroabietin

IV. Dehydroabietane

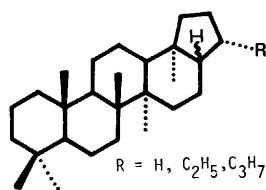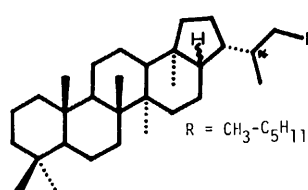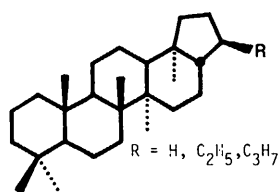V. Simonellite

VI. Retene

VII. Extended tricyclic terpanes
$R = C_2H_5-C_8H_{17}$
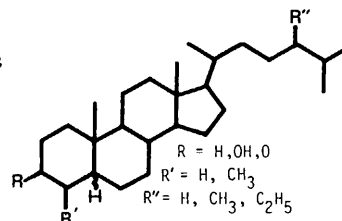
VIII. Hopanes
$R = H, C_2H_5, C_3H_7$
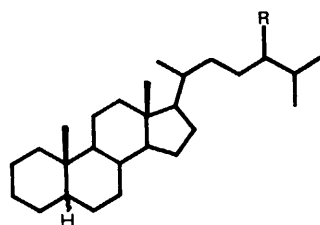
IX. Extended hopanes
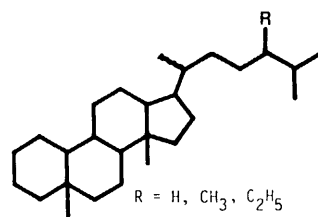$R = CH_3-C_5H_{11}$

X. Moretanes
$R = H, C_2H_5, C_3H_7$
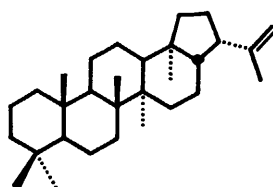
XI. Diploptene

XII. Steroidal derivatives
$R = H, OH, O$
$R' = H, CH_3$
$R'' = H, CH_3, C_2H_5$

XIII. Steranes, $5\alpha/\beta(H)$
$R = H, CH_3, C_2H_5$

XIV. Diasteranes
$R = H, CH_3, C_2H_5$