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Generation and Migration of Light Hydrocarbons

John M. Hunt

Summary. Light hydrocarbons (containing from 1 to 14 carbon atoms) are formed from disseminated organic matter in sediments at the parts-per-billion level by biological and low-temperature (<50°C) chemical reactions and at the parts-per-million level by high-temperature (>50°C) cracking reactions. The cooler reactions produce mainly branched hydrocarbons, whereas the hotter reactions yield more straight chains. Hydrocarbon generation zones in the subsurface can be recognized on the basis of hydrocarbon distribution patterns. Hydrocarbons with tertiary carbon atoms form at lower temperatures than those with quaternary carbons. Methane and ethane migrate vertically through fine-grained shales by diffusion and solution, whereas many of the C_{3+} hydrocarbons show little or no vertical migration. Concentrations of light hydrocarbons, including methane, in fine-grained source rocks decrease to low values in deep, high-temperature (>200°C) sediments. This decrease may be one reason why no economic accumulation of gas has been found to date deeper than 8.2 kilometers (27,000 feet).

Natural seeps of oil and gas have been known since the beginning of recorded history, but only recently have investigators begun to understand how these important fuels are formed. It is now well documented that practically all petroleum originates from the decomposition of organic matter in marine and lacustrine sediments of the earth's crust. The process occurs in three stages. During the first stage, diagenesis (<50°C), methanogenic bacteria form methane from substrates in the sediments. Traces of C_2 to C_{14} hydrocarbons and about 15 percent of the C_{15} to C_{40} hydrocarbons in crude oil also are formed as a result of low-temperature biological and chemical reactions (*1*). During catagenesis (50° to 200°C), about 85 percent of the oil and 75 percent of the gas are formed from the cracking of the organic molecules (kerogen) in the sediment (Fig. 1). Some asphalt also is formed either as a by-product or as an intermediate in the reactions. In the last stage, metagenesis or metamorphism (>200°C), only gas is formed in appreciable quantities. An unknown number of intermediate reactions are involved in the overall reaction:

$$\underset{\text{kerogen}}{2C_{10}H_{14}} \rightarrow \underset{\text{oil}}{C_{10}H_{18}} + \underset{\text{gas}}{2CH_4} + \underset{\text{pyrobitumen}}{2C_4H}$$

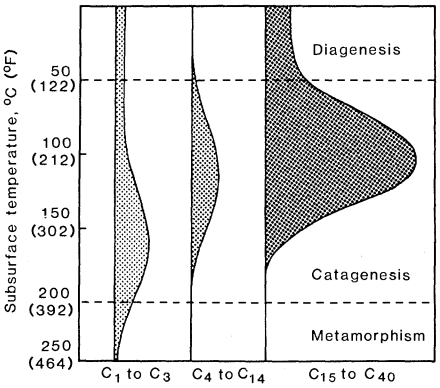
Graphitic pyrobitumen residues have been found in many sedimentary rocks. If the oil is subjected to higher temperatures with greater burial, most of it is converted to gas. The oil floor in sedimentary basins, the depth below which there are no oil accumulations of economic value, varies between about 3 and 7 km (10,000 and 23,000 feet), depending on the geothermal gradient (*1*).

Petroleum geochemists are now turning their attention to the more difficult problem of working out the details of the generation processes and determining the mechanisms by which the oil and gas migrate from the source beds into reservoirs. Most of the early techniques developed to define petroleum source beds depended on tracing the distribution of the hydrocarbons spatially in the subsurface by grinding up sediment samples and extracting their hydrocarbons and associated bitumens with nonoxidizing organic solvents (*1*). The hydrocarbons were separated from the solvent by distillation and analyzed by liquid and gas chromatography and mass spectrometry. This procedure came to be known as the C_{15+} extraction technique since it separated the hydrocarbons from about C_{15} to C_{40}. The light hydrocarbons, containing fewer than 15 carbon atoms, were lost during removal of the solvent. Currently, this technique is widely used in the petroleum industry for determining the subsurface depth at which hydrocarbons are forming and for correlation. The C_{15} to C_{40} hydrocarbons include a wide variety of individual hydrocarbons derived from living organisms, such as steranes from sterols (for example, cholesterol), which can be used to correlate reservoir oils with oils remaining in source rocks and to estimate stages of maturation (*2*).

In the first extractions of the light hydrocarbons (below C_{15}) about 20 years ago, high molecular weight solvents were used that did not interfere with the isolation of the hydrocarbons (*3*). Since then much more sophisticated techniques have been developed, such as headspace analysis which involves disaggregating wet sediments in a helium atmosphere and analyzing the hydrocarbons released into the gas space (*4*). Also, light hydrocarbons have been steam-distilled from wet sediments with various pyrolysis units and have been removed by hydrogen stripping techniques (*5*).

The light hydrocarbons have proved to be a useful supplement to the heavier fractions in unraveling the details of the petroleum generation and migration processes. In the C_1 to C_{10} range it is

The author is in the Department of Chemistry at Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543.



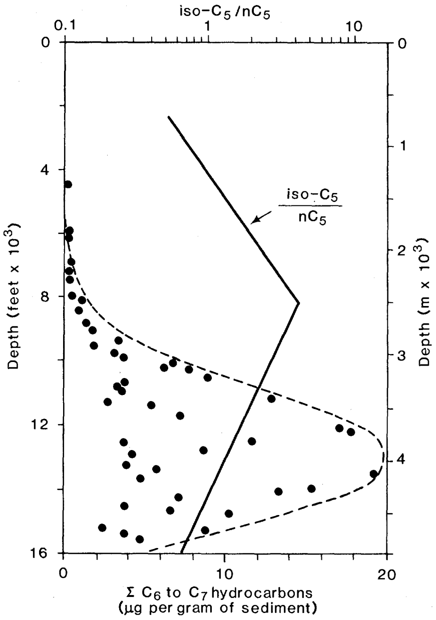


Fig. 1 (left). Distribution of hydrocarbons in sedimentary rocks. Molecular sizes are indicated by the number of carbon atoms: gas, C_1 to C_3; gasoline, kerosene, and jet fuel, C_4 to C_{14}; heavy gas oil, lubricating oil, and residuum, C_{15} to C_{40}. Fig. 2 (right). Distribution of hexanes and heptanes (dots) compared to the ratio of isopentane to *n*-pentane in sediments (cuttings) from a well drilled off the shore of South Padre Island, Texas.

possible to separate all the individual hydrocarbons and to monitor their individual generation-migration patterns. This is difficult in the high molecular weight range except for the more characteristic molecules. Moreover, the light hydrocarbons migrate by all three of the recognized migration mechanisms: diffusion, solution, and oil-gas phase. In contrast, the dominant migration mechanism for the high molecular weight hydrocarbons is the oil-gas phase. In addition, the light hydrocarbons are of interest commercially since they include the most valuable energy products: gas, gasoline, kerosene, jet fuel, and the lighter part of diesel fuel.

The earliest analytical techniques were not capable of detecting extremely low concentrations of hydrocarbons. Light hydrocarbons were not detected at the parts-per-million level in recent sediments except for methane, but they were found to be present in high concentrations in petroleum source rocks (*3*). As analytical techniques improved, the light hydrocarbons were found throughout the sedimentary column at the parts-per-billion level in shallow sediments and at the parts-per-million level in deep sediments (*1*). Methane is an anomaly in this group because it is found in high or low concentrations in both shallow and deep sediments.

Generation

There are three major sources for methane that have been clearly documented by both laboratory and field research. Methane is produced by (i) methanogenic bacteria utilizing substrates such as carbon dioxide and hydrogen in near-surface sediments, (ii) the thermal degradation of organic matter disseminated in sediments, and (iii) the thermal degradation of coal and oil. There has been speculation over a deep mantle origin of methane, but as yet there is no proof that this source contributes significantly to known accumulations.

The biological production of methane can occur from near the surface to sediment depths of 300 m or more in both lacustrine and marine environments. Thermogenic methane is formed mainly in the subsurface temperature range between 100° and 200°C. It forms within and below the oil generation zone. It tends to disappear in deep sediments when the ratio of hydrogen to carbon in the organic matter drops below 0.25; generation of methane stops apparently because of a lack of readily available hydrogen.

The C_{2+} light hydrocarbons of recent near-surface sediments appear to be formed by a combination of biological and low-temperature chemical reactions. Traces of ethane, ethylene, propane, propylene, butane, and pentane have been formed by microbial fermentation processes (*6, 7*). The microbial degradation of terpenoids has yielded butenes, pentenes, hexenes, and toluene (*8*), but these compounds are not major metabolic products of the microorganisms. Instead, they apparently represent the reduction of degradation products occurring incidental to the microbial activities and they vary with the nature of the substrate.

