

THE ORIGIN OF NATURAL GAS AND PETROLEUM, AND THE PROGNOSIS FOR FUTURE SUPPLIES

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INTRODUCTION

Any estimation of future supplies of hydrocarbons—oil and gas—is necessarily bound up with the question of the origin of these deposits. The theory of a biological origin, which has become accepted almost universally, would place fairly sharp limits on what the earth might provide. The total volume of sediments, the proportion of organic matter they may contain, and the fraction of this that may have been converted into accessible hydrocarbons have all been estimated. So long as many areas of sediments on the earth remain unexplored by the drill, a prognosis based on such evaluations can be a rough judgment at best. Still, it will give some indication of what can be expected, and it is not likely to be in error by orders of magnitude.

In the early 1970s, estimates based on these considerations had indicated that oil was running out—that the earth could provide for no more than 20 to 40 years' supply at the present rate of consumption. These estimates were widely accepted, resulting in drastic increases in the price of oil. It was the estimates, and not an actual shortage, that prompted these changes, with their profound effects on the world economy.

But what if the source material for oil and gas were not limited to organic deposits, but instead these substances derived wholly or in part from materials incorporated deep in the earth at the time of its formation? This

possibility has been considered in the past, and again in recent times with modern data (1–10). In that case one would make quite different and very much more optimistic estimates of future supplies. But is there any possibility of that? Is anything coming up from deep sources in the earth?

There is little doubt that large quantities of certain fluids—the so-called “excess volatiles”—have made their way up through the crust over geologic time (11). The water of the oceans, the nitrogen of the atmosphere, and the large quantities of carbon now resident in the carbonate rocks of the sediments must have been supplied in that way. The erosion of the basement rocks that produced the other components of the sediments would have provided only a very small fraction of these substances.

There is no agreement (and very little discussion) of the form in which the “excess” carbon came to be supplied to the surface, although it is clear that much of it was at some stage in the form of atmospheric CO_2 , which then dissolved in the ocean water and finally precipitated to form carbonate rocks. The amount of CO_2 in the atmosphere or the oceans at present is a very small fraction of the quantity that has cycled through the system to produce the large deposits of carbonate rocks, which amount to as much as 20% of the mass of all the water in the oceans.

The usual assumption seems to have been that all this carbon came up from its original deep sources already in oxidized form, namely as CO_2 . There is no compelling reason for such an assumption, and there are several good reasons for considering an alternative possibility, namely that methane or other hydrocarbon fluids were involved. In the oxidizing circumstances of the outermost crust and the atmosphere, most of the carbon would end up as atmospheric carbon dioxide in any case, and the subsequent deposition process of the carbonate rocks would be the same. What would be different is the identification of the unoxidized forms of carbon that we find in the outer crust and in the sediments.

When it was thought that the supply of carbon had all been in the form of CO_2 , any unoxidized carbon had to be considered the result of photosynthesis in plants, in which sunlight had supplied the energy necessary for the dissociation of CO_2 . The burning of such fuels, then, constituted the regaining of this “fossil solar energy.” But if the primary carbon had come up from depth in the form of methane or other hydrocarbon fluids, the situation would be quite different. A small fraction of this, arrested on the way up and contained at accessible levels in the outer crust, could constitute an enormously larger energy resource than all the biological deposits. The methods of prospecting for oil and gas would then be quite different, and many new locations would come under consideration, which would have been excluded if one was looking for biological deposits only.

The Opposing Viewpoints

Why should we doubt the biological origin of the earth's hydrocarbons? Has not an immense amount of work demonstrated that the locations of hydrocarbon deposits, the chemical natures and contents of the oils, and the isotopic composition of the carbon, all fit the biogenic theory? Has the biogenic theory not provided the basis for the exploration which has been so successful in the past?

This is what is generally said, but when we look at the various points in detail the situation turns out to be not nearly so clear-cut. Several leading investigators, in both geology and chemistry, have expressed doubts. Hollis Hedberg, a well-known petroleum geologist, wrote, "It is remarkable that in spite of its widespread occurrence, its great economic importance, and the immense amount of fine research devoted to it, there perhaps still remain more uncertainties concerning the origin of petroleum than that of any other commonly occurring natural substance" (12). Sir Robert Robinson, the British organic chemist and Nobel laureate, who investigated the chemical nature of petroleum, wrote, "Actually it cannot be too strongly emphasized that petroleum does not present the composition picture expected from modified biogenic products, and all the arguments from the constituents of ancient oils fit equally well, or better, with the conception of a primordial hydrocarbon mixture to which bioproducts have been added" (13). And again, "It is believed that the arguments for a biological *and* an abiological origin of petroleum are alike incontrovertible. Hence a duplex origin of mineral oil is envisaged" (14). Today we have a great deal more information, which, although rarely examined from that viewpoint, greatly strengthens the duplex origin theory.

One way of discussing this complex subject, with its numerous, apparently conflicting clues, is to discuss the historical evolution of the ideas. The theory of a biological origin became quite firmly established in the second half of the last century, although at that stage no very detailed chemical arguments could be used. Coal, found mainly in sediments, and often with fossils, was firmly regarded as a biological product, and based on this, it was considered that immense amounts of plant material had been laid down over geologic time in circumstances where they escaped destruction by oxidation. It seemed reasonable to think that some fraction of this was converted into the hydrocarbon molecules of gas and oil.

Mendeleev was on the other side of the argument. His paper (in 1870) on the origin of petroleum ended with the words: "The capital fact to note is that petroleum was born in the depths of the earth, and that it is only there that we must seek its origin" (1). He provided many arguments for his

conclusion, among them the regional patterns of petroleum occurrence and their relationship to underlying structures rather than to the nature of the sediments.

The Formation of the Earth

Until the middle of this century, it was thought that the earth had formed as a hot body, had been a ball of liquid rock, as such no doubt well mixed, and had then gradually cooled, producing a differentiated crust overlying a homogeneous mantle. In such an evolutionary history, there could not have been any hydrocarbons in the early earth, for even if they had been initially supplied in the formation process, they would surely have been destroyed. To account for the supply of excess carbon to the surface, one then thought in terms of oxidized carbon only, since that would be the stable form expected in such a case. Carbon dioxide was found to come out of volcanoes, apparently confirming this viewpoint.

The present understanding of the formation process of the earth is different. It has become quite clear that the earth, as well as the other terrestrial planets, accreted as solid bodies from solids that had condensed from a gaseous planetary disk. The primary condensates, ranging in size from small grains to asteroid-sized "planetesimals," all contributed to the formation of the final earth. An accretion from small grains only, could have led to a final body that was inhomogeneous with depth, since at successive epochs different materials might have been acquired. However, when such an accretion process was punctuated by major impacts of competing bodies that had formed on collision orbits, then an orderly, layered composition would be turned into an erratic patchwork. This appears to have been the case in the formation of the earth, just as it was in the formation of all other solid planetary bodies, demonstrated by the ubiquity of impact craters on them.

There is now a great deal of evidence from trace elements and their isotopes that have come up from depth, in various parts of the earth, that the mantle is indeed quite inhomogeneous (15, 16) and its chemical composition patchy, confirming that it has never been all molten. What melting has taken place seems to have been only a small proportion at any one time, but since this partial melting resulted in outpourings that formed the entire outer crust, it produced the impression of an earth cooled from liquid.

Abundance of Hydrocarbons in Solar System

Another part of the discussion, where the outlook in earlier times was quite different from that of today, concerned the derivation of hydrocarbons in the solar system. Hydrocarbons used to be thought of as substances that

were specifically biological. Methane and other hydrocarbons were clearly the results of biological processes, and there was little indication that these molecules would be produced in other ways. In fact, when methane was first detected in the atmosphere of Jupiter, this resulted in publications suggesting that some form of life on Jupiter must be responsible.

Now we know not only that there is methane in the atmosphere of Jupiter, but that by far the largest proportion of the carbon in the entire planetary system is in the form of hydrocarbons. The greatest quantity is in the massive outer planets and their satellites. Jupiter, Saturn, Uranus, and Neptune have large admixtures of carbon in their extensive atmospheres, chiefly in the form of hydrocarbons—mainly methane. Titan, the satellite of Saturn, has methane and ethane (CH_4 and C_2H_6) in its atmosphere. Its clouds are composed of these substances, and it is likely that liquid methane-ethane mixes are on the surface below, and perhaps make up oceans, rivers, and frozen polar caps, more or less as water does on the earth. The asteroids—that swarm of minor planetary bodies between Mars and Jupiter—also seem to have hydrocarbons on their surfaces, and most probably in their interiors. These small bodies cannot retain any atmosphere, and therefore gaseous hydrocarbons cannot be present there. But their dark surfaces and details of their reflection spectra give the strong suggestion that tarlike substances are prominent on their surfaces.

The meteorites are considered to provide us samples of the materials from which the planets formed. One class—the carbonaceous chondrites—contain some volatile substances, and it is this class that is thought to have supplied the earth with most of its complement of volatiles. While carbon is a minor constituent of the other types of meteorites, it is present at a level of several percent in the carbonaceous chondrites, mostly in unoxidized form, with a certain fraction in the form of hydrocarbon compounds (17). The meteorites we now see would have lost any more volatile compounds in their $4\frac{1}{2}$ -billion-year flight as small objects through the vacuum of space, but one would judge that at the time of their condensation in a dense nebula, other more volatile components, including the lighter hydrocarbons, would have been present also. If this type of material was incorporated in the earth, and later subjected to heat and pressure, it would separate out some of these volatile components. The mobile forms of carbon that would be expected would be chiefly methane, with an admixture of heavier hydrocarbon molecules. The pressure, temperature, and chemical surroundings in the earth would then determine what products of this would reach the near-surface domain.

There is no abundant meteoritic material that would outgas carbon dioxide, nor would such material be expected in the chemical circumstances that are believed to have existed at the time of planetary formation. Carbon

dioxide may, of course, result from the oxidation of the hydrocarbons at depth, or on their way to the surface, but it is unlikely that oxidized carbon was the primary material that was incorporated at the formation, and provided all the surface carbon we now have.

The Stability of Hydrocarbons at Depth in the Earth

Another area where the arguments have changed greatly, especially in recent times, is the stability of hydrocarbons. It used to be thought that temperatures above about 600°C would dissociate methane, and that temperatures of 300°C were sufficient to destroy most of the components of natural petroleum. Since such temperatures are reached at depths of a few tens of kilometers in the crust, it seemed pointless to discuss an origin of hydrocarbons from nonbiological sources in the mantle. If the origin had to be found in the upper and cooler parts of the crust, then there was really no alternative to the biological theory.

This viewpoint about the thermal instability of hydrocarbons came about simply because the experiments had not been done at the appropriate pressures. Hydrocarbons appear to be greatly stabilized against thermal dissociation by high pressures, and we must therefore discuss the question of stability in the pressure and temperature regime that exists in most of the crust of the earth.

Figure 1 shows the approximate relationship between pressure (or depth) and temperature in continental and oceanic regions. Only intensely volcanic zones would fall outside the band so defined. The theoretical pressure-temperature line on which methane would begin to be destroyed (more accurately defined as the line where in equilibrium 95% would remain methane in the presence of hydrogen from the remaining 5%) is entirely above the pressure-temperature regime in the earth to a depth of 30 km. Down to that depth methane appears to be essentially stable against thermal dissociation. Even below that depth it would be only partially dissociated down to a depth of more than 300 km, where the fraction remaining as methane would have decreased to 10%. Perhaps somewhere around the 600-km depth one can place the lower limit of the possible existence of methane in the earth.

The question of the stability of hydrocarbons against oxidation, with oxygen that is available in the rocks, is bound up with the details of the outgassing process. If the gases ascend in regions of magma, then each bubble that forms has access to the oxygen available at the constantly changing surface of the bubble in the liquid rock. If the chemical equilibrium were then to favor the oxidation of the hydrocarbons and the partial reduction of the magma, this would indeed take place. For many types of magma, and for the high temperatures and low pressures that occur

at shallow depths in a volcanic region, chemical equilibration would certainly go in that direction, and so it is no surprise that volcanoes generally emit carbon mainly in the form of CO_2 , with only minor amounts as CH_4 .

Where gases make their way through solid rock, as we shall discuss later, the process involves pore spaces and pathways held open by the gas pressure. In that case, no chemical equilibrium between the rock and the gas need be expected, since the gas comes into contact with only a very limited

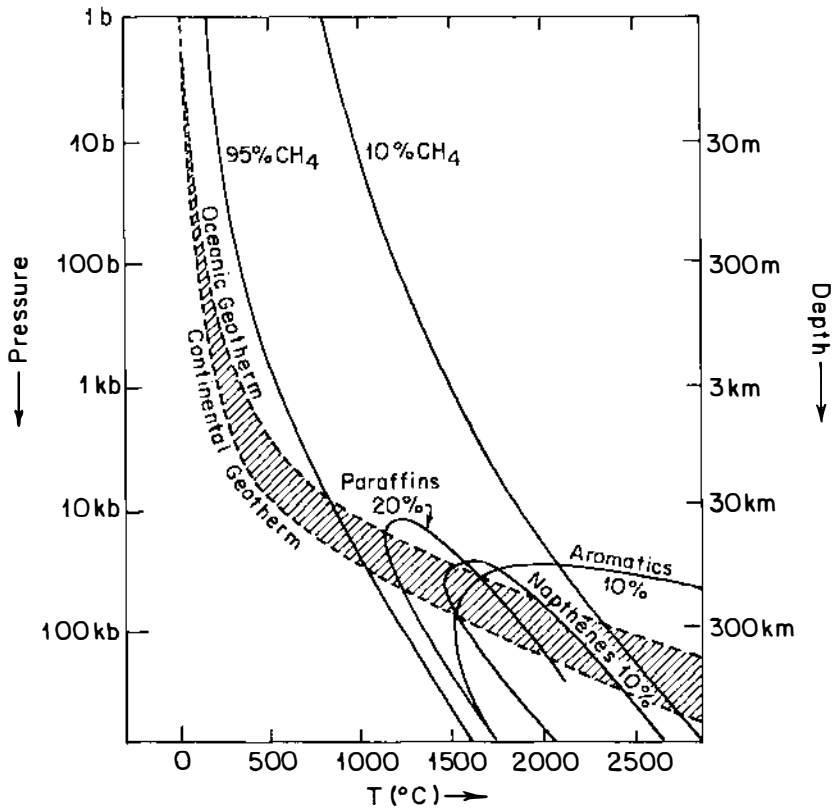


Figure 1 The shaded area represents the relation between temperature and pressure (or depth) in nonvolcanic areas. The stability limits of methane are indicated (known from experiments to approximately 1500°C). The beginning of the domains of equilibrium production of the major constituents of petroleum are shown, as deduced from thermodynamic calculations by Chekaliuk (22).

amount of rock on the surfaces of the pores. The amount of oxygen that can be made available by the rock surfaces bordering the gas-filled cracks is limited, and once this oxygen is used up no further oxidation will take place along any particular pathway. Methane has indeed been found deep in granitic rock in many locations (18–20), including the superdeep hole drilled in the Kola Peninsula (21).

What about the other hydrocarbon molecules that make up the bulk of petroleum? Thermodynamic calculations (22) have suggested not only that most of these molecules are stable in the pressure-temperature regime at a depth between 30 and 300 km, but indeed that they would form in equilibrium in a mix of carbon and hydrogen in that regime (Figure 1). If the carbonaceous chondrite type of material were packed in the earth, then, in that depth range, methane and a mix of heavier hydrocarbon molecules could be expected.

Transport of Heavier Molecules by Methane

At the high pressures ruling deep in the earth, methane, though technically a gas, behaves much like a liquid. It is a good solvent of other hydrocarbons (23, 24), and it will therefore mobilize heavier compounds, which on their own would have had viscosities too high to be mobile. It is such streams of methane that may have been making their way up towards the surface over most of geologic time and that may have supplied the bulk of the surface carbon. Heavier hydrocarbon molecules, as well as organometallic compounds and other trace substances, would be transported upward in that stream, and no doubt chemical processes would change the detailed molecular structure on the way up, as different pressures, temperatures, and catalytic actions of minerals were encountered. At shallow levels, as the pressure drops to values at which the solubility in methane becomes small, the heavier molecules will be deposited, resulting in the concentrated deposits of carbonaceous matter, including the deposits of petroleum.

Very high pressure experiments are required to define these data more precisely and to explain what chemical changes such a stream would suffer on its way to the surface.

Diamonds provide evidence that unoxidized carbon in very pure form does in fact exist at depths below 150 km. This is the depth required to produce this high-pressure form of carbon. A carbon-bearing fluid that could flow at such levels and deposit the very pure carbon must have been present to allow the mineralization to take place. Methane seems to be the best candidate for this. Fluids in high-pressure inclusions in natural diamonds have been analyzed and methane was, indeed, found to be one of the components (25, 26).

THE EVIDENCE OF "MOLECULAR FOSSILS"

The biological origin theories obtained their strongest support when molecules thought to be strictly biological were discovered to be present in most petroleum. Porphyrins and certain isoprenoids were the classes of complex molecules that seemed to be derived from molecules that are common constituents of plants and animals. It is not quite certain where we have to draw the line, especially in view of the findings in meteorites. The carbonaceous chondrites contain molecules built up almost certainly without the aid of biology, yet their virtual indistinguishability from biological products is striking. "If found in terrestrial objects, some substances in meteorites would be regarded as indisputably biological"—chemist Harold Urey concluded in 1966 (27). Quite probably some of these complex molecules form readily without the help of biology, and biology, when it developed, adopted them for its own purposes.

But even if we ignore the complex molecules in petroleum that we also find in meteorites, there still remain some specific biological markers. But do they point to the origin of the bulk substance, or merely to a contamination it has acquired? Most oils are found in porous sediments, which contain some biological materials. Oil is a good organic solvent, and, on migrating through the sediments, would necessarily pick up some of these materials. Recently, however, another important source of biological contamination has been identified; petroleum from many different sources, as well as coal, contain a class of molecules—hopanoids—derived from bacterial cell walls (28). It appears that none of these fuels were free from substantial alteration and contamination by bacteria. There is no suggestion that these bacteria provided the bulk of the unoxidized carbon compounds that led to the deposition of oil and coal; they merely invaded many, and perhaps all, existing deposits. While previously it was thought that one could distinguish biodegraded from nonbiodegraded petroleum, it now seems that a certain amount of degradation is essentially universal. All the specific biomolecules may be due to this bacterial processing, and therefore their presence does not give any evidence that the bulk source material itself was of biological origin.

Certain other properties of natural petroleum have also been identified as the results of biological contamination. Optical activity—that is a rotation of the plane of polarization of light—is rarely seen in nonbiological liquids. In petroleum, different boiling point fractions have shown various degrees of this effect, and of both signs (right-handed and left-handed). This implies that certain molecules that can form as either right- or left-handed show a numerical preference for one or other of the two types. This is common in

biology, where the whole genetic system and the enzymes it creates are all asymmetric in this way. Without biology such asymmetries could also arise, but only in rather special circumstances.

What has now been seen is that these asymmetries are totally absent in oils found in reservoirs above a certain temperature (29). A sharp cutoff for the effect appears at about 66°C, and as this is much too low a temperature to result in the destruction of all the molecules concerned, this can only be interpreted as being a temperature at which a particular type of bacterial action (by no means all bacterial action) has ceased.

A similar situation exists with respect to another biological indicator frequently present in petroleum. This is the greater abundance of molecules with an odd carbon number than an even one in the paraffin component, for molecules with a carbon number in the range 20–40. It seemed improbable (though not impossible) that the frequent occurrence of this odd-even effect could be due to any nonbiological buildup or breakdown of such molecules, while biological processes were known to produce such effects. It has now been demonstrated that in the same circumstances in which the optical activity disappears in the oils of a region, as one goes from one level to a deeper and warmer one, the odd-even effect also disappears. Philippi (29) has demonstrated this for the oils of five geographically widely separated basins, and has concluded that this sharply temperature-dependent effect can be attributed only to a microbial action in which certain molecules are preferentially destroyed. He observes that this goes in step with other chemical transformations that must also be attributed to microbial action.

Biological markers are clearly abundant in petroleum. It is no longer clear, however, that any of them point to an origin of the bulk substance as a surface biological sediment produced with the aid of photosynthesis, as had been generally assumed. Microbiology in the ground is much more widespread than had earlier been recognized, and it has certainly introduced many, and quite possibly all, the biological evidence seen in petroleum.

THE CARBON ISOTOPE RATIO

The precise ratio of the two stable carbon isotopes, carbon-12 and carbon-13, is sometimes taken to identify carbonaceous material of biological origin. The organic carbon in plants is generally depleted in carbon-13 relative to the carbon-dioxide of the atmosphere, from which it was mostly derived. This is due to a selection favoring the light isotope in the chemical processes of photosynthesis. The resulting change in the abundance ratio of the two isotopes is rather large, and no comparably strong isotopic fractionation effect is noted in any single nonbiological chemical process in

nature. As it was found that most petroleum and, even more, most natural methane, showed a marked depletion of the heavy isotope, it was natural to consider that this confirmed the theory of a biological origin for these substances.

It is beyond the scope of this report to go into the details of the numerous discussions in the literature of the carbon isotope evidence in relation to petroleum and natural gas (30). There is evidence, however, essential to the present discussion, for a progressive isotope fractionation process in the migration of gas and petroleum through the crust, leading to cumulative effects. As in industrial isotope fractionation processes, the final result can be a much larger fractionation than that produced in any single step. The simple argument—that the fractionation produced by biological processes is larger than any other, and that material showing such fractionation must be biological—is therefore invalidated (8). This fractionation process is discussed briefly in the appendix.

THE MECHANISM OF FLUID ASCENT THROUGH THE CRUST

If fluids bring up hydrocarbons from deep sources, it is important for several reasons to understand the details of the migration processes involved; chemical composition, trace element content, and especially the geographic and vertical distribution of deposits of oil and gas may depend on these details.

Diffusion of fluids from deep levels through the rocks of the crust is too slow to be important, even on the long time scale of geology. Only a bulk motion through cracks could provide a significant flow through the solid rocks. Transport from deep levels to the surface must therefore occur in two steps.

First, fluids must be assembled by diffusion over small distances into cracks, which are generated and held open by the fluid pressure. That, of course, is a process which must occur to initiate any form of outgassing. Volatile substances liberated under heat must separate out from the solids and build up pressure in the pores. If this process generated only small pores, diffusely distributed and separated from one another, no movement would result.

The second step in the upward transport process can only occur if a region contains a sufficiently concentrated source of fluids, so that the pores that are generated create an interconnected domain of fracture porosity (by a process of hydraulic fracturing, often called “hydrofracking” when done artificially). If such a fluid-filled domain grows to a sufficient size and volume, then buoyancy forces exerted on the light fluid in the denser rock

will drive it upward. This would occur in the following way. The connected fluid-filled pores have a pressure gradient in them given by their density; the denser rock must have a higher pressure gradient in it over the same height interval. When such a porosity domain has a sufficiently large vertical extent, the pressure difference between fluid and rock will become so large that the strength of the rock is insufficient to withstand it. The fluid pressure will then become excessive at the top of the domain and force open new pore spaces, while at the same time it will be insufficient at the bottom of the domain to hold the pores open, against the greater rock pressure. In this way the fluids will force their way upward through the largely stationary rock (9, 10).

One can estimate the maximum vertical height that a domain can have before it must start this upward migration. This depends of course on the density of the fluid at that depth, on the density of the rock, and on the strength of the rock in tension (at the top of the domain) and in compression (at the bottom of the domain). Depending on these quantities, estimates would range mostly between 2 and 10 km.

This process will have many important consequences for oil and gas exploration. First it implies that only high concentrations of fluids can become mobile. Where there is an upward stream, it will soon use up all available oxygen on its pathways, and will then be largely protected from further oxidation.

At the shallow levels at which oil is found, it could have been carried only in small proportion by the stream of gas, which by then has reached a low pressure. Therefore a large amount of gas must have escaped in a region in order to have left behind a substantial deposit of oil. Chemical evidence of methane seepage at the surface overlying oil fields should then be the rule, and may make chemical prospecting much more helpful than had previously been thought. Oxidation products of methane, as well as helium and various organometallic complexes carried up in the stream, may all be useful for this purpose. Gas reservoirs, even of large size, can occur in regions of less prolific supply. They do not represent the residue of the stream, but the stream itself, and there is no need for a great oversupply to have been provided.

Regional and vertical patterns must be expected to result from such a mode of supply, in which oil and gas deposits are densely packed, and essentially fill all available zones of porosity that have adequate caprocks. Other local characteristics in the same region, such as the geologic age and setting of a formation, the type of sediment, and its present depth, should be of secondary importance. The significant questions to ask in any area would be whether it belongs to a generally petroliferous region, whether a

rock there has sufficient porosity to become a reservoir, and whether there is an adequate caprock over it.

ACCESSIBLE DOMAINS OF HIGH FLUID PRESSURE

As we drill downward from the surface in most areas of the earth, we find some porosity and permeability in the rocks, and it is usual to have the pore spaces filled with water. The fluid pressure in the pores at any level is therefore determined by the height of the water column above it. This is generally referred to as "ordinary" or "hydrostatic" pressure. The pressure in the rock, determined roughly by the density of the rock, increases about $2\frac{1}{2}$ times as fast. With increased depth, the two pressures therefore get progressively more out of step, so long as there is sufficient permeability to maintain the pore-pressure at the hydrostatic value. Since the strength of the rock is limited, there must be a depth at which the rock fails and the pores are crushed shut. A layer of very low or zero permeability will result, which we have termed the "critical layer" (see Figure 2).

This situation is indeed often observed, and, depending on the type of rock and its strength, an effectively impermeable level is encountered in sedimentary rock at a depth that lies most commonly between 10,000 and 20,000 ft. Very often a continuous decline of porosity and permeability is

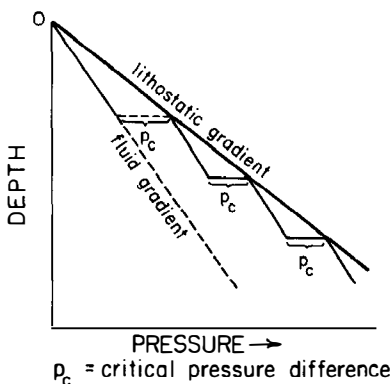


Figure 2 Schematic showing relation of pressure in rock and in fluid-filled pores. Fluids are lighter than rock, and the pressure gradient in a connected system of pores will therefore be smaller than the pressure gradient in the rock. When the compressive stress in the rock is not adequately compensated by the pore-fluid pressure, the rock collapses and closes the pores. Another fluid domain underneath the "critical layer" can then have a higher pressure in it, and thus hold the pores open again. In this way a stacked system of fluid-filled domains would set itself up, wherever there is a supply of fluids from below. The step-wise pressure system in the fluid would be an approximation to the pressure in the rock, with the difference between the two always limited by the maximum stress the rock can bear without collapsing.

observed as one drills to this effectively impermeable level, and this observation has been taken to suggest that no adequate porosity for production of oil or gas could be expected at still deeper levels. In several instances, however, where drilling was nevertheless continued to deeper levels, another zone of porosity and permeability was encountered, with a fluid pressure much in excess of the hydrostatic value, and sometimes quite close to the pressure given by the overburden weight of rock (the "lithostatic" value). It is clear that in these cases the fluid pressure, now disconnected by the impervious layer from the hydrostatic domain above, was at a pressure sufficiently high to balance the rock pressure and maintain porosity and permeability. This lower domain can exist only when it has an effective seal against the hydrostatic domain above. Otherwise the high-pressure fluids would, of course, simply be expelled upward, the pressure would drop, and the pores would collapse.

A layer of low permeability to shield and maintain a high-pressure domain below can arise in a variety of other ways as well, and it can then be at shallower levels than that at which it would be enforced by the ultimate crushing strength of the rock. Strata of very dense media, such as shale or salt, may serve this purpose, or dense layers may be generated by the cementing action of minerals deposited by the fluids. Whatever the origin, any such layer may serve to protect an underlying domain in which there is a pressure in excess of the hydrostatic one.

It used to be thought that the probability of encountering such "overpressured" domains with expanded porosity was very low, and that some special local circumstance would have been required to create it. Indeed, if the source materials for the fluids had all derived originally from surface deposits, this would be true. If, however, fluids have been penetrating from below, they will always arrive at each level at the pressure at which they will fracture the rock, a pressure which in practice is very close to the lithostatic one. In this case, no special circumstances are required to set up the high-pressure domain—it would be normal to expect such a domain under each petroliferous area that had obtained its supply from below.

The structure of permeable domains of limited vertical height, disconnected from each other by impermeable layers, is the only one in which fluids and rock can coexist in a static, or nearly static, condition. The finite strength of the rock, and the different densities of rock and fluid, allow no other configuration. The uppermost such domain is open to the surface, and therefore to atmospheric pressure. The first critical layer encountered on the way down, then, allows the transition to a higher pore pressure. In a strictly static case, one can expect such a series of domains to continue downward, making the fluid pressure approximate in a stepwise fashion to

the lithostatic pressure. Where such a structure of vertically stacked domains has been established, a further supply of fluid from below must of course also allow an upward transportation to take place. It will not now be the process discussed earlier, which was that of a domain ascending through an initially tight and unfilled rock. In the present case the flow must take the form of a spillover from one domain to the next one above, either by a momentary rupture through the sealed layer between them, or by a gradual leakage through it, but in either case preserving the basic stepwise pressure profile.

High-pressure domains filled with methane or methane-saturated water, underlying oil and gas fields, have been seen in many instances. Paul Jones (31) has investigated this phenomenon and has concluded that "All Cenozoic oil-producing sedimentary basins of the world are geopressured at depth." The production of gas from such high-pressure domains has been very successful in Oklahoma, Texas, Louisiana and other locations, and many of the deep wells have flow rates and life expectancies rarely equalled by shallow wells.

If a region is petroliferous, due to its location overlying a productive area of the mantle, one would expect to see similarities in the chemical makeup of the fluids and in the trace elements that they carry, irrespective of the various traps in which the fluids may be found in the area. These chemical characteristics may be impressed not only on the oil found in a region, but also on the solid carbonaceous materials there, which in the conventional theories of petroleum origin have come to be regarded as source materials. Such patterns have indeed been identified, and appear to be the rule.

THE GEOGRAPHIC DISTRIBUTION OF OIL, GAS, AND ASSOCIATED TRACE ELEMENTS

Mendeleev, in 1870 (1), and many authors since (2-5, 8) have noted that the occurrence of petroleum seems to be more closely related to large-scale tectonic features of the crust than to the magnitude of organic sedimentary deposits. Within petroliferous provinces it is indeed common to find many different levels that are productive, and also to find that the detailed chemistry of the gas or petroleum, and the trace elements they carry, show striking similarities, even when quite different ages and geologic settings of individual oil and gas fields are involved.

The outstanding example of an oil province showing these features is the region of the Middle East, with the oil fields of Iraq, Iran, the Persian Gulf States, and Saudi Arabia. It is thought that 60% of the world's recoverable oil that has been discovered so far is in this region, whose area amounts to only 1/200 of the earth's land surface. Clearly some unifying feature has to

be found that can explain this extraordinary concentration. One could not think that independent circumstances in different part of this region would have conspired to make it all so hydrocarbon-rich; that different epochs, different organic deposits in different geologic circumstances, and different caprocks could have been involved, and that it was merely a matter of chance that they had all, independently, been so favorable in this area.

Yet no common feature of all these fields has been noted. Some are in the folded mountains of Iran, some in the flat deposits of the Arabian desert. The oil and underlying gas fields span over quite different geologic epochs, have different reservoir rocks, and have quite different caprocks (32). The search for organic source rocks responsible for the world's largest oil fields has not led to any consensus. In different parts of this petroliferous province, sediments of quite different type and age have been suggested as the source rock, and evidently quite different materials serve as caprocks. The quantities of organic sediments have been regarded as inadequate for the production of all the oil and gas (32, 33), and would probably be seen to be much more inadequate still, if one allowed for the large natural seepage rate of the area, which has been known since ancient historical times. Thus Kent and Warman, who report on their detailed geologic studies of the area, write: "It is a remarkable circumstance that the world's richest oil-bearing region is deficient in conventional source rocks." And also: "The oil is distributed in reservoirs varying in age from middle Jurassic to Miocene, with maxima in the middle Cretaceous and Oligo-miocene. Despite this range of age and type of reservoir, there is a notable homogeneity in chemical composition of the oils, and there is a presumption that they have a common stratigraphic origin." It has also been noted that "most of the reservoirs are conspicuously full to the spill level" (34).

On the basis of a deep origin, this and many other regional concentrations of hydrocarbons would be ascribed to patches of a particularly hydrocarbon-rich mantle underlying the area. The mantle underneath the crust is in any case known to be of uneven composition, and the scale of this unevenness is recognized in other instances also to be much larger than the scale of crustal features and topography. A hydrocarbon-rich area of mantle will make the overlying crust oil- and gas-rich by filling and overfilling every available trap, no matter whether these traps are in flat plains or steep mountains, in old or young porous rock, or with deep or shallow caprocks.

Another petroliferous province that can be singled out as demonstrating a large-scale tectonic, rather than regional sedimentary relationship, is the island arc of Java and Sumatra and its tectonic continuation into Burma. The volcanic chain and the clearly associated earthquake belt begins in the East, at the western tip of New Guinea, and then runs through the small

islands, to Java, Sumatra, and the Andaman Islands and then northward through Burma into China. The petroliferous province is mostly a belt to the inside of the active volcanic arc, almost over the entire length, and although the geologic setting varies greatly, as between the islands and the folded mountains of Burma, the oil fields seem to follow the arc with remarkable consistency.

The global map of seismically active areas, and of volcanic areas, shows an incomplete but significant relationship to the map of known hydrocarbon deposits (7). Different explanations for these relationships have been advanced, but it could be readily understood as due to an accelerated fluid transport in zones of active faults penetrating the crust.

Trace elements carried in oil and gas frequently show regional patterns that also seem to be unrelated to the sediments of the locality. The noble gas helium is clearly seen concentrated in petroliferous areas, and indeed all the world's commercial production of helium is obtained by separation from natural gas. Helium-rich regions are generally coincident with petroliferous regions. This clear relationship, which has been observed globally, will need to have an explanation in any theory of the origin of hydrocarbons.

Most of the helium that the earth possesses has resulted from the radioactive decay of uranium and thorium since the time of formation of the earth. A small proportion appears to have been incorporated as helium at the time of formation (35). The ratio of the two stable isotopes of helium, helium-3 and helium-4, is quite different in the two types. The helium produced by radioactivity is all helium-4, and only a very small admixture of helium-3 can result from a certain nuclear reaction with terrestrial lithium; the primordial helium, thought to be of an isotope ratio similar to that in the sun, has a much higher proportion of helium-3.

Chemical or biological processes cannot have concentrated the inert helium. However, uranium and thorium, the progenitors of helium-4, have undergone chemical concentrations, and helium-4 may show the resulting regional patterns. Where helium is found with an isotopic ratio higher in helium-3 than could have been produced on the earth, it has to be in part primordial. Any concentration of such helium is therefore indicative of a primary outgassing process that has channeled up helium from its diffuse distribution in the original rocks, from levels sufficiently deep not to have been outgassed before.

Methane containing such helium has been identified in numerous locations. The East Pacific Rise, the great rift of the Pacific Ocean, emits such gases along most or all of its length (36, 37). Methane in the volcanic rocks of Japan (38), methane in the rift of the Red Sea (39), and methane in the African Rift Valley (40) have all been found to have an admixture of this primordial helium, and this is suggestive that the methane, like the helium,

is derived from deep sources, a suggestion strengthened by the absence of substantial organic deposits in some of the cases.

Nikonov (41), who has studied the global distribution of helium and the relationship to other gases, concluded that: "All the largest helium deposits are related to combustible gases and petroleum." Moreover, he showed that there is a clear relationship between the helium concentration and the distribution of the different types of hydrocarbon molecules; the highest helium concentrations occur typically in oil-gas fields and not in "dry" gas (42). In total quantity, one sees frequently more helium than could be accounted for by production from uranium and thorium within the sedimentary basin, and an inflow from elsewhere must have been responsible (43).

Helium occurrence shows geographical patterns on a much larger scale than those of individual oil and gas fields. Thus, almost all oil and gas fields of West Texas, New Mexico, Arizona, Kansas, Colorado, Utah, Wyoming, and Montana have higher helium contents than almost any oil or gas field east of that region (44, 45). These relationships cannot be accounted for in terms of radioactive minerals in each sedimentary domain, and it is difficult to see any way in which helium of an independent origin would have mixed with such consistency with organically produced materials, whose local density must surely span a wide range of values. It is also difficult to see on that basis why one does not find much helium unmixed with methane, or why the detailed mixture of the hydrocarbon molecules in a field should show any relationship to the proportion of helium present.

The noble gas argon, and in particular argon-40, the decay product of potassium-40, is present in some gas fields in extraordinarily high concentrations. A discussion of one instance by Pierce et al (43) contains the remark: "Explaining the radiogenic argon (0.1 percent by volume) in the Panhandle field presents a problem similar to that of helium. Calculation shows that the reservoir rock would have had to be about a hundred percent potassium to supply the argon present; the argon therefore also (like the helium) must have been derived from an external source."

Numerous other trace elements in oil and gas tell a similar story. Almost all oils of South America are peculiarly rich in vanadium (46). The vanadium-to-nickel ratio in oils tends to be characteristic of large geographic regions that span over many oil fields in a variety of geologic settings (47). Mercury is so abundant in some oil and gas regions that its detection at the surface is used for hydrocarbon prospecting (48). All these observations are not adequately explained by the individual properties of the sedimentary deposits, and one must assume that they reflect a larger scale pattern that exists at a deeper level.

CONCLUSIONS

If hydrocarbon fluids have been streaming up through the crust over geologic time, and have been responsible for supplying the great quantity of surface carbon of all the carbonate rocks and other carbon deposits, then the earth must have contained, and presumably still contains, quantities of these fluids that are many orders of magnitude larger than the quantities in all known oil and gas fields. Most of this is out of reach, at depths far too great for any foreseeable drilling technology. The practical importance lies in the quantities that have been arrested, temporarily on a geologic time scale, in the shallow depth range that can be economically exploited. Present drilling techniques seem to place the limit at a depth of approximately 30,000 ft.

Most of the oil and gas exploration has been in the shallow domain, whose pore spaces are generally open to the surface and where special caprocks of particularly low permeability were required to hold down an accumulation of oil or gas. It is this domain, of generally hydrostatic fluid pressures, that contains almost all the oil that has so far been found. Below the first critical layer, where the pressure is above the hydrostatic value, gas is common, but oil is rare. This distribution of oil and gas has usually been attributed to the inability of oil to survive for long periods at the higher temperatures at that depth. The alternative possibility is that oil is deposited from the stream at the levels where the sudden pressure drops occur and where the solubility of oil in gas is thereby diminished.

It is the shallow domain where oil is found that has formed the basis of conventional estimates of future supplies. If, however, gas has been streaming up from deep levels, then the type of reservoir where an expanded porosity has been built up underneath the first critical layer can be expected to constitute a major global resource. Instead of finding this an anomaly, in some special circumstances, it would now be the expectation that in all petroliferous areas, and in many such areas not yet identified, such reservoirs may exist. These reservoirs may have quantities of gas corresponding to the major carbon outgassing process of the earth, and not just to the small fraction that would be given by biological materials from the surface that have been buried in such a way as to avoid near-surface oxidation.

Gas exploration geologists who have opened up gas production from the deep domain foresee tapping enormous resources there. Robert A. Hefner III, a leader in this field, estimates that at least 140 trillion cubic feet of gas, and quite possibly as much as 300, can be produced from levels below 15,000 ft in the Anadarko Basin of Oklahoma alone. From extensive

drilling experience there, he concludes that the entire deep high-pressure domain in this basin is one common reservoir. The productivity of the individual wells is of course dependent on the permeability of the local formation, but in no case is it limited by the availability of gas in the region. Will numerous other deep basins, still unexplored at depth, tell a similar story?

Deep sedimentary basins would continue to be the major target for exploration, simply because sedimentary rocks generally make the best reservoirs. The volumes of unexplored sediments in the world below 15,000 ft are still immense, and if a large fraction of these is as productive as the few areas that have been explored at that depth, the global resources of gas would be very many times larger than all the hydrocarbon resources that have been discovered to date. Not only large sedimentary basins, but many rift valleys that have been filled up with sediments, may turn out to be good reservoirs, as well as good conduits for the ascent of gas. Gas from this deep level may then be not only a much larger total resource, but also a resource much more widely distributed in the world than gas from the intensely petroliferous areas that produce oil; a globally much more even supply of fuel could result from this.

While sediments would still be the first choice, igneous and metamorphic rocks can also receive serious attention. Some types of volcanic rock have developed high porosities, and some faulting in them has produced media of good permeability. This is the case, for example, in the "Green Tuff" of Japan, where gas and oil production from volcanic rock is in progress (38). Metamorphic rocks may also have substantial porosity in zones of severe faulting. Also, ancient meteoritic impacts that have smashed crystalline rock can be expected to have produced large volumes of buried porosity (51). One such location in Sweden, the Siljan Ring, is at this time under intense investigation, and gives evidence of being a strongly petroliferous area.

What will be the effects of such a general outlook on the strategies and techniques of prospecting? Identifying areas of hydrocarbon-rich mantle, and of good conduits to the surface, will be a first priority. Extensions from known petroliferous areas, deep-seated tectonic patterns, and rifts and faultlines will assume greater significance. Source rocks and the biological contents of sediments will be unimportant, although the presence of such carbonaceous materials as have previously been regarded as source materials may be an indication of hydrocarbon flow in the area. They will then serve as indicators of hydrocarbon presence, but now just as likely below them as above.

Regions below existing oil and gas fields, including the exhausted ones, would now be promising. Locations that showed shallow oil and gas, in

which deep drilling was abandoned because of declining porosity, may have to be re-explored to somewhat deeper levels to find regions of expanded porosity in the high-pressure domain below.

The extensive areas of tar sands may give evidence of massive outgassing, and may therefore point to underlying gas fields.

Porous volcanic or metamorphic rocks may be as promising as sedimentary ones. Very ancient rocks that are thought to predate the widespread occurrence of plant life, should equally come under consideration.

Chemical surface prospecting is the means of finding past or present surface seepage of methane and the substances with which it is frequently associated. This would assume a greater importance, first because it would be clearer why it should be successful, when one recognizes that massive seepage generally goes together with a large content. Second, the task is made easier than it was thought to be, when the estimated seepage rates may be so much larger than had seemed possible previously. Most oil in the world was discovered by following up surface oil seeps. It is likely that most gas will also be discovered by following up gas seeps. Whereas oil can be recognized by any person walking over the land, identifying gas seeps generally requires more sophisticated methods.

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APPENDIX

Progressive Fractionation of Carbon Isotopes

It has long been noted that methane in the same vertical column in the ground tends to be progressively more depleted in carbon-13 as one goes from deep to shallow levels (30). To ascribe different origins to the methane at different levels seems improbable when it is so often found that the same region is methane-rich at all levels probed. It seems more likely that one is seeing methane at all stages of its expected upward migration. In that case, the isotopic change, so consistent in many instances, has to be attributed to an ongoing effect that continues to remove preferentially the heavy isotope during this migration.

A product of this process has now been discovered, namely a particular form of carbonate that lies characteristically over oil and gas fields (49). Methane and other hydrocarbons appear to have been oxidized, and the CO₂ so produced seems to have combined with oxides of calcium and other metals in the rocks to produce this "anomalous" carbonate. The carbonate is enriched in carbon-13 relative to the local methane and other hydrocarbons, showing that isotopic fractionation has progressively depleted the upward-moving hydrocarbon stream of carbon-13. Nevertheless, this carbonate usually has a lower carbon-13 content than "normal" carbonate derived from atmospheric CO₂, and for this reason is readily distinguishable from it.

Such a fractionation depends not only on the isotopic selection in the chemical processes that are involved, but also on differences in molecular diffusion speed, wherever diffusion in pore spaces, rock, or water is involved. For methane the latter effect is particularly large (3% slower speed for the heavy isotope, and therefore a longer residence and an enhanced chance of oxidation on a given path), and this probably accounts for the fact that methane shows a much larger fractionation effect than any other hydrocarbon.

At shallow levels, where this type of evidence has been obtained, the oxidation process appears to be mediated by bacteria. At deeper levels, where the temperature is too high for any of the methane-oxidizing bacteria to exist, this process, and the resulting fractionation, should be absent. Presumably at very much deeper levels, where the temperature is so high that oxidation can be thermally induced, there can again be such fractionation. The final carbon isotope ratio of upwelling hydrocarbons sampled at a particular level will then depend on (a) the original ratio of the deeply embedded carbonaceous source material (which may have different values in different regions); (b) the isotopic fractionation that occurs in the cracking process that splits off the more mobile components; and (c) the cumulative isotopic fractionation in the upward migration, as a proportion is lost to oxidation. The final product may then show a larger depletion in carbon-13 than any single-step biological process could have produced. Biology is involved in a sense, in that one fractionation process is due to selective bacterial destruction. The situation here is similar to that of the optical activity or the odd-even effect; in each case biology enters through the selective removal of some components, leaving the remainder with a biological imprint.

The quantities of anomalous carbonates that are seen overlying some oil and gas fields deserve comment; they often imply that the seepage of methane, and possibly of other hydrocarbons, has amounted to much larger quantities than those now thought to be in the underlying sediments.

The township of Cement in Oklahoma is one such example (50), where an area of approximately ten square miles has an abundance of such carbonate cement, sufficient to discolor and harden the surface soil, and to fill the porosity of the sedimentary rock beneath, down to a depth of at least 2000 feet. This patch overlies very neatly the most productive oil and gas fields of the region, and it appears that the cementing of the pore spaces actually helped to improve the quality of the caprock. An estimate of the mass of the isotopically anomalous carbon in place there, derived from an estimate of 15% porosity that is so filled, amounts to almost one billion tons. It would have taken more than 50 trillion cubic feet of methane to lay down this carbon. Presumably only a fraction of the seeping methane was converted into this carbonate and the quantity lost in the area must have been much larger still. The highest estimate of the entire gas content of the Anadarko Basin of Oklahoma, of which this area is a small part, amounts to 300 trillion cubic feet. While no claim for the accuracy of these figures can be made, they show that the production of this carbonate can be a major item in the discussion of both the quantitative aspects of the gas's source material and of the isotopic fractionation that has taken place.

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