DEVELOPMENTS IN GEOCHEMISTRY AND THEIR CONTRIBUTION TO HYDROCARBON EXPLORATION

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Abstract. This paper considers the exploration significance of developments in organic and other areas of geochemistry. The utility of geochemical criteria in early reconnaissance and developmental stages of exploration of sedimentary basins for crude oils and natural gases is discussed and illustrated with case histories. References to surface (land) and marine hydrocarbon survey technology, source bed determination, hydrocarbon maturation and migration phenomena, post-migration alteration and transformation, correlation processes and non-conventional hydrocarbon sources are made. Advances in spectroscopic techniques such as high resolution GC-mass spectrometry, nuclear and electron spin resonance, infrared and UV-fluorescence and their relevance in correlation of hydrocarbons with stratigraphic units and reservoirs are discussed. Results of an updated literature review on the theories of oil and gas formation will be presented. The role of stable isotopes of carbon, nitrogen, and sulphur in elucidating problems in evolution migration and alteration of petroleum is treated. Hydrocarbon gases, N–S–O organic compounds, and other elements as proximity indicators of petroleum reservoirs will be evaluated.

Résumé. On étudie l'influence des progrès réalisés en géochimie, et surtout en géochimie organique. On discute de l'utilité des critères géochimiques dans les phases de reconnaisance initiale et d'exploration approfondie des bassins sédimentaires pour le pétrole et le gaz, et on l'illustre par la description de cas réels. On fait référence aux techniques d'études de surface des hydrocarbures sur terre et en mer, de détermination des roches-mères, des phénomènes de maturation, de migration des hydrocarbures, de transformation et d'altération après leur migration, des procédés de corrélation, et aux sources d'hydrocarbures non conventionnels. On évoque les progrès réalisés dans le domaine des techniques spectroscopiques, telles que la chromatographie en phase gazeuse couplée avec la spectrométrie de masse à haute résolution, la résonance magnétique nucléaire et la résonance paramagnétique électronique, la fluorescence par infrarouges et ultraviolets, et leur importance dans les corrélations entre hydrocarbures, unités stratigraphiques et réservoirs. On présente les conclusions d'une revue des publications récentes sur les théories concernant la formation du pétrole et du gaz naturel. On traite aussi du rôle que jouent les isotopes stables du carbone, de l'azote et du soufre dans la solution des problèmes de l'évolution, de la migration et de l'altération du pétrole. On évalue également la valeur des hydrocarbures gazeux, des composés organiques de N, S et O, ainsi que d'autres éléments comme indicateurs de proximité des accumulations de pétrole.

INTRODUCTION

The search for oil and natural gas has evolved into a highly sophisticated technology drawing from many disciplines as it is practised today. The simple act of discovery of a hydrocarbon occurrence in the earliest days of the petroleum industry usually imposed technical challenges and responsibilities on the pioneer explorer. First, the discovery had to be contained for safety and other practical reasons, then production techniques had to be devised. It is not unreasonable that the petroleum industry was destined from the beginning to require an integration of skills which today embrace the earth sciences as well as more traditional areas of science, mathematics and engineering. It is also not unreasonable that

geochemistry should play an important role in the industry—the object of the search for petroleum and natural gas is in essence a chemical mixture. For many years, however, the search for petroleum concentrated on the trap—and structural geology provided the basis for pursuit. The advent of modern geophysics further emphasized the search for formations suitable for oil and gas containment. Chemical considerations were of secondary importance in the search for the easy-to-find oil. Today's explorer must consider source as well as migration and accumulation aspects in the search for the 'more difficult' to find reserves of oil and natural gas.

It is the purpose of this review paper to explore some of the current ideas and methods of geochemistry as they contribute to hydrocarbon exploration.

GEOCHEMISTRY IN EARLY RECONNAISSANCE EXPLORATION

Surface geochemical prospecting represents one of the oldest prospecting methods for petroleum. Surface seepages guided the earliest explorers to subsurface geological features which were drilled for their hydrocarbon potential. Many of the world's largest oil fields were marked by oil and gas issues near the crest of anticlines or the apices of domes. De Golyer[5] reported in 1940 that visible oil and gas seeps had resulted in the discovery of more oil and gas fields than any other single method. Geophysical methods, particularly seismic technology with 'bright spot' processing enhancement, have introduced powerful new tools for structural determination. Continued refinement of the geophysical methods can best be accomplished with the assistance of geochemical techniques to confirm and detail chemically the actual presence of hydrocarbons. Geochemical methods have found utility primarily when used in conjunction with available geological and geophysical information. The necessity for an integrated exploration approach cannot be over-emphasized. Fedynsky *et al.*[1] reviewed the application of geochemical methods at the 9th World Petroleum Congress, emphasizing the widespread use of geochemical surveys in the Soviet Union to evaluate structures located by geophysical methods and to search for oil in lithological, stratigraphic and tectonic traps. Considerable technical advances have been made since 1975 in establishing the validity of surface geochemical methods. Jones[2] presented evidence from extensive studies on the composition of light hydrocarbons present in the near-surface soil gases which show striking similarity to the compositions of the underlying known production. He showed that soil–gas geochemistry is a technique which is capable of predicting whether oil or gas is more likely to be discovered in the prospect area. These oil vs. gas predictions are made by using the percent compositions and ratios of methane to ethane and propane. Typical average values determined from soil–gas surveys are:

	% Methane	Methane/ ethane	(Propane/ methane $\times 1000$
dry gas	100–90	200–20	2–20
gas-condensate	90–75	20–10	2–15
oil	75–45	10–4	60–500

Intermediate values are expected for many hydrocarbon accumulations.

Extensive studies compiled and reported in the literature have clearly shown that reservoired hydrocarbons contain varying amounts of methane and heavier homologues. Frequency histograms of the sum or ratio of methane homologues illustrate that gas from gas deposits is quite distinguishable from that of oil deposits. Gases from gas-condensate or combined oil and gas provinces plot intermediate between those of gas or oil only provinces as expected.

Light hydrocarbon ratios have been used successfully to predict the petroleum potential of a formation by monitoring C_1—C_5 hydrocarbons from a steam-still reflux gas sampling system during routine mud-logging operations (Pixler[3]). Individual ratios of the C_2—C_5 light hydrocarbons with respect to methane have been demonstrated to provide discrete distributions which reflect the true natural variations of formation hydrocarbons between oil and gas deposits. Analyses of these same ratios for soil–gas hydrocarbons yield nearly the same limits for delineation of oil and gas potential. This correspondence with the actual formation gases shows that the upward migration of reservoired light hydrocarbons into near-surface soils represents a viable mechanism, allowing near-surface geochemical exploration techniques to be utilized for prospect evaluation.

Figure 1 shows the variation in methane content of near-surface gases in the Sacramento and San Joaquin Basins, California. Predominantly dry methane gas is produced in the northern part of the Sacramento Valley and is reflected in the methane composition in excess of 90%. Oil and gas condensate production in the San Joaquin is indicated by the lower methane values.

Figure 2 illustrates the results obtained on a regional line across the San-Joaquin Basin, California. Methane and propane profiles are presented for gases from shallow bore holes along a line which parallels state route 46 and crosses the Lost Hills oil field and Semitropic and Wasco oil and gas fields. Good correlation with the reservoirs was obtained. Figure 3 shows the geochemical signature obtained over a gas storage area in the Pleasant Creek Gas Field, Sacramento Valley, California. The location of the storage sand is indicated on the seismic section.

Figure 4 shows the results of a geochemical survey in the Idaho–Utah–Wyoming Thrust Belt area. A predominantly methane anomaly is present over the Coalville Gas Storage Area where gas stripped of its lighter components is re-injected into the subsurface. Leakage is along major fault systems in the area. The signature of the oil production associated with the Pineview field is manifested by an anomaly composed of propane and butane hydrocarbons. In the vicinity of the surface exposure of the Tunp Thrust on the eastern edge of the cross-section another methane type anomaly is displayed.