Recent sediments also contain a variety of more complex C_{2+} hydrocarbon structures that are believed to form from low-temperature carbonium ion or free-radical reactions which yield branched hydrocarbons as the dominant products. Such reactions have been observed in the laboratory, and their occurrence in sediments is inferred from the change in the ratio of branched to straight chain hydrocarbons. In most surface sediments, the ratio of a branched pentane or hexane to its straight chain homolog varies from 0.21 to 0.5. With increasing depth and burial, these ratios increase to a peak between 2 to 5 (*9–11*). This peak coincides with the threshold of intense oil generation, which is at about 2.4 km in Fig. 2. This shows the concentration of total C_6 to C_7 hydrocarbons in the fine-grained shales obtained from a well drilled off the shore of Texas in the Gulf of Mexico east of South Padre Island. Only trace amounts of these hydrocarbons are found above 2.4 km. In the interval from 2.4 to 3 km, equivalent to a subsurface temperature of 100° to 110°C, there is an exponential increase in the concentration of these hydrocarbons due to the thermal cracking of the organic matter (kerogen) in the shales. The concentrations decrease at depths beyond 4.3 km as a result of three factors: decreased generation of hydrocarbons, migration of the hydrocarbons out of the source rock, and cracking of the hydrocarbons to smaller molecules, mainly methane through propane. Within the depth range from 3.7 to 4.3 km, not all samples show high concentrations; the range in the concentrations is due to variations in the generating capability of different kerogens within this interval and to early migration along more permeable bedding planes (*10, 12*). Hydrocarbon concentrations in Figs. 2 and 3 are plotted relative to the sediments rather than to organic carbon as the latter was fairly constant in this well (0.9 to 1 percent).

The solid lines in Fig. 2 are best-fit lines for the ratio of methylbutane (isopentane) to *n*-pentane. The peak is just about at the threshold of increased hydrocarbon generation. This ratio continues to decrease with depth because the high-temperature thermal cracking reactions form predominantly straight chain hydrocarbons. A similar peak is observed in the ratios of isobutane to *n*-butane and 2-methylpentane to *n*-hexane in Gulf Coast wells (*10*).

The generation peak in Fig. 2 represents the sum of 14 hydrocarbon structures that contain six or seven carbon atoms per molecule. Distribution patterns for individual hydrocarbon molecules indicate that different hydrocarbon structures are generated preferentially at different depths. Figure 3 shows the depth concentration patterns for two hydrocarbons with tertiary carbon atoms (ethylcyclopentane and 3-ethylpentane) and one with a quaternary carbon (2,2-dimethylhexane). The former show increased generation at 3 km, whereas the latter shows an increase at 4.1 km. The threshold of intense generation for 2,2-dimethylbutane and 2,2-dimethylpentane, both containing quaternary carbon atoms, was about 914 m deeper than for the corresponding 2,3- homologs (*12*). Increased generation of 1,1-dimethylcyclopentane also occurs about 610 m deeper than for 1,2-dimethylcyclopentane. In all these cases, the hydrocarbon that requires a greater depth and higher temperature to form contains a quaternary carbon atom. It is believed that the hydrocarbons with tertiary carbon atoms form earlier because of the greater stability of the intermediate tertiary carbonium ion or free radical. The generation of the *n*-alkanes peaked at about the same depth, around 4.3 km, as that of the hydrocarbons with quaternary carbon atoms in the South Padre well.

These observations are not confined to Gulf Coast sediments. Shale cuttings from the Inigok No. 1 well on the North Slope of Alaska showed the threshold of intense generation of isopentane to be at about 2.7 km, whereas that of neopentane with a quaternary carbon was at 3.4 km. The Kugrua No. 1 well on the Alaska North Slope showed that generation of 2,2-dimethylbutane and 3,3-dimethylpentane continued about 610 m deeper than that of the corresponding C_6 and C_7 homologs (*10*).

Erratic changes in the ratios of individual light hydrocarbon concentrations occur in shallow recent sediments as a result of differences in the organic matrix. These anomalies tend to smooth out with depth, but the type of organic matter is always a factor controlling hydrocarbon generation even in the deepest samples. Leythaeuser *et al.* (*11*) found that the ratios of iso- to normal alkanes for butanes, pentanes, and heptanes were significantly lower for hydrocarbon mixtures generated from marine organisms than for those generated from terrestrial organic matter in Jurassic shales buried to a depth of 3800 m.

The Austin Chalk of South Texas is a carbonate rock containing some glauconite and pyrite but almost no clay minerals. It is a major oil-producing formation, but there have been arguments over whether it is both a source and a reservoir of oil because of its lack of clay, which is thought to be needed for thermocatalytic reactions. Carbonates, however, contain metal impurities that can act as catalysts (*1*). Grabowski (*13*) was able to demonstrate after a large number of extractions and related geochemical tests that the Austin Chalk is a source of C_{15+} hydrocarbons in the depth range from 1.8 to 2.7 km. Hunt and McNichol (*14*) have shown that intense generation of the C_2 through C_{14} hydrocarbons occurred within the same depth range in this chalk.

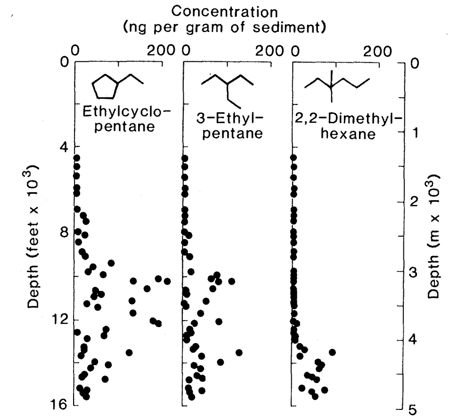


Fig. 3. Distributions of three branched hydrocarbons in the South Padre well cuttings [from (*12*)].

When the quantity and type of organic matter are very similar throughout a sedimentary column, as in the South Padre well, the oil generation interval is recognized as having a smooth increase and decrease in hydrocarbon yield as shown by the dotted line enveloping the data points in Fig. 2. Some wells such as the Kugrua No. 1 in the Meade Basin of the North Slope of Alaska have organic matter that is not so uniform. Consequently, hydrocarbon yields are erratic within the oil generation zone (Fig. 4). This makes it more difficult to determine whether an early hydrocarbon concentration increase, as at 1 km in Fig. 4, is due to generation or to migration from a deeper generation zone.

Other geochemical techniques, in addition to the analysis of simple hydrocarbon yields, have been developed for recognizing the beginning of oil generation. One of these is vitrinite reflectance. Vitrinite is a coal maceral (*15*) that constitutes about 75 percent of most humic coals. It is also found finely disseminated in about 80 percent of all sedimentary rocks. It is derived from disseminated organic debris carried by rivers into sedimentary basins. As vitrinite particles are buried deeper and are subjected to higher temperatures, their molecular structure develops an orderly pattern that causes greater reflectance of monochromatic light. In near-surface sediments vitrinite particles reflect about 0.2 percent of the incident light, whereas in deep samples, where the rocks become metamorphic, reflectance may reach 7 percent. Studies have shown that the beginning of intense oil generation starts at vitrinite reflectance values between 0.5 and 0.6 percent, depending on the type of organic matter generating the oil (*1*). In the South Padre well (Fig. 2) oil generation started at a reflectance value of about 0.6 percent (3 km), whereas in the Kugrua well (Fig. 4) the reflectance value of 0.55 percent at a present-day depth of 914 m indicates that the hydrocarbon peak near this depth is due to generation. The apparent shallower hydrocarbon generation in the Kugrua well is believed to be due to deeper burial in the past and more recent uplift of these sediments. Hydrocarbon generation in the Kugrua well extends from 914 to 2652 m, but the yields of free hydrocar-

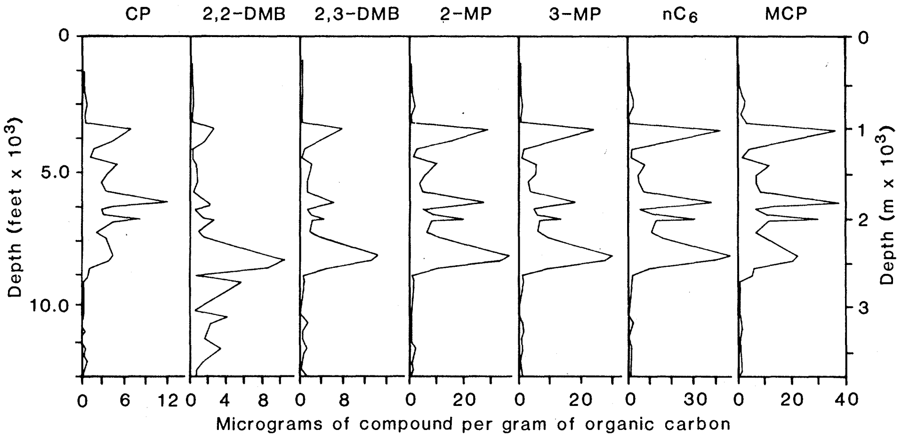


Fig. 4. Hydrocarbon distributions in the Kugrua No. 1 well drilled in the Meade Basin, North Slope of Alaska. Abbreviations: CP, cyclopentane; 2,2-DMB, 2,2-dimethylbutane; 2,3-DMB, 2,3-dimethylbutane; 2-MP, 2-methylpentane; 3-MP, 3-methylpentane; *n*C_6, normal hexane; and MCP, methylcyclopentane.

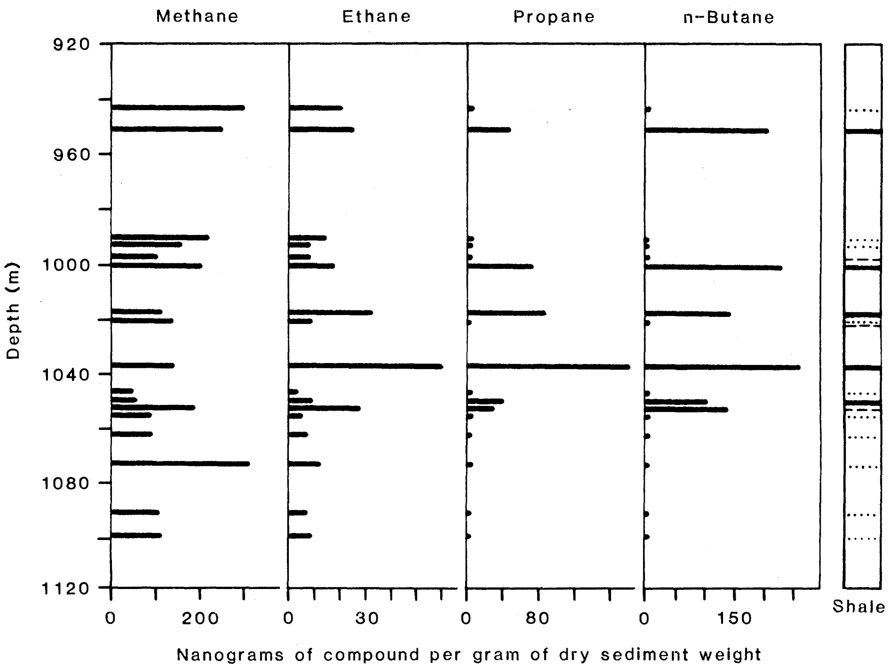


Fig. 5. Variation of gaseous hydrocarbon concentrations with depth and sediment type in DSDP Hole 530A drilled near Walvis Ridge off the west coast of Africa. Green shales, dotted lines; gray shales, dashed lines; black shales, solid lines.

bon within that interval vary from 0.5 to 31 mg of hydrocarbon per gram of organic carbon. The yield of hydrocarbons produced when the kerogen is cracked by laboratory pyrolysis at 400+°C ranged from 3 to 102 mg of hydrocarbon per gram of organic carbon in the depth interval from 914 to 2652 m. This high variability means that only parts of the generation zone can make significant contributions to hydrocarbon accumulations. The hydrocarbon with the highest yield in this group below 2652 m is 2,2-dimethylbutane, which has a quaternary carbon atom.

Migration

Recent studies by Leythaeuser *et al.* (*16*) have emphasized the importance of diffusion as a mechanism for transporting light hydrocarbons from source to reservoir-type rocks. They found that the concentration of C_2 to C_7 alkanes showed a large decrease across a siltstone (source)–sandstone (reservoir) boundary for the C_4 to C_7 molecules but a relatively small decrease for C_2 and C_3. They attributed this difference to diffusive transport, which is faster for the smaller molecules. There also may be a solubility effect because the aromatic hydrocarbons, benzene and toluene, had anomalously high migration rates. These aromatics are more soluble in sediment pore waters than the C_2 through C_7 alkanes.

Although the combination of diffusion and solution mechanisms causes hydrocarbon migration across sand-shale boundaries, the evidence is less convincing that extensive verticle migration occurs by these mechanisms within fine-grained shales except for methane and ethane. On Leg 75 of the Deep Sea Drilling Project (DSDP), Hole 530A was cored off the west coast of Africa through alternating gray and green shales of Cretaceous age with a few organic-rich black-shale laminae. Figure 5 shows the hydrocarbon distribution from methane through butane for the section from 920 to 1120 m (*17*). Although this section is geologically old, it has never been heated to temperatures above 50°C, so any migration mechanism would not involve a thermal input. This could result in slower transport rates than reported by Leythaeuser *et al.* (*16*). Analyses of the samples [see (*17*) for details] showed that the low-temperature hydrocarbon generation originates mostly from the black shales with a small amount from the gray and little or none from the green shales. Propane and the higher hydrocarbons were found concentrated in the black and gray shale source beds, whereas methane and ethane were found distributed through all three lithologies.

An enrichment factor, the ratio of the hydrocarbon normalized to organic carbon in a green shale to the same hydrocarbon normalized to organic carbon in a black shale, was calculated. The results indicated that methane and ethane were enriched in the green shales through migration from the black shales by factors up to 28 for methane and 7 for ethane. Enrichment factors for propane and the higher hydrocarbons were less than 1, indicating no migration for them from black to green shales even over distances of a few centimeters. The interpretation that methane is not generated in the green shales would hold no matter whether the methane is formed microbially or chemically in this section, because studies of DSDP cores over the last several years have indicated that methanogens are not active in green shales like these with organic carbon contents less than 0.5 percent.

The Inigok No. 1 well has been studied in great detail by the U.S. Geological Survey and a number of oil companies (*18*). Figure 6 shows the distribution of four C_7 hydrocarbons compared to that of methane and ethane in this well. The dashed lines represent formation boundaries. A major source of the giant oil accumulations on the North Slope of Alaska has been interpreted, from these studies, to be the Kingak shale of Jurassic age (*18*). In the Inigok well, the Kingak shale extends from 2822 to 3722 m. It is overlain by the Pebble Shale unit and underlain by the Shublik Formation, both of which may be minor contributors to the oil accumulations. The present-day temperatures of the Kingak shale range from about 95°C at the top to 110°C at the bottom. Vitrinite reflectance values range from 0.75 to 2 percent. Figure 6 shows that the highest concentrations of the four C_7 hydrocarbons are in the Kingak shale source rock. The threshold of intense generation for these hydrocarbons, however, starts at about 2.4 km in the overlying Torok Formation where the vitrinite reflectance value is 0.65 percent. There is no evidence of downward migration of these C_7 hydrocarbons and only a suggestion of upward migration of the most water-soluble hydrocarbon, toluene. Likewise, ethane shows only small increases in concentration outside the Kingak shale source. Methane, however, shows comparatively high concentrations in the top 914 m and in the zone below the Kingak shale. It is the only hydrocarbon in this group that is migrating, or being generated, in appreciable quantities outside the Kingak and lower Torok shales.

Deep Gas

In most sedimentary basins, the petroleum geochemist can define the oil floor, that is, the depth below which no oil is being generated. The gas floor is more controversial. My studies of several wells on the North Slope of Alaska and in the Gulf Coast suggest that, when the ratio of hydrogen to carbon in the organic matter of the sediment becomes less than 0.25, the generation of methane is terminated. This is in the range of a vitrinite reflectance value of 4 to 5 percent. The deepest producing well in the world today is the Chevron No. 1 Ledbetter well in Wheeler County, Texas, producing gas at 8 km. The deepest dry hole was drilled to 9.6 km in Oklahoma's Anadarko Basin in 1974. Although about 400 wells have been drilled deeper than 6.1 km in the United States in the last 5 years, none have found commercial gas deeper than the 1977 Chevron well.

Several years ago, LeTran *et al.* (*19*) showed that the generation of methane from source rocks of the Aquitaine Basin of France peaked at a subsurface temperature of ~150°C; at greater depths the methane yields decreased sharply. Since then, the analyses of many deep well cuttings by geochemical service laboratories in the United States have also shown that methane concentrations in the fine-grained sediments decrease to low values in the deepest (2.6 km) high-temperature formations. These observations argue against the possibility that most of the methane found in sedimentary rocks could be diffusing from deep sources in the mantle.

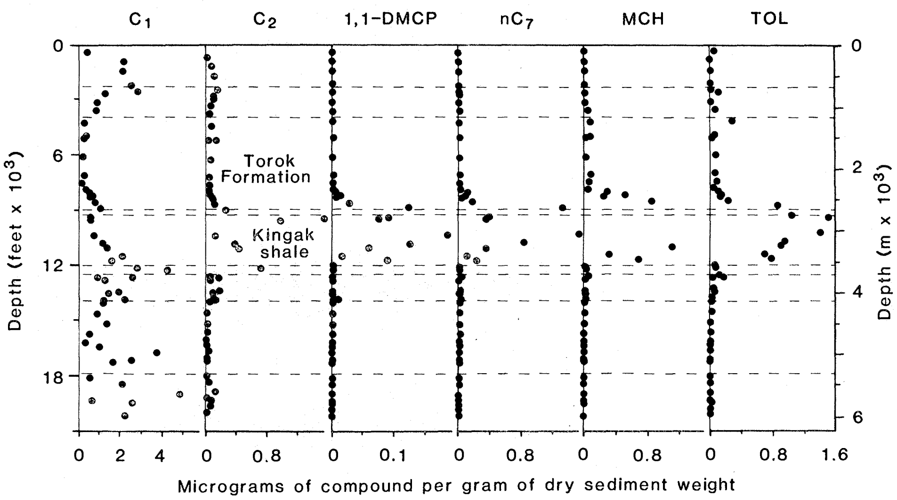


Fig. 6. Distribution of four C_7 hydrocarbons, 1,1-dimethylcyclopentane (1,1-DMCP), normal heptane (nC_7), methylcyclohexane (MCH), and toluene (TOL), compared to that of methane (C_1) and ethane (C_2) in the Inigok No. 1 well drilled in the Ikpikpuk Basin, North Slope of Alaska.

Conclusions

Several types of reactions appear to be involved in light hydrocarbon (C_1 to C_{14}) formation. These include (i) biological origin, (ii) low-temperature (<50°C) chemical reactions, and (iii) high-temperature (>50°C) cracking reactions. The light hydrocarbons are formed from the organic matter of fine-grained sediments at parts-per-billion levels by the first two types of reactions and at parts-per-million or parts-per-thousand levels by the third type of reaction. The lower temperature reactions tend to produce the branched-chain light hydrocarbons, whereas the higher temperature reactions yield increasing amounts of straight chains. This causes a reversal in the ratio of branched to straight chain alkanes at the threshold of intense hydrocarbon generation. Hydrocarbons with tertiary carbon atoms form earlier than those with quaternary carbons because of the greater stability of the intermediate tertiary carbonium ion or free radical.

Hydrocarbon generation zones (oil windows) in wells drilled through sedimentary formations can be recognized on the basis of the distribution patterns of the light hydrocarbons. Generation curves normally show an exponential increase and decrease. In some cases, as in the Kugrua well of Alaska, light hydrocarbon distributions within the oil generation zone are erratic because of variations in the generating potential of the kerogen. If petroleum source rocks within the generation zone are interbedded with sands, there will be some depletion of hydrocarbons from the shales as a result of migration into the sands. The transport mechanism across shale-sand boundaries for the light hydrocarbons is believed to be a combination of diffusion and solution.

Methane and ethane were found to migrate vertically over tens of meters through all lithologies in immature Cretaceous sediments off the west coast of Africa at temperatures below 50°C. In contrast, the C_{3+} hydrocarbons showed essentially no verticle migration in fine-grained shales over distances of centimeters.

In the Inigok well on the North Slope of Alaska, high concentrations of four C_7 hydrocarbons were found to occur only within the oil generation zone of the Kingak shale and the immediately overlying Pebble Shale and Torok units. There was no evidence of downward migration of these hydrocarbons, although some upward migration may have occurred with toluene as a result of its greater solubility in pore fluids. High ethane concentrations were confined mainly to the oil generation zone, but methane was distributed throughout the well.

The methane distribution in Fig. 6 could be interpreted as due to migration from gas-generating organic matter both within and deeper than the Kingak shale. Or it could be a generation profile with biogenic methane formed in the top kilometer and thermogenic methane formed from sediments deeper than 3 km.

Interpretation of the C_{3+} hydrocarbon distributions is more definite. There is no appreciable vertical migration up or down in both the DSDP Cretaceous and the deeply buried Alaska North Slope fine-grained sediments. Yet we know that these hydrocarbons do migrate from source to reservoir rocks in sedimentary basins. This suggests that the migration pathways are not through the fine-grained rock but are along more permeable avenues such as faults, fractures, bedding planes, unconformities, sheet sands, and other large pore openings that permit migration as an oil or gas phase. Migration by this latter mechanism can occur even in microfractures with openings of a few hundred nanometers but not in the fine-grained shale where pore diameters are estimated to be less than 5 nm in the oil window (*1*). Within these shales the vertical transport mechanisms are dominantly diffusion and solution. This limits long-distance vertical migration to the smallest hydrocarbon molecules such as methane and ethane unless the rock is fractured.

Future Work

There are still many important questions to be answered such as how deep can methane be generated. Drillers have the capability to go to 15 km, but will they find anything? Methane tends to move upward through the sedimentary column because of buoyancy, and so the generation floor is probably the production floor. Methane is thermodynamically stable to temperatures higher than those that exist in sedimentary rocks, but it can be oxidized in the presence of water and sulfur compounds (*1*). The No. 1 Bertha Rogers well drilled to 9.6 km in the Anadarko Basin of Oklahoma produced some molten sulfur at a bottom hole temperature of 260°C in Cambro-Ordovician sediments but no methane. Was its absence due to lack of generation or to chemical destruction?

Many more detailed studies are needed to clarify hydrocarbon migration within fine-grained sediments and across lithologic boundaries. Today the exploration geologist wants to know how much oil may be in the reservoirs of an unexplored area. We can make realistic estimates of the amount of oil generated, but estimates of the quantities expelled, trapped, and lost are still based on comparisons with heavily explored areas rather than on a complete understanding of the processes involved.

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15. Coals are composed of macerals just as rocks are composed of minerals. However, macerals vary in chemical composition and physical properties and are not crystalline. The term "maceral" describes the shape and nature of recognizable constituents of coal as determined by reflected light microscopy. The three dominant macerals are vitrinite, liptinite, and inertinite. For further details, see E. Stach, *Coal Petrology* (Gebruder Borntraeger, Berlin, 1982).
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Intrinsic Mechanisms of Pain Inhibition: Activation by Stress

Gregory W. Terman, Yehuda Shavit, James W. Lewis
J. Timothy Cannon, John C. Liebeskind

Our understanding of the neural and neurochemical mechanisms of pain perception has greatly increased since the time when Melzack and Wall presented their gate control theory of pain (*1*). One development presaged by that theory was the discovery of a central nervous system substrate whose normal function appears to be pain inhibition. This substrate includes cells of the medial brain stem and fibers descending from them to the spinal cord dorsal horn. In the cord, the transfer of nociceptive information from peripheral fibers to ascending paths is modulated by these descending controls.

Stimulation-Produced Analgesia

Until recently, most of the evidence for an intrinsic pain-suppressive system came from studies of stimulation-produced analgesia (SPA). Electrical stimulation of the midbrain periaqueductal gray and other portions of the medial brain stem in awake rats caused profound analgesia (*2, 3*) without consistently causing deficits in other sensory or motivational functions. These findings suggested a natural pain-inhibitory role for these brain regions (*3*). Such studies have been amply reviewed (*4, 5*), and need be only briefly summarized here as follows:

1) Pain inhibition appears to result from activation of centrifugal controls since even spinally mediated nociceptive reflexes are blocked by SPA (*3*). That nociceptive responding of dorsal horn cells is inhibited by stimulation at SPA sites supports this view (*6*). Also, lesions of the nucleus raphe magnus and spinal dorsolateral funiculus can disrupt SPA and block the inhibitory effect of SPA on dorsal horn cells, suggesting a bulbar relay and spinal path responsible for these descending effects (*7*).

2) SPA requires the integrity of certain neurotransmitters (*8*), suggesting an active process of inhibition in which the pain-inhibitory message is transmitted across synapses by means of those substances (*3*). Chemical activation of the periaqueductal gray with glutamate excites nucleus raphe magnus cells (*9*) and causes analgesia (*9, 10*). Morphine and enkephalin increase neuronal ("multiple unit") activity only or best in SPA areas, only in awake animals, and to a degree that is closely correlated with their analgesic action (*11, 12*). Supporting the view that this activation during SPA causes animals to feel less pain is the finding that rats self-administer electrical stimulation at certain SPA sites only when concomitant noxious stimuli are also being applied (*3, 13*). Also the results of neurosurgical trials indicate that valid pain suppression occurs with medial brain stem stimulation in man (*14*).

3) An idea of heuristic value was that SPA shared with opiate drugs both central sites and mechanisms of action (*3*). Thus, for example, brain areas supporting SPA and analgesia from opiate mi-

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G. W. Terman and Y. Shavit are graduate students in the Department of Psychology at the University of California, Los Angeles 90024. J. W. Lewis is a NIDA postdoctoral fellow in the Mental Health Research Institute at the University of Michigan, Ann Arbor 48109. J. T. Cannon is an assistant professor of psychology at the University of Scranton, Scranton, Pennsylvania 18510. J. C. Liebeskind is a professor of psychology and anesthesiology at the University of California, Los Angeles 90024.