Abiogenic Methane and the Origin of Petroleum

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INTRODUCTION

The concentration of carbon at the surface of the Earth is the result of a gradual seepage of carbon-bearing gases from the deeper layers. There is a growing body of evidence that these gases are not always oxidized, as had been generally assumed, but that a substantial proportion emerges as methane. Complex organic molecules of non-biological origin are very abundant in some meteorites and must have been incorporated by the accreting Earth. Methane generated from such materials in the mantle would ascend through zones of weakness in the crust and there contribute to natural gas deposits directly and to petroleum deposits by polymerization. Much of it would ultimately reach the surface, in volcanic eruptions (with most of the CH_4 oxidized to CO_2), by slow seepage, or during earthquakes. The seismic precursory phenomena are interpreted as symptoms of deep gas pressure variations. If this viewpoint is correct, a revised strategy is indicated in the search for gas. Very large quantities can then be expected, but generally at deeper levels where present exploration is minimal. In this paper we further develop some of the ideas previously published,[1,2] and briefly respond to some objections raised by Dr F. K. North.[3]

COSMOCHEMISTRY AND THE ORIGIN OF THE VOLATILES

Carbon is the fourth most abundant element in the solar system, after hydrogen, helium and oxygen. In the Sun, in the outer planets and their satellites, in comets, asteroids and meteorites, carbon or complex organic carbon compounds are very much in evidence. The bulk of the Earth, however, seems to contain relatively little carbon, if the average carbon content in igneous basement rock (about 0.05%) is any indication. Yet on the surface of the Earth and in its sedimentary layers, carbon is very abundant. Some 3% by mass of the sedimentary rock is carbon. Limestone (calcium carbonate) and other carbonate rocks form a major part of the sediments that have accumulated over the course of geologic time. This carbon is far in excess of what could be accounted for by any grinding up and weathering of the igneous rocks.

Did the carbon then fall in late as the last addition to the forming Earth? Or was it concentrated on the surface by the migration of some carbon-containing fluid upward from the mantle? There is clear evidence for an outgassing process bringing up carbon gradually over all or most of geologic time. The carbonate sediments were derived mainly from atmospheric carbon dioxide which was dissolved in sea water and combined there with calcium oxide (and some other oxides).

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At present this process is dominated by the action of micro-organisms, but it also occurs without the intervention of biology, so that carbonate deposition did not have to wait for the advent of biology. It seems that there has been a supply of CO_2 available for this process from the earliest times until the present.

Estimates have been given for the total amount of CO_2 that would have been required to produce all the sedimentary carbonates, ranging from about 15 to 80 kg/cm^2 over the surface of the Earth. We adopt a value of 50 kg/cm^2, equivalent to some 50 atmospheres. There was probably never a very large amount of CO_2 in the atmosphere at any one time, but rather it seems to have been put away into limestone more or less as fast as it was supplied. In contrast, Venus, the 'sister' planet of the Earth (with comparable size and density), has outgassed about 95 atmospheres of CO_2, all of which remains in its atmosphere to this day, as there is no ocean to precipitate it. The outer mantle of Venus is much hotter than that of the Earth, and it is likely to have been more completely outgassed.

Evidently, some process in the Earth is continuously exhaling CO_2 and/or some other carbon compound that turns into CO_2 either on the way up or once it is in the atmosphere. What is the source of this carbon-bearing material, what are the pathways by which it comes up, what are the detailed physical and chemical processes that take place?

In order to attempt some answers to these questions, we must consider the environment in which the Earth itself was assembled. The evidence of cosmochemistry (of meteorites, comets, and planetary atmospheres) has led to general agreement that the planets must have formed out of a hydrogen-saturated 'solar nebula,' by a temperature controlled process of condensation into grains. The more refractory materials will have condensed nearer the Sun, the volatile materials only further out. The bulk of the Earth is composed of the refractory substances, with very little of the volatile ones.

Elemental carbon (graphite) is a refractory substance, but little of the terrestrial carbon seems to have been originally present in that form. The evidence is in the meteorites, which are thought to be the last remnants of the materials that long ago accreted to form the bulk of the Earth. Among the meteorites there is just one type that contains a substantial amount of carbon, the so-called carbonaceous chondrites.[4] They are believed to represent the most primitive (chemically unaltered) material in the solar system, and the carbon they contain is almost entirely in the form of complex organic molecules (up to 5% by volume). It thus appears that the dominant carbon-bearing materials in the solar nebula were hydrogen compounds, most of which are volatile. This is probably the reason for the low abundance of carbon in the refractory materials.