Stable carbon isotope studies (C^{13}/C^{12}) have contributed widely in environmental identification of organic source materials. They have also been useful in evaluation of the influence of migration, recog-
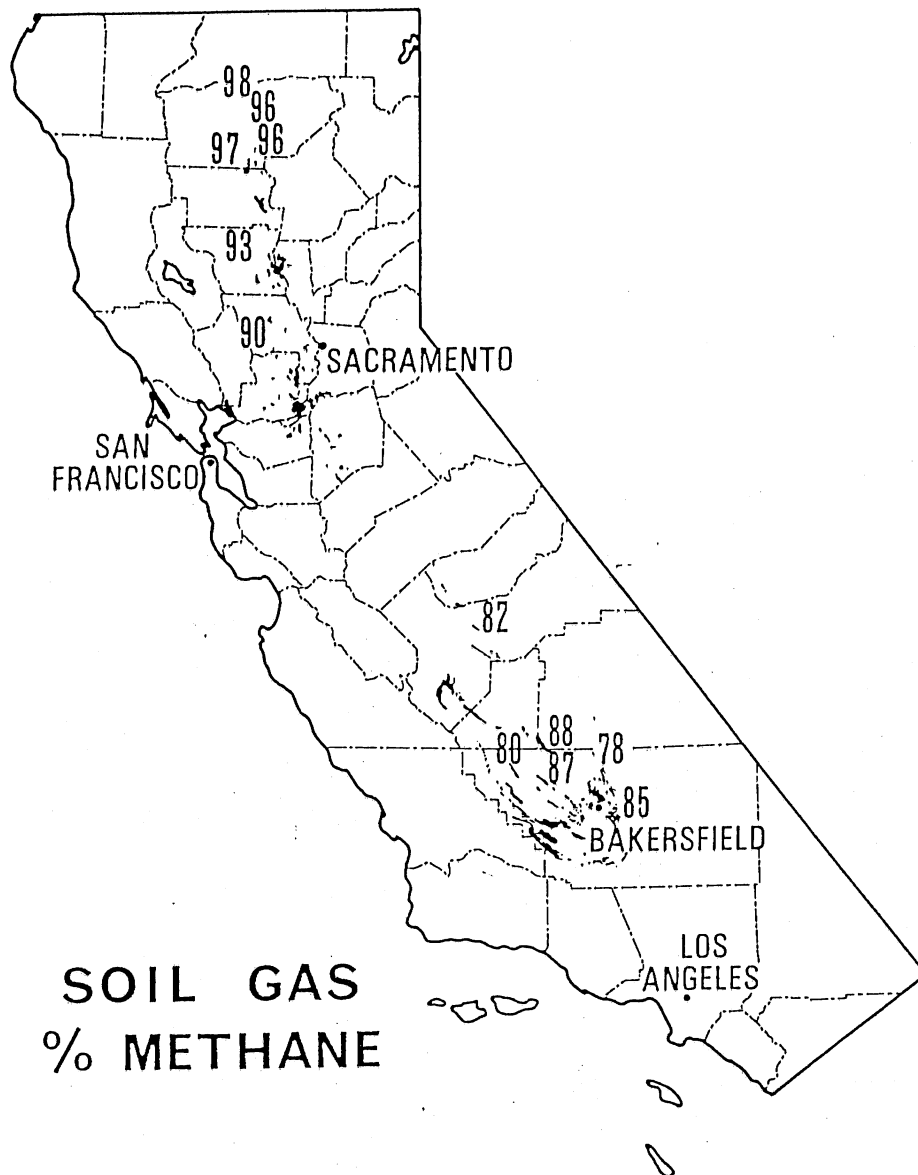
Fig. 1. Variation in methane content of near-surface hydrocarbon gases in Sacramento
and San Joaquin Basins, California

nition of bacterial degradation, quantitative deter-
mination of the maturity of CH_4-producing organic
source materials, characterization of and differen-
tiation between various crude oil accumulations and
correlations of crude oils with source rocks.[6,40]

Horvitz has examined tens of thousands of near-
surface sediment samples from both onshore and
offshore areas for the saturated hydrocarbons
through pentane. Recognizable hydrocarbon dis-
tribution patterns were observed over known fields.
Similar patterns were found in areas which has been
examined but not yet tested for hydrocarbon produc-
tion. Follow-up studies indicate a high percentage
of anomalies in originally unexplored areas

subsequently were found to be associated with
petroleum accumulations. Recently, Horvitz[4] utilized
carbon isotope data in search for evidence linking the
hydrocarbons measured at the surface with those
found in the reservoir. Methane desorbed from a soil
sample taken at 4 m depth from an anomalous area
observed over the Francitas field in Texas, yielded a
δC^{13} of −44.0‰ relative to the PDB standard. Inter-
stitial methane extracted from a 4 m sample at
another location within the same hydrocarbon halo
yielded a value of −40.8. Reservoir methane from
the Francitas field showed δC^{13} values ranging from
−41.0 to −43.8‰, almost identical to those of the
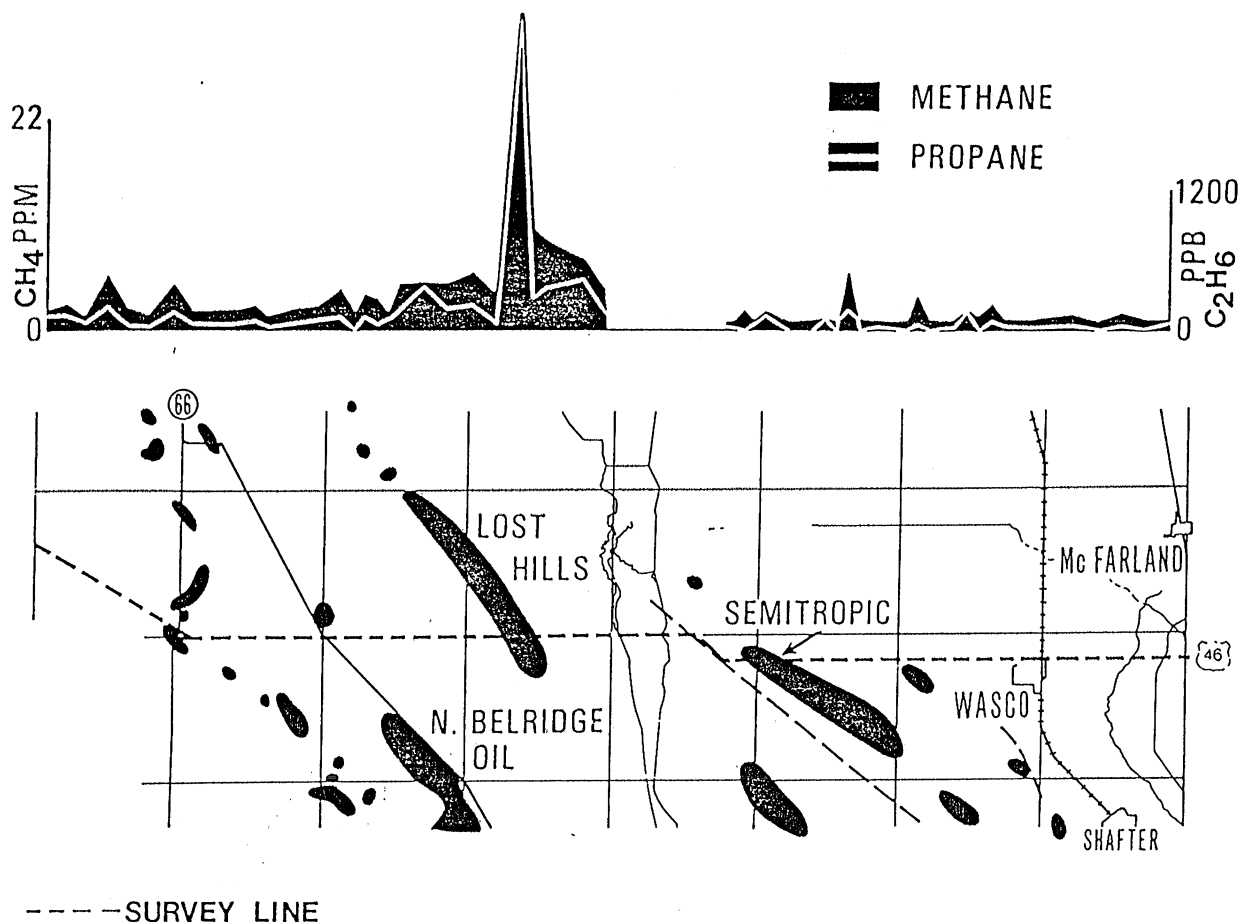near-surface methane.

Fig. 2. Regional geochemical survey line—San Joaquin Valley, California.

Relationships of carbon isotope ratios of gases desorbed from near-surface sediments samples from the Anadarko Basin and North Sea have been related to geochemical data of the deeply situated, pooled hydrocarbons in both areas by Stahl.[10]

Microbiological surveys also hold promise in surface detection of reservoired hydrocarbons.[11] Techniques which follow the uptake of specific light hydrocarbon gases from gas-consuming microorganisms present in the near surface over oil reservoirs have been applied with success in the US and USSR. Microbial studies were used to delineate production over the Bell Creek field, Montana, Recluse field, Campbell County, Wyoming and Hyde oil field, Washington County, Colorado. Such studies appear useful to the explorer, particularly when carried out in conjunction with surface geochemical work or geophysical–electrochemical surveys. In many instances the results of one type of survey, although not convincing on a stand-alone basis, are reinforced by the findings of the other disciplines. The interdisciplinary role in modern petroleum and natural gas exploration cannot be too strongly emphasized.

Workers at the USGS, Denver[12,13] have conducted investigations into near-surface and surface manifestations of subsurface oil and gas occurrences by cost-effective airborne and satellite imagery geophysical means. Low molecular weight hydrocarbons seeping from buried accumulations of petroleum commonly are chemically or biochemically oxidized near the surface. When seepage is long continued, the resulting carbon dioxide reacts with calcium ions and, sometimes, magnesium ions dissolved in ground water to produce isotopically distinctive pore-filling carbonate cements in otherwise porous surface rocks. Distinctive trace elements are also incorporated. Localized reducing conditions resulting from the upward passage of hydrocarbons and (or) their associated compounds through surface rocks tends to reduce ferric iron minerals and dissolve and remove the more soluble ferrous iron, commonly causing a discoloration. This colour change in the surface rocks may be subtle to marked, depending in general upon the efficacy and rapidity of the leakage, and the original colour, iron content, and oxidation state of the altered rocks. Other metals are also mobilized and redistributed. These complex
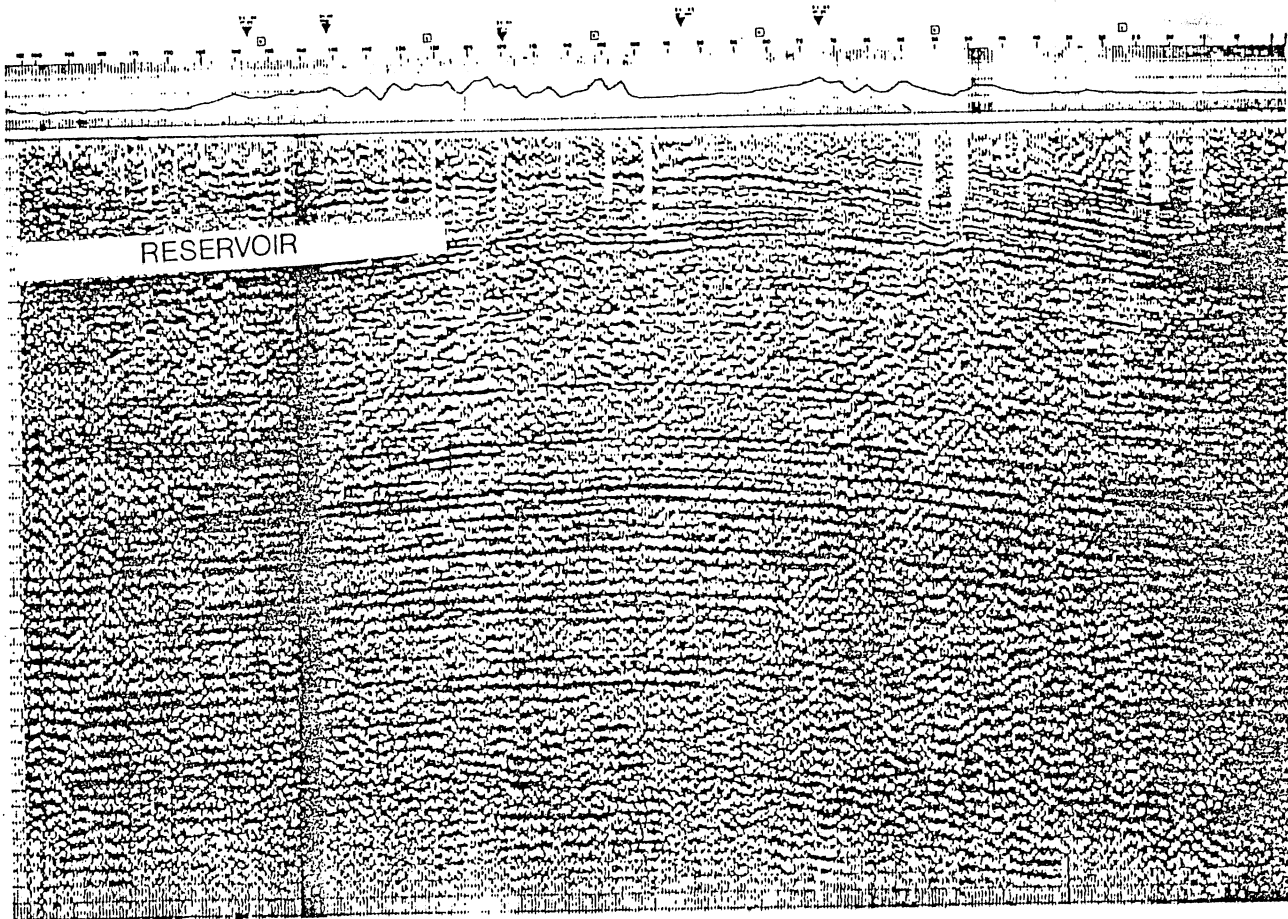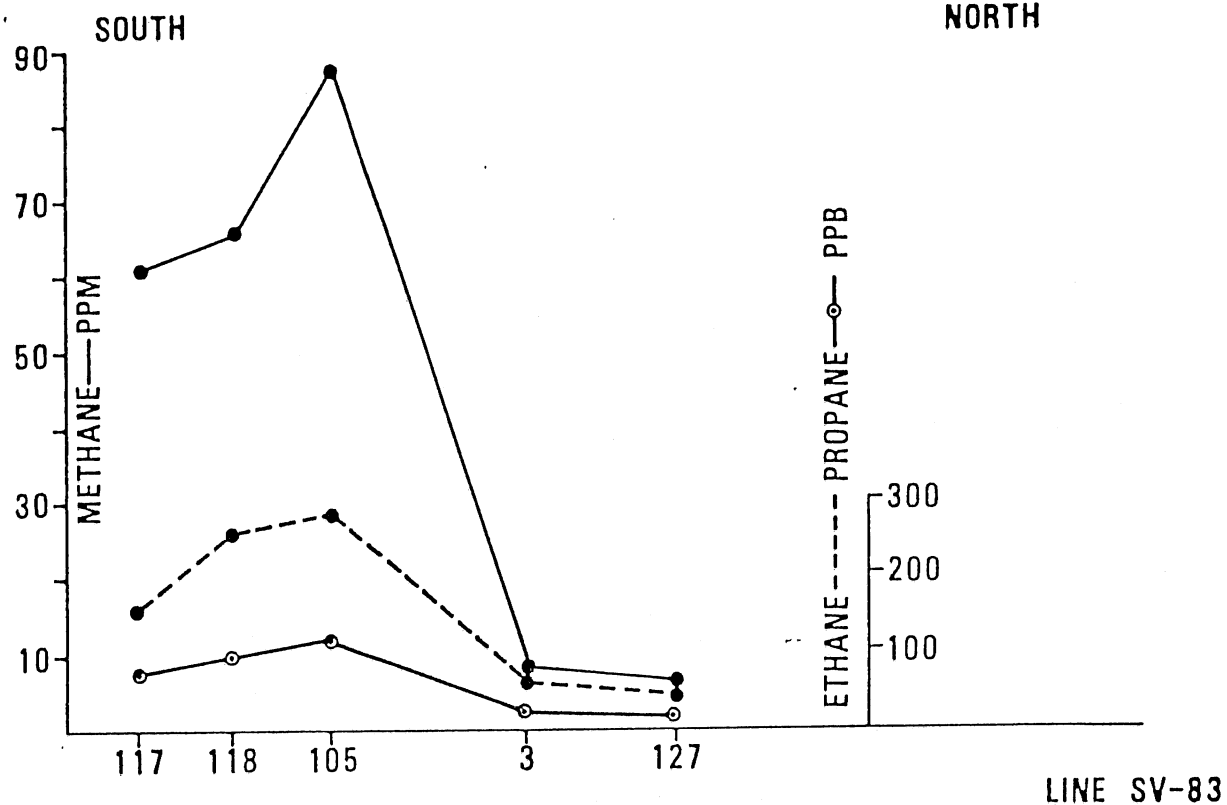
Fig. 3. Geochemical profile—Pleasant Creek gas storage field, Sacramento Valley, California.
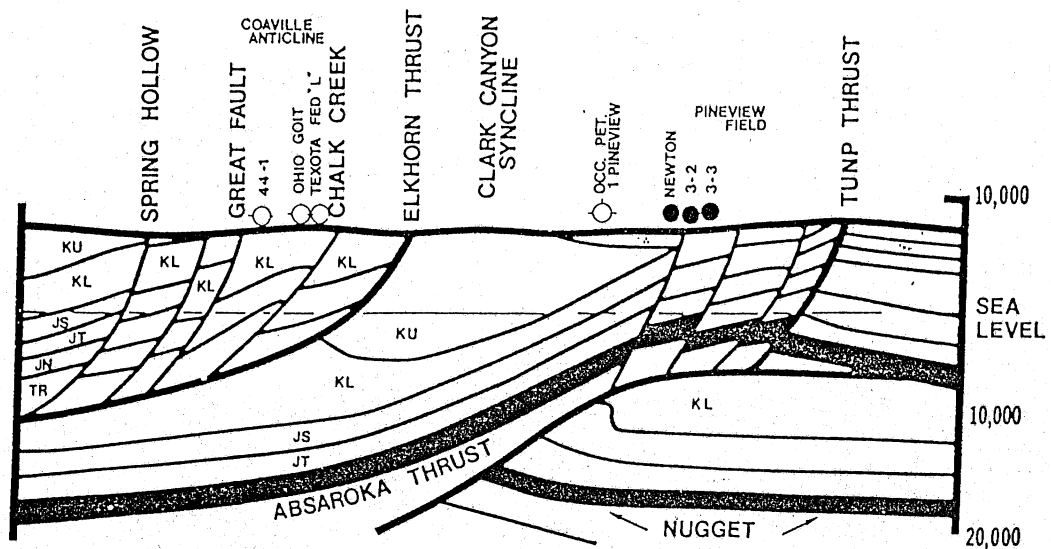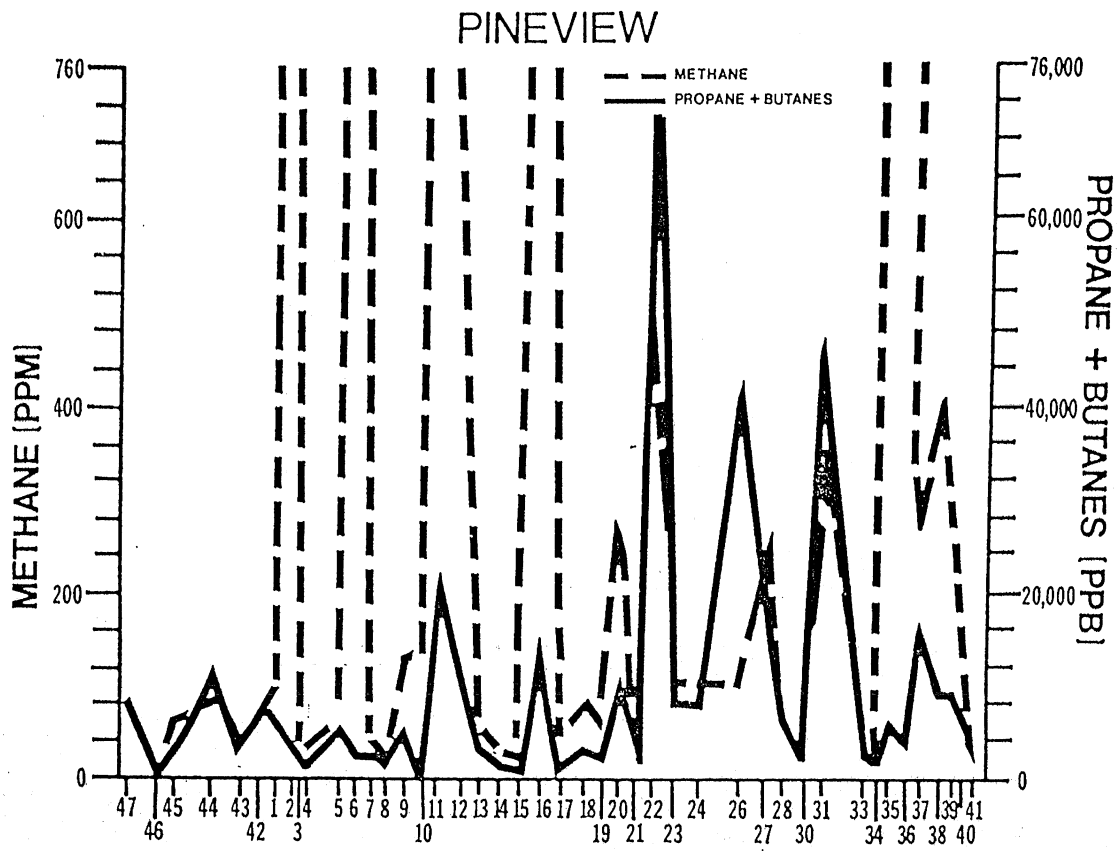
Fig. 4. Geochemical profile, Idaho–Utah–Wyoming thrust belt area.

alterations in surface rocks are fossil evidence of long continued seepage which result in areally restricted changes in the physical properties of rocks which are correlatable with the subsurface occurrences of petroleum.

Remote sensing techniques, if developed, could have an enormous impact on the exploration for hydrocarbons. In addition, satellite imagery might provide strategic information about the location of future world resources.

OTHER GEOCHEMICAL PROXIMITY INDICATORS

Several additional techniques which are employed as proximity indicators for petroleum exploration are worthy of mention in this review. A number of hydrochemical methods are used. Aromatic hydrocarbons such as benzene and toluene are present in formation waters associated with oil fields. Their concentration in subsurface brines recovered from drill-stem tests has been shown to be related to proximity to the oil accumulation. The hydrocarbons are thought to diffuse into the brines from the contact with the oil pool. Although the method was introduced in the late 1960s, case histories on many early predictions are still being developed. Results of this method have been encouraging.

Iodine and ammonia dissolved in formation fluids also hold promise as petroleum proximity indicators.

Microseepages of petroleum in soils and in muds of the seafloor provide another potential tool for the explorer. Often the concentrations of these hydrocarbons are at exceedingly low levels. Detection and quantitative determination is possible through the application of fluorescence spectroscopy to solutions of the extracts from the soils or muds. Surveys are carried out on this basis. Interpetation of the fluorescence analysis is complicated by the fact that some of the compounds present contain soil and plant bitumens which also fluoresce but are unrelated to petroleum. Refinements to this technique offer challenges to the exploration researcher.

Carothers[14] reported the presence of aliphatic acid anions in oil-field waters and studied their relevance on the origin of natural gas. Earlier studies suggested the possibility of using these chemical components as proximity indicators for petroleum. Re-evaluation of the role of these anions in formation fluids appears justified.

MARINE HYDROCARBON SURVEYS

One major application of marine geochemistry to the continental margins lies in the technique known colloquially as 'sniffing'. This technique attemps to locate oil or natural gas seeps by measuring the concentration of gaseous hydrocarbons in the sea. It is assumed areas of anomalously high hydrocarbon concentration have been caused by a seep.

Other compounds from petroleum could also be used as seep indicators but for practical reasons (primarily difficulty of analysis) the technique is usually restricted to the measurement of the gaseous hydrocarbons.

In the practice of this detection technique, petroleum and natural gas companies have acquired systems and capabilities to rapidly collect data on the amount of these compounds present in the ocean. The large volume of data generated could make a major contribution to a growing literature on gases in the ocean. Most contributions to date have come from the academic and government communities.

One vessel, the R/V HOLLIS HEDBERG and also its predecessor, the R/V GULFREX, have circumnavigated the earth and done extensive detailed surveying in areas such as the Gulf of Mexico.

As an example of the capabilities of a marine hydrocarbon detector the R/V HOLLIS HEDBERG system employs three separate water inlets which continuously supply sample streams from the near surface, intermediate depths and deep depths. The deep towed sample inlet can operate to nearly 600 ft depths while the ship is underway at normal seismic survey speeds. Each sample stream is analysed for seven hydrocarbon gases once every three minutes with a sensitivity which depends upon the hydrocarbon but, for example, is about 5×10^{-11} l of propane at STP per litre of seawater.

The basic philosophy upon which the exploration interpretation of these data rests is that local areas of enhanced hydrocarbon concentration are due to seepage from oil or natural gas accumulations. Figure 5 illustrates one form in which the 'sniffer' data can be used as an exploration tool. It shows geochemical data from a deep tow inlet in profile form superimposed to scale on the seismic profile. Such records are produced at sea to aid the explorer in making real time evaluations of hydrocarbon potential of structurally significant areas. The anomaly represented on the right of Fig. 5 is termed a 'localized' anomaly because of the relatively short duration of the hydrocarbon signal and the magnitude of the hydrocarbon concentrations relative to regional background. Several 'bright spots' may be seen on the seismic section at depth as well as shallow gas-charged reservoir sands presumably sourced by migration along the observed fault plane.

Figure 6 illustrates a second type of anomaly frequently observed and referred to as a 'broad' anomaly owing to its time and areal persistence. Note
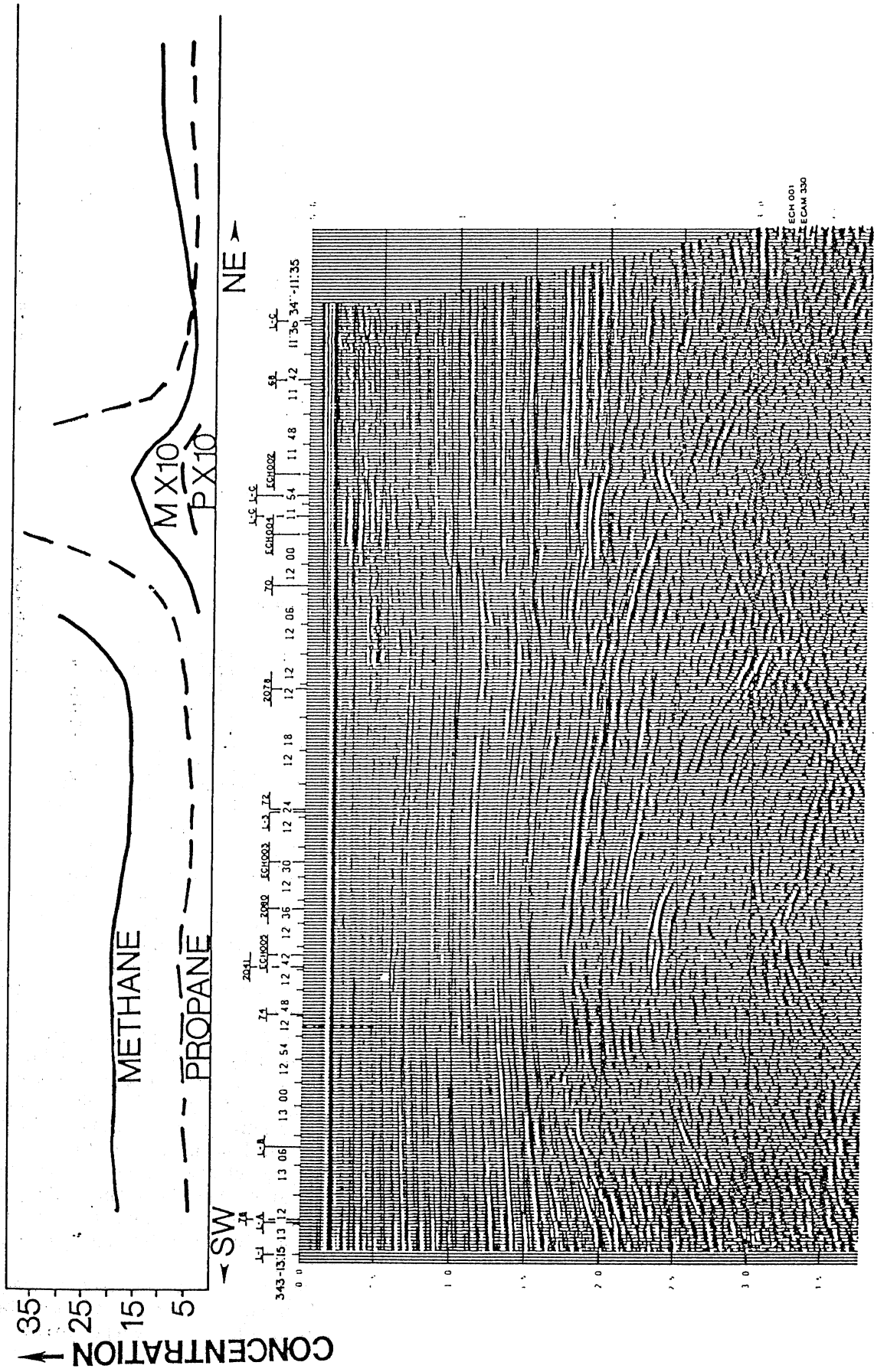
Fig. 5. Marine hydrocarbon and seismic profile showing localized anomaly over faulted reservoir.
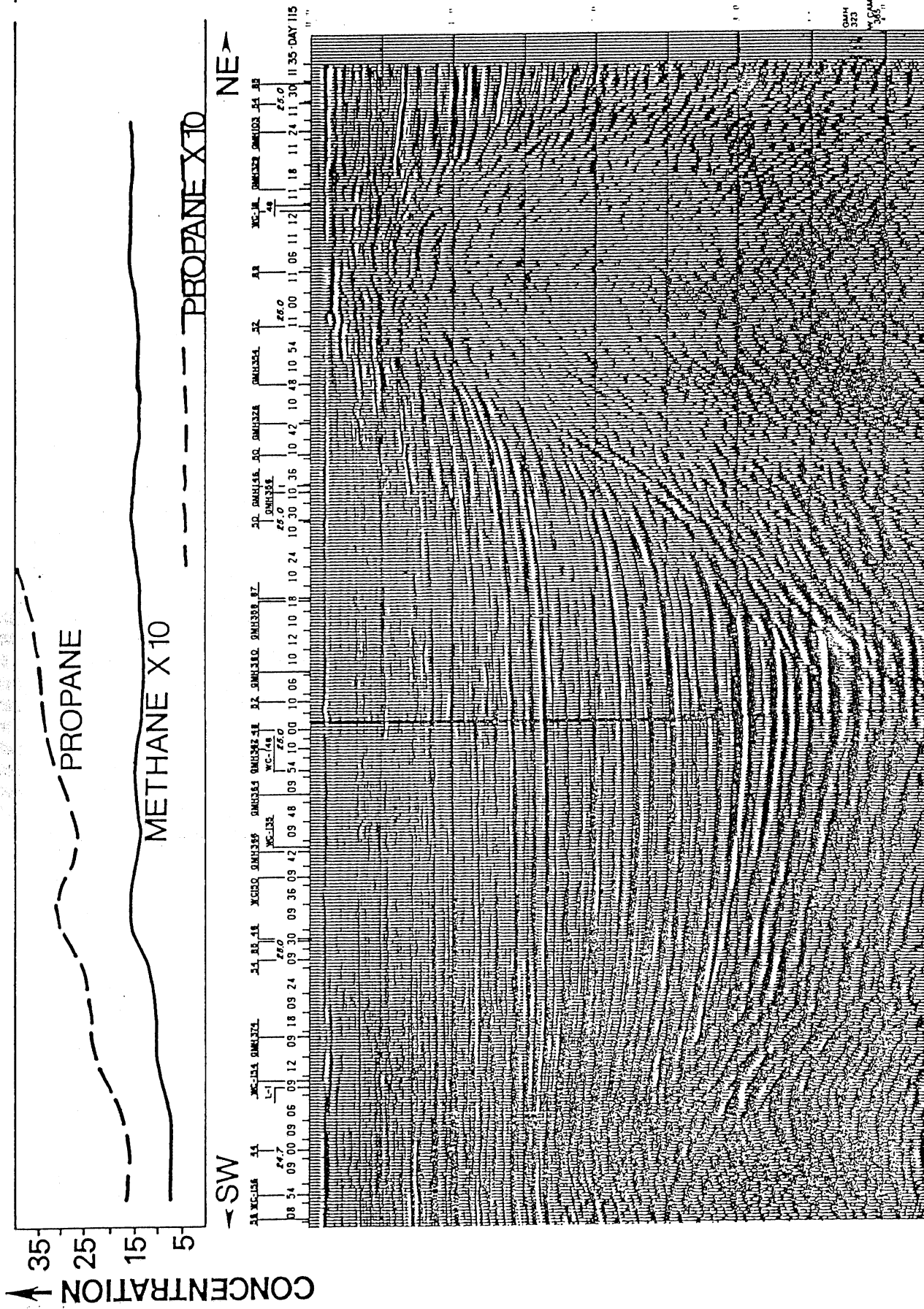
Fig. 6. Marine hydrocarbon survey profile showing broad anomaly over structural feature.

the relative constancy of the methane signal while the propane concentration increases as the vessel approaches the seismic structural feature indicated on the right of the figure. This type of behaviour is characteristic of an oil as opposed to a gas prospect.[31] Reitsema[32] observed methane arising from both biological and thermal sources. Differentiation was made on the basis of methane to ethane ratios. Multiple sources are observed for methane but not for ethane or propane. Petroleum production activities did not increase the hydrocarbon content of the non-surface water beyond that often found above petroliferous structures. To avoid surface contamination valid seepage information is obtained near the sea floor.

Sackett and co-workers[33,34] have carried out extensive studies on C^{13}/C^{12} content of hydrocarbons removed from sea waters to characterize their sources as biogenic or petrogenic. Crossplots of C^{13} content vs. C_1/C_n provide diagnostic classification of the gases.

EXPLORATION ASPECTS OF OIL GENESIS AND TRANSFORMATION

Present geochemical concepts of petroleum and natural gas formation are based on the deposition of organic-rich, fine-grained sediments under conditions favourable to preservation of the organic matter. Transformations in the chemical character of this organic material begin immediately after deposition where microbial activity is one of the primary agents. Methane is the component of this phase of transformation which is of exploration significance. Bacterially produced gas is often found in shallow reservoirs.[25]

The generation of oil and gas is a function of both the type of original organic matter and its thermal history. The principal phase of oil generation requires a temperature threshold of 50–60 °C. This temperature is not usually reached at burial depths of less than 3000 ft and will be significantly deeper for areas having a lower than normal (1.4 °F/100 ft) geothermal gradient.

The type of original organic matter plays an important role in determining the relative amounts of oil and gas and their rate of generation. The composition of sedimentary organic matter varies as a function of proximity to sources of algal and terrigenous plant remains. Algal remains are characterized by high atomic H/C and low O/C ratios and terrestrial plant debris is characterized by low atomic H/C and high O/C ratios. Organic debris rich in algal remains is associated with open marine or freshwater lacustrine environments and is recognized as an excellent source of the more common crude oil types.

Terrigenous remains are associated with nearshore environments. They consist of epicuticular waxes, spores, pollen, resinous and woody organic matter. The waxes are regarded as a rich source of paraffinic-base crude oils commonly associated with intermontane basins,[15] while the spores, pollen and resinous matter are considered a more prolific source of gas. The woody organic matter is also regarded as gas-prone and produces little or no oil during thermal maturation.

A thorough source evaluation must first provide a quantitative measure of the total organic carbon content of the rock. Shales and siltstones with above average organic carbon content (minimum values of 0.4%) are regarded as favourable source rocks. Carbonates with organic carbon content in excess of 0.3% may be also good oil source rocks while sandstones are commonly regarded as having little or no source potential.

For practical purposes the organic matter is divided into a soluble (extractable by organic solvents) and an insoluble fraction (kerogen) freed from the rock by acid digestion. By its very nature the soluble organic matter is more amenable to quantitative analysis by standard analytical techniques than are the insoluble fractions. The soluble organic matter provides a quantitative estimate of oil source potential in terms of the concentration of petroleum-like hydrocarbons present in the rock. A threshold value of 500 ppm extractable organic matter is generally regarded as the lower limit for a favourable oil source rock.

Field studies carried out in several sedimentary basins have shown that sedimentary organic matter undergoes a progressive change in character with increasing depth of burial. These changes are reflected in both the soluble and insoluble organic matter and are observed to vary as a function of the type of organic matter and the geothermal gradient. Increasing depth of burial is accompanied by an increase in the quantities of extractable matter. More importantly, the gross composition and relative abundances of individual hydrocarbons also undergo a significant change. Shallow samples are characterized by an abundance of the heavier and more condensed structures characteristic of the original organic matter. This represents the pre-petroleum generation stage and is representative of an immature source sequence. With further burial thermal cracking of the insoluble organic matter (kerogen) occurs. Petroleum-like hydrocarbons are generated, giving rise to a progressive dilution of the original heavier hydrocarbons inherited directly from the higher plants and algal forms incorporated in the sediments. At this point, the extractable matter takes on the character of a petroleum and the source rock is regarded as having reached a thermally mature stage.[39] The maturation stage is recognized by solid-liquid chromatography (SLC) of the extractable

matter and gas–liquid chromatography (GLC) of the saturated hydrocabon fraction. SLC provides a quantitative measure of the hydrocarbons (saturated and aromatic), resins and asphaltenes, fractions common to all crude oils.

The quantity of organic carbon, extractable organic matter and its gross composition (SLC; GLC) are basic information to a source rock evalution. These data are essential to the characterization of a source rock and correlation of a source rock with a specific crude oil.

Kerogen microscopy by both transmitted and reflected light provides another approach for determining favourable zones for oil and gas generation. Kerogen, the insoluble organic matter, represents in excess of 90% of the total organic matter present in a sedimentary rock. Kerogen may be described as a mixture of highly polymerized macromolecules bearing alkyl chains and aromatic ring systems. The complex nature of kerogen and the experimental difficulties inherent in obtaining pure kerogen for subsequent chemical analysis imposes several practical limitations on its routine use for estimating quantitatively the source potential of a particular interval.

Kerogen microscopy, however, offers the simplest and most direct method for estimating the thermal maturity of sedimentary organic matter and the depths at which oil or gas generation is likely to occur. The use of kerogen analysis for measuring the degree of maturation is based on parallelism between the processes of coalification and petroleum formation. A highly refined method for estimating the maturation stage of organic matter involves measuring the light-reflectance of microscopic size vitrinite particles present in the sediments. Geochemists have shown that the principal phase of petroleum generation occurs when the coaly matter contains between 30% and 40% volatile matter. Calibration curves have been developed relating the volatile matter content to reflectance and indicate that the main oil generation stage corresponds to reflectance values between 0.5% and 1.4%. Lower levels are indicative of immature organic matter (pre-generation stage) and higher values above 1.4% are indicative of post-mature organic matter.

A second, more subjective, kerogen evaluation technique is the examination of the particulate organic matter in transmitted light. Whereas reflectance microscopy examines vitrinite particles transmitted light microscopy examines all the organic particles present in the residue. These particles include amorphous matter, algae, spores, pollen and cuticle and woody remains, as well as coaly fragments. The visual kerogen examination includes an estimate of the concentration, color and state of preservation of these remains providing information on the type of original organic matter and, therefore,

the hydrocarbon product (oil or gas) most likely to be generated during thermal maturation.

The color of the particulate organic matter has been observed to vary as a function of its type and thermal history. With increasing burial the organic matter undergoes a color change from yellow, representing essentially unaltered material, to brown and black, the latter stage representing essentially complete carbonization of the organic debris. A numerical thermal alteration scale of 1 through 5 has been developed based on both experimental and field observations. This scale provides a relative estimate of the maturation stage of the organic matter pertinent to oil and gas generation.

Pyrolysis techniques have recently been developed by members of the Institut Français du Pétrole (Espitalie[27]) which are rapidly gaining acceptance by the industry. Van Krevelen type evolutionary paths for the thermal decomposition of various types of kerogen associated with source rocks are evoked. The method consists of the selection, detection and quantitative analysis of oxygenated and hydrocarbon type compounds issuing from the pyrolysis of sedimentary rocks in an inert atmosphere and with programmed temperature. The visual display results in three peaks on an analogue recorder. Peak areas are diagnostic. The first peak corresponds to the free hydrocarbons present in the rock. The second corresponds to the hydrocarbon type compounds produced by the cracking of the kerogen up to 550 °C, is indicative of the residual petroleum potential of the rock and referred to as the 'Hydrogen Index'. The third peak corresponds to the CO_2 produced by the pyrolysis of the organic matter in the rock and is called the 'Oxygen Index'.

The fourth parameter obtained by the method is the temperature corresponding to the maximum hydrocarbon generation in peak #2. This T(max) shows promise of providing another indicator of the maturation stage of the kerogen and will be a useful supplement to currently used vitrinite reflectance measurements.

Hydrocarbon source evaluations seek to identify organic-rich intervals with the requisite thermal history for oil or gas generation. The quantities generated and the ratio of oil to gas will depend on the quantity and type of organic matter originally deposited. These geochemical studies may be carried out on either surface or subsurface samples. Data based on a single well are not meant to imply knowledge of migration and accumulation in reservoir rocks. Such interpretations are possible only when adequate control points throughout a basin are available. Geochemical data must be integrated with knowledge of the geological history of the basin and current geophysical data if meaningful evaluations regarding migration and accumulation are to be reached.

CHEMICAL IDENTIFICATION OF INDIGENOUS AND MIGRATED PETROLEUM

One of the most difficult questions facing the petroleum geochemist today is the problem of primary migration. Despite numerous studies which have served to elucidate the origin and maturation of organic matter as a function of time and temperature, very little is known of the time and mechanism of hydrocarbon expulsion from source rocks. This lack of knowledge has given rise to two schools of thought. Geochemists, on the one hand, maintain that significant oil expulsion and subsequent migration from the source rock occurs only as a result of the burial of the source rocks to depths where temperatures are sufficient to form crude oil-like mixtures. Many practising exploration geologists, on the other hand, maintain that empirical data call for expulsion and migration of oil after only shallow burial of source and reservoir rocks. In essence, the main point of contention centres on the vertical migration distances required of the late generation hypothesis. In order to account for many shallow oil accumulations, particularly in Tertiary reservoirs, geochemical data frequently necessitate vertical migration of over several thousand feet.

In this regard, geochemical data for the Tertiary age sediments of the Niger Delta are comparable with data generated from similar age rocks of the Gulf Coast, MacKenzie Delta and Tertiary basins of California. Kerogen microscopy reveals low levels of thermal maturation for fine-grained rocks associated with reservoirs in these basins. The paucity of the oil prone amorphous organic matter in these rocks is a further indication that generation of significant levels of oil-like mixtures is unlikely. Further support for this conclusion is to be found in a critical evaluation of the rock extract data. Chemical composition has been widely used as an indicator of thermal maturity, the ultimate goal being to identify that point in the burial history at which the chemical composition of the source rock extract is virtually identical to oil produced within the basin.

Philippi's study[16] of Miocene source sediments of the Los Angeles and Ventura Basins of California represents one of the first attempts at the use of the chemical composition of a rock extract for the identification of mature source facies.

Dow[17] discussed the role of Continental slopes and rises in deposition of organic-rich sediments and their transformation into petroleum. Migration and accumulation are most efficient where reservoir sequences prograde over source beds in areas of structural complexity.

The discussion of oil generation in source rocks presented in this review paper is necessarily brief and sketchy. The comprehensive book by Tissot and Welte[18] on petroleum formation and occurrence is recommended to the reader desiring more information on the subject.

OIL AND SOURCE ROCK CORRELATION

Geochemists are most frequently called upon by the explorers to provide information concerning similarities or differences in crude oils encountered during exploratory or production drilling. Oils which appear physically different may be encountered in reservoirs within a given field. The question is posed whether, in fact, the oils are from a similar source or have widely different origins. Chemical separation techniques developed by researchers from academic, industrial or research institutions working on oil characterization have been quite similar—probably as a result of the presence of several recognizable groups of compounds present in oils and the limited number of practical methods which permit their separation for subsequent characterization.

An illustration of the application of source rock and crude oil correlation is shown in Fig. 7. A regional study was undertaken to assess the source potential of Paleocene/Eocene sediments in the Danish sector of the North Sea. Cuttings and core samples were processed from selected intervals from ten wells shown on the index map and located from Ekofisk in the southern Norwegian sector to the O-1X well in the Danish area A-SW. Chromatograms of the saturated hydrocarbon fractions extracted from cuttings and cores as well as the corresponding fractions isolated from crude oils obtained from the wells are shown in the cross-section. Thermal alteration data obtained by both transmitted light and reflectance microscopy are indicated. Temperatures based on vitrinite reflectance data are also shown.

Crude oils and oil shows encountered in the Danish sector may be broadly classified into four distinct types. One, a condensate type collected during testing of the 6750–6728 ft interval of the E-2X well. Two, a bacterially altered crude oil evidenced by the oil shows in the M-1X well. Third, an admixed oil consisting of a bacterially altered oil and the condensate type. These are represented by the oil show at 6708–6723 ft in the E-2X well. Fourth, and most important from a source correlation point of view, is the paraffinic base oil typified by gas chromatograms of the saturated hydrocarbon fraction of oil shows from the Jurassic reservoired oil in the Q-1X well; Lower Cretaceous and Jurassic reservoired oil in the E-1X; Upper Cretaceous reservoired oil in the N-1X well; and production in the Ekofisk field. This oil type is directly correlatable with the saturated hydrocarbon fraction of extractable matter from Jurassic shales. This correlation indicates that Jurassic or, on the basis of data from the Q-1X well, older rocks are

TABLE I

Mass spectrometric group analysis of saturated hydrocarbon fractions

| | McMurray Oil | Lower Cretaceous | | Devonian Leduc Oil |
		Lloydminister Oil	Grand Rapids Oil	
Alkanes	0	0	0	28
Noncondensed cycloalkanes	40	42	40	39
Condensed cycloalkanes	41	38	40	21
Benzenes	16	17	17	11
Naphthalenes	3	3	3	1

the probable source rocks for oil present in the Danish sector.

Regionally, there is little evidence to support the contention that Tertiary or Cretaceous sediments have generated significant quantities of hydrocarbons. Where the younger sediments contain adequate organic matter of the proper type, such as in the O-1X and I-1X wells, the thermal history has been too mild for significant generation. Extraction data and crude oil correlations indicate there has been significant updip migration of oil into the younger sedimentary sections. This is further supported by the recognition in the N-1X well of extractable organic matter which was previously associated with an evaporitic sequence. The evidence supports the view than underlying Jurassic or older sediments are essential to the presence of petroleum.

RECOGNITION OF ALTERED CRUDES— EXPLORATION SIGNIFICANCE

The development of rapid, inexpensive gas chromatographic methods for analysis of hydrocarbons separated from crude oils and source rocks has resulted in widespread acceptance of the techniques. Recently, gas chromatographs have been linked with mass spectrometers to provide an even more effective tool for the explorer. Mass spectrometry was applied to saturate fractions of Lower Cretaceous oils from Lloydminister and Grand Rapids and Devonian Leduc oil and compared with similar extracts from the tar sands at Ft. McMurray (Table I). The results show the Leduc oil to be different from the oil of the McMurray and the McMurray to be similar to the Lower Cretaceous oils. It was concluded that the McMurray crude oil in the Athabaska oil deposit does not represent oil which has escaped from the Upper Devonian sediments but was most likely generated from Cretaceous sources.

The mass spectrometry clearly showed the absence of n-paraffins in the oil fraction. Deroo[19] presented a study of alteration of crude oils from eastern Alberta in the western Canada sedimentary basin. Systematic

changes were observed progressively from unaltered oils in deeper pools to heavier oils in shallower reservoirs and, finally, severely altered oils near the surface and in the Athabaska tar sand. Microorganisms are thought responsible for the degradation with selective removal of the n-paraffins. In western Canada, consistent with the trend of increasing bacterial degradation is an increase in sulfur content of the crude oils. The role of the bacteria in causing the addition of sulfur to the crude oils is unknown. However, free sulfur is produced by the action of *Desulfovibrio* on sulfate. This free sulfur may react directly with the oil. Reactions of saturate hydrocarbons from the Lloydminister Lower Cretaceous crude oil with elemental sulphur carried out by the author produced resins similar in composition to the naturally occurring resins in the Lloydminister crude and those present in the McMurray bitumen (Table II).

TABLE II

Mass spectrometric group analysis of natural and synthetic resins

	McMurray Resins	Lloydminister Natural Resins	Lloydminister Synthetic[a] Resins
Benzenes	11.1	11.3	12.3
Indanes	7.2	4.3	6.3
Dinaphthene-Benzenes	5.1	5.1	10.6
Naphthalenes	11.6	11.3	12.5
Benzothiophenes	13.3	10.8	10.8
Phenanthrenes	6.2	6.9	4.9
Dibenzothiophenes	10.2	10.3	8.2
Pyrenes	6.3	7.0	5.8
Chrysenes	2.0	1.5	2.8
Naphthobenzo-Thiophenes	3.4	3.2	2.4
Acenaphthylenes	12.0	15.7	11.8
Acenaphthenes	11.7	12.6	11.6

[a] Synthetic resins produced by reaction of elemental sulfur with Lloydminister saturate hydrocarbon fraction.
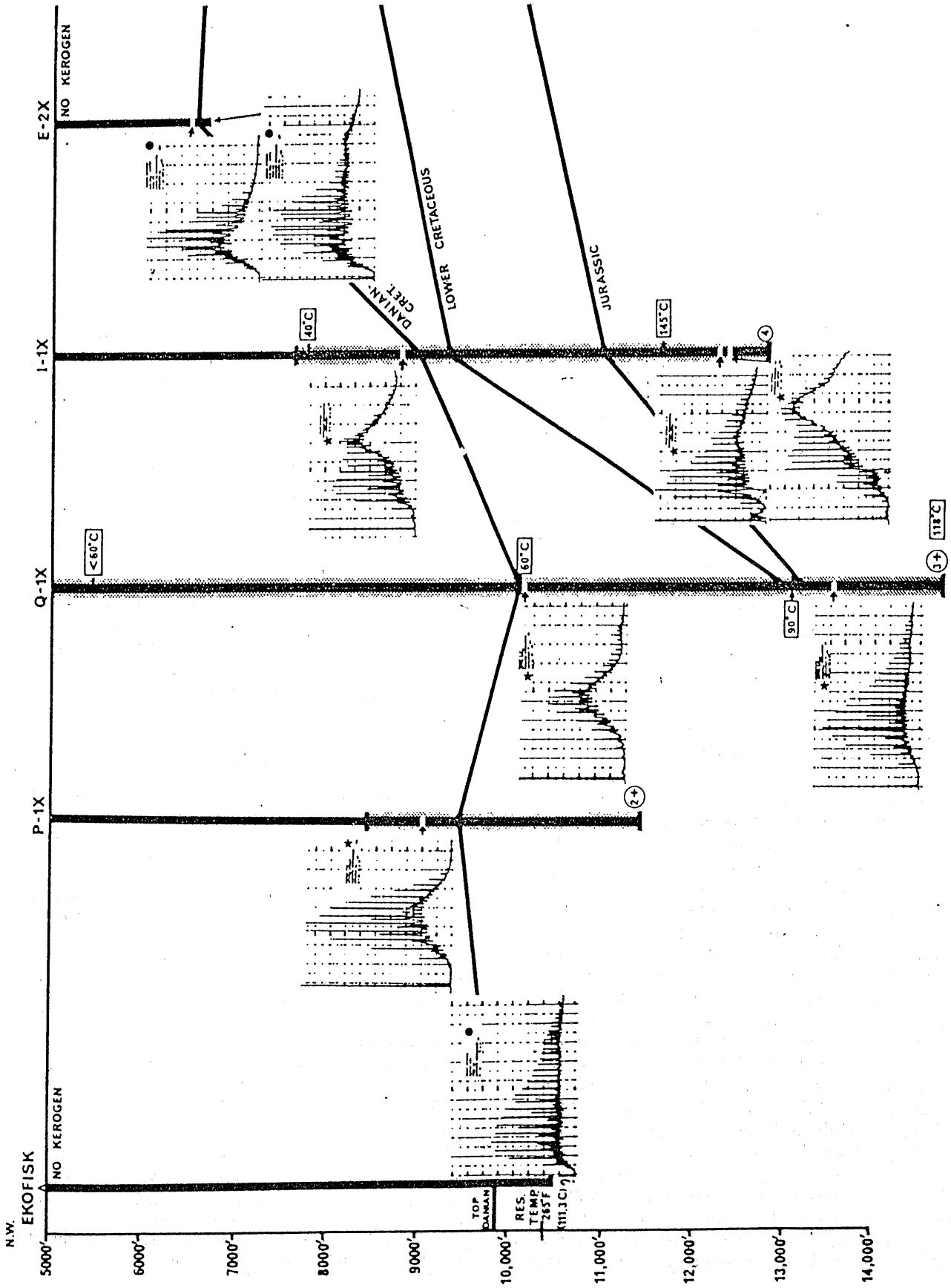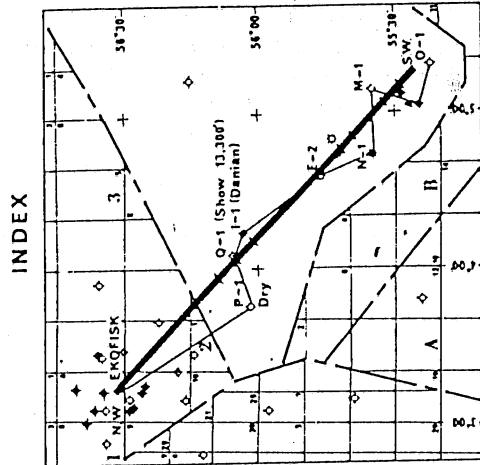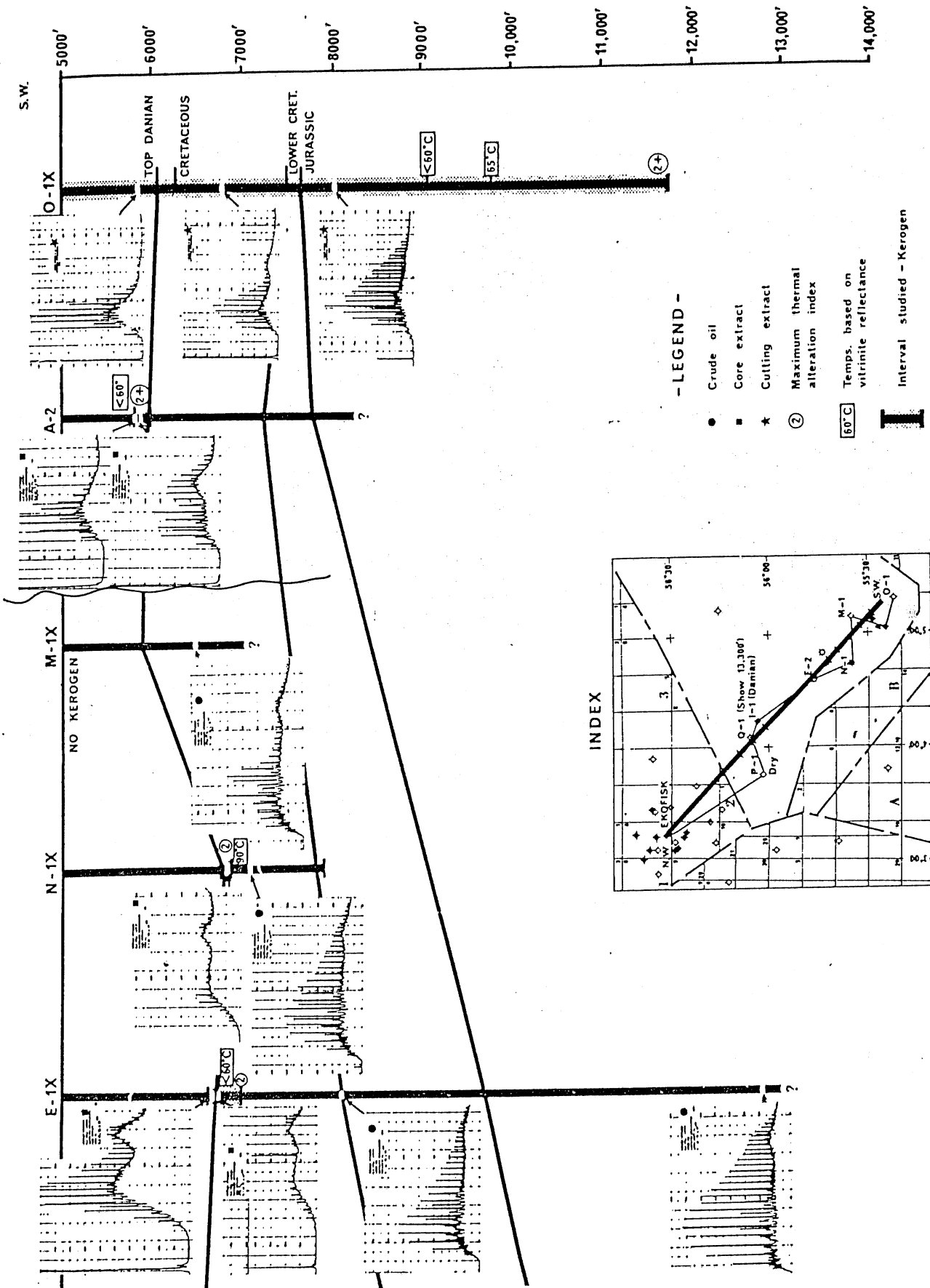
Fig. 7. Thermal maturation and chromatographic correlation of reservoired oils and source rock extracts of North Sea Danish and Norwegian sectors.

Fig. 7—continued.

Hunt[20] has postulated that in the deep (hot) portions of sedimentary basins, sulfur in elemental or polysulfide form could effectively destroy light hydrocarbon liquids and gases. Valitov[21] has further demonstrated the oxidation of hydrocarbons with elemental sulfur at 175 °C.

THERMALLY INDUCED EARLY MATURATION

Rashid and McAlary[22] provided an example of early maturation of organic matter and genesis of hydrocarbons as a result of heat from a shallow piercement salt dome. The Primrose Prospect is characterized by Jurassic salt that has pierced Early Cretaceous sediments and uplifted Late Cretaceous and Early Tertiary beds to provide localized structural closure, shale compaction and anomalously high heat gradients in the younger sediments overlying the salt mass. Reservoir rocks interbedded with the compacted shales contain wet gas, condensate and 31° API oil. Thermal gradients as high as 3.5 °C/100 m were calculated. Mature hydrocarbons were encountered in shallow reservoirs on the crest of the halokinetic structure and thought to be the result of maturation of amorphous organic matter via the temperature and pressure exerted by the salt dome. Coeval beds beyond the salt indicate lower levels of thermal alteration as exhibited by kerogen properties.

AGE DATING OF HYDROCARBONS IN OILS

A goal of many geochemists has been to devise a method for age dating of oils similar to those used in radioactivity dating of minerals ($K^{40} \rightarrow A^{40}$, etc.). The short half life of C^{14} (5730 ± 40 years) and detection limits of approximately 10 half-lives render application of radiocarbon data practically useless in petroleum exploration with the exception of very recent sediment studies. Young *et al.*[23] have devised a method based on the idea that compositional changes of petroleum may be used to estimate the duration of the petroleum generation and maturation processes. Hydrocarbon-age calculations are made for two ranges of hydrocarbons: the light gasoline range (C_5–C_7) hydrocarbons and the heavy ($C_{15}+$) hydrocarbons. Gas chromatographic methods to determine the composition of the light hydrocarbons and mass-spectrometric analysis of the saturated $C_{15}+$ hydrocarbon fraction were used. Matrix methods for calculating the relative amounts of paraffins and the various ringed naphthenes are employed. The calculation of hydrocarbon ages for the gasoline range hydrocarbons is based on the apparent disproportionation of naphthenes to give paraffins and aromatics. Ten naphthenes ranging from cyclopentane

through ethylcyclopentane, 17 paraffins including isopentane through *n*-heptane and benzene and toluene aromatics are used. Kinetic expressions are developed using first order kinetics with a temperature dependent reaction rate function replacing a reaction rate constant. In addition to the analytical results stratigraphic information for the section with which the oil samples are associated and temperature information for calculation of geothermal gradients are required. The agreement of calculated age and known gelogical age of reservoirs containing the oils is better for oils from Cenozoic reservoirs than for those from older reservoirs. Likewise, agreement is better for clastic than carbonate reservoirs.

TIMING OF OIL GENERATION, MIGRATION AND OIL WINDOW

Understanding of the timing of oil gas migration is of importance to the explorer in evaluating a geological target. At the time of sourcing, suitable geologic traps must have been formed in order to accept and retain the expelled hydrocarbons. Periods of erosion, salt movement and other active tectonism should be considered along with timing of periods of oil generation and expulsion from source rocks in basin evaluation. Magara[35,36] dissects the conventional peak oil accumulation curve associated with the oil window concept to include an early stage of peak oil formation followed by a later stage of peak thermally generated gas formation. Tissot[37] has presented a mathematical model to simulate the thermal degradation of kerogen and the formation of petroleum. Warren[38] has incorporated basin source potential and the sedimentological-trap type classification of the basin to yield an estimate of total basin reserves and a field size distribution.

POST-ACCUMULATION CHANGES

Post-accumulation transformation processes have been recognized by many workers in geochemistry.[24] Five principal processes are operative. Devonian Leduc reef oils from Alberta, Canada represent examples of thermal alteration (maturation). Six oils belonging to a single family on the basis of geological considerations and geochemical correlation criteria were examined. With increasing reservoir depth, coinciding with maximum paleodepth of burial, increasing alteration was observed. This consisted in (1) an increase in paraffins and naphthenes (saturates); (2) a slight decrease in low-ring aromatics (four or less rings); (3) a marked decrease in high-ring aromatics (>four rings) and NSOs (resins); and, (4) a slight decrease in asphaltenes. Gas-deasphalting is the precipitation of asphaltenes from crude oil in the

reservoir by an increase in solution gas, generated externally or internally by maturation. Deasphalting is largely restricted to the deeper or hotter parts of basins. Young or shallow oils are usually not affected. Three transformation processes are usually inter-related; biodegradation, water-washing and oxida-tion. Oxidation involves the thickening or drying of an oil deposit through evaporation of gases and lighter fractions where exposed to the atmosphere. The alteration of oils by contact with meteoric waters results in the flushing away of light hydrocarbons via their solubility in water. Oils from Paleocene sands in the Gippsland Basin, Australia appear to have been altered by water washing and/or biodegradation. In two closely spaced pools one oil is paraffinic while the second is naphthenic. Biodegradation is evident in the Cretaceous Bell Creek field, Montana; other areas include MacKenzie Delta Beaufort Basin oils, Louisiana Gulf Coast salt dome pools and Santa Maria Basin, California.

CONSIDERATION IN OIL AND GAS EXPLORATION AT GREAT DEPTHS (BELOW 7000 m)

The existence of oil and gas accumulations at great depth has been a topic of concern to the petroleum industry. Geoscientists are divided on the subject. Theorists present convincing arguments for the possibility of deep gas generation via non-con-ventional or abiogenic methods.[28] Abiogenic gas is thought to originate from igneous rock by the combination of the *in situ* carbon and hydrogen to form nearly pure methane. Since carbonaceous chondritic meteorites do contain hydrocarbons, including graphite, it is possible that the earth's mantle might contain hydrocarbon molecules.[29] Lack of reservoirs is a major concern.

Because of the limits placed on deep drilling by current drilling technology little first hand informa-tion relative to the actual occurrence of these non-conventional gas sources is available. Deep tests of approximately 31 000 ft in the US have been drilled.

This review author conducted an investigation into the possible association of dry gases in the Sacramento Basin and the Delaware and Val-Verde Basins with high thermal activity. Based on C^{13}/C^{12} studies on the methane and CO_2 in wells from these basins, it was conluded that there was a possibility of igneous action. Either the igneous instrusives pro-vided the thermal regime necessary to promote maturation of conventional source bed organic matter or sources of carbon from deep within the earth were brought to the reservoir sands via the igneous activity.[30]

Price[26] has presented a case to accommodate large amounts of hydrocarbons such as petroleum in water solution at temperatures in excess of 180 °C. He suggested a model calling for deep origin of hydro-carbons and primary migration in molecular solution at elevated temperatures along fault pathways of vertical migration to shallow sediments and reservoir sands. Primary migration by molecular solution may be operable to depths of as much as 40 000 ft until all deep basinal pore water has been removed by compaction. Exsolution via salting-out and tempera-ture reduction in the shallow depths is a key feature of Price's model.

Most petroleum company geochemists accept the organic origin theory of petroleum and natural gas. They are convinced of the regularity in trans-formation of organic compounds as they pass through the temperature regime known as the oil window (50–150 °C). Thermodynamic considerations indi-cate that at temperatures above 200 °C all hydro-carbons except methane are unstable in the sedimen-tary environment. At temperatures above 550 °C, methane decomposes. However, these temperatures would not be expected in the sediments except in the immediate contact with igneous intrusions.

Geologists maintain gas phase-out with depth would occur because of a loss of permeability and porosity rather than chemical destruction or migra-tion. Hunt[20] reports oil phase-out will occur between 14 000 and 25 000 ft depending upon the geothermal gradient and depositional rate. Gas phase-out will occur at depths greater than 25 000 ft.

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