The carbonaceous chondrites are also the only type of meteorite containing significant amounts of bound water, mostly in the form of hydrated silicates (up to 20%). It appears unlikely that water could have condensed directly in the part of the solar nebula as close to the Sun as where the Earth formed. There are several reasons to believe that most of the terrestrial water and the carbon were brought to the Earth from farther out by bodies of the carbonaceous chondrite type, mainly during the final stages of accretion.[5] There might also have been a substantial contribution from the comets, which are thought to consist principally of water ice with an admixture of carbonaceous chondritic material.

Like the carbon, the water at the surface of the Earth is also the product of outgassing. But most of the deep rocks are generally anhydrous and would soak up water rather than expel it. Thus in order for water to have been outgassed, it must have arisen from local sources in the mantle with a water concentration much higher than the average. For both the carbon and the water, a material like that of the carbonaceous chondrites is the obvious candidate. A layer or a patchwork of this type of material was probably deposited within the outer few hundred kilometers of the Earth's surface. It would later give rise not only to the oceans but also, in our view, to most of the petroleum and natural gas.

Sokoloff [6] seems to have been the first to suggest, in 1888, that petroleum is quite representative of the hydrocarbon chemistry of extraterrestrial materials. The resemblance has been noted by many others. According to Sylvester-Bradley,[7]

> 'If carbonaceous chondrites had originated on Earth, they would certainly be regarded as bio-

> genic, for they contain many organic compounds indistinguishable from some of those also found in crude oil and in kerogen.'

Most investigators believe that these compounds in meteorites are not of biological origin but rather are the result of a Fischer-Tropsch type synthesis (involving carbon monoxide and hydrogen gas with mineral catalysts) in the solar nebula.[8]

In what form would carbon be supplied to the Earth's surface from such materials? Buried under conditions of high pressure and temperature, the source concentrations of complex organics would expel carbon mainly in the form of methane. Other hydrocarbons would also be produced, but methane is the most stable one. Hydrogen gas and water would be additional mobile products. Methane would then be the principal fluid bearing carbon towards the surface. Additional methane might be formed from ascending hydrogen, deriving the carbon from solids in the rocks along the migration pathways.[31]

This outlook is very different from the conventional one in petroleum geology. The prevalent belief is that virtually all of the methane and other forms of unoxidized carbon in the crust were derived exclusively from the biological reduction (via photosynthesis) of atmospheric carbon dioxide. The question of the origin of the CO_2 itself has had little attention, most investigators being satisfied with the information that CO_2 is observed to be the main carbon-bearing gas that comes out of volcanoes. This observation, however, tells us nothing about the chemical form of the carbon at the source, which might well have included hydrocarbons. What has gone largely unnoticed is the fact that any primordial methane that might be bubbling up through liquid rock in the low pressure, high temperature circumstances of a volcano would almost all have been oxidized to CO_2 before venting at the surface. The same is true of other hydrocarbon gases. The oxygen for this combustion is provided from metal oxides in the liquid magmas. No case has been made that oxidized carbon was the principal original source of all the surface carbon, and from the viewpoint of cosmochemistry it seems very unlikely.

It has sometimes been objected that any methane at great depths would be oxidized due to the high temperatures, but this overlooks the stabilizing effect of the high pressures. The stability regime of mantle methane in temperature–pressure space is determined by the amount of oxygen in the surrounding rock buffer (indicated by the oxygen fugacity). Until recently it was generally assumed that the oxygen fugacity of mantle rocks was relatively high, about the same as that of erupted magmas (with the quartz-fayalite-magnetite or QFM buffer); this would favor CO_2, rather than CH_4, as the dominant carbon-bearing gas phase in chemical equilibrium with mantle rocks. However, recent measurements of the oxygen fugacity of actual mantle rocks (peridotites) by Arculus and Delano[9,10] have given values as much as four orders of magnitude lower than for QFM, comparable instead to the iron-wüstite (IW) buffer, suggesting that methane is stable in the upper mantle and may well be a dominant gas there.

In Fig. 1 we have plotted in pressure–temperature space the curve for equal concentrations of CO_2 and CH_4 in the presence of an IW buffer. The data were taken from calculations of C–H–O equilibria at high temperature and pressure, which involve a number of simplifying assumptions,[11] and we emphasize that these results must still be regarded with caution. Nevertheless it appears likely from this figure that methane in the upper mantle is stable and potentially present in significant concentrations.[12]

The pressure axis is labelled with depth below the surface, which allows us to plot theoretical curves of temperature versus depth (the continental and oceanic geotherms). Gas slowly migrating upward from the mantle will in general remain in temperature equilibrium with the appropriate geotherm, and we see that along such a 'cold' pathway, any deep-source methane will emerge at the surface unaltered. However, any such methane that finds its way to a 'hot' pathway through volcanic magma will be maintained at a high temperature as the pressure is reduced, and at a depth of only a few kilometers most of it will be oxidized to CO_2.

We have also plotted the centroid of the region in which diamonds are believed to be formed. If the rocks there have an oxygen fugacity comparable to that of the IW buffer, it appears that the dominant carbon-bearing gas able to contribute to diamond formation will be methane. Inclusions

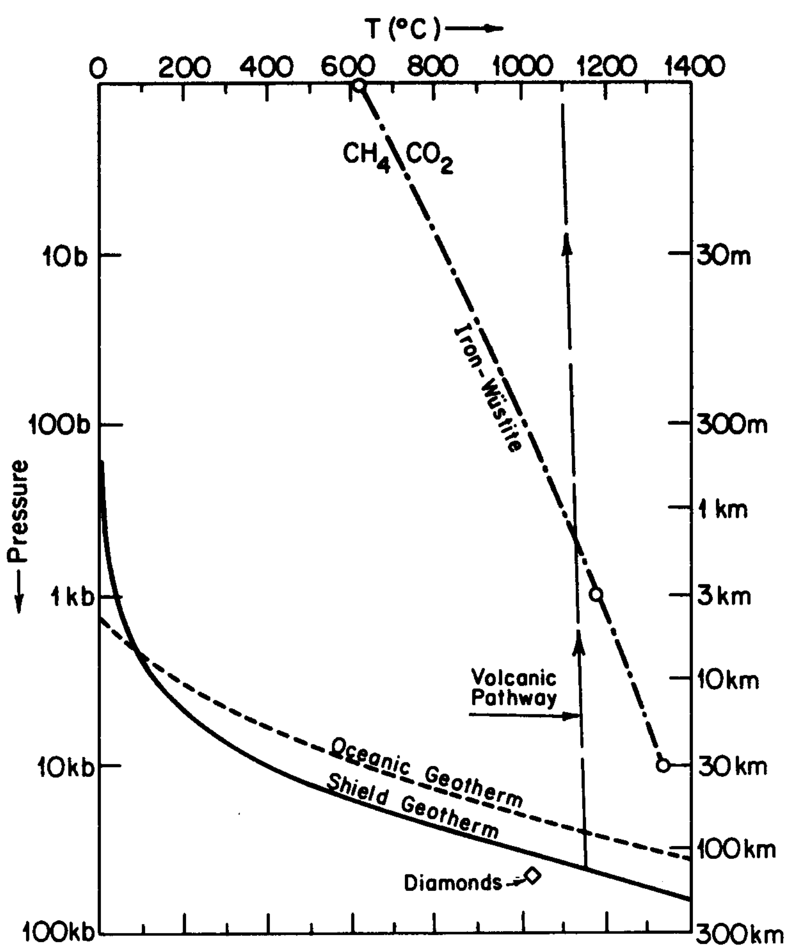

Fig. 1. Pressure–temperature regime for gas-phase carbon in the crust and upper mantle. The dot-dash curve is the calculated locus of points at which the equilibrium concentrations of methane and carbon dioxide are equal when maintained in the chemically reduced environment of mantle rock. The latter is characterized by oxygen fugacity values similar to that of an iron-wüstite buffer.[9,10] Below the curve, most of the gas-phase carbon will reside in methane, which is stabilized by the increasing pressures at depth despite the higher temperatures. Carbon-bearing fluids emerging from depths of a few hundred kilometers will in general remain in temperature equilibrium with the geothermal gradient (calculated values indicated for both oceans and continents). According to the figure, the carbon will then emerge at the surface as methane (neglecting oxidation by bacteria at shallow depths). But any such fluids that manage to rise along a volcanic pathway will go to lower pressures while still at high temperatures and most of the methane will be oxidized at a depth of a few kilometers. The figure also indicates the region around which most diamonds are believed to be formed, which lies well on the methane side of the extrapolated iron-wüstite curve. This suggests that if diamonds are precipitated from gas-phase carbon, methane is most likely to be involved. Caution is advised in interpreting this figure: The iron-wüstite curve is derived from preliminary calculations which are based on a number of approximations. Also, most crustal rocks have an oxygen fugacity some four orders of magnitude larger than that of the iron-wüstite buffer; however, if mantle gases stream through the same venting regions over geological times, it is likely that most of the oxygen along the way will be scavenged, reducing the fugacity to a low value dominated by the source fluid region.

in diamonds contain the gases CH_4, CO_2, and H_2, and we believe that the partial dissociation of methane is the most likely origin of the very pure carbon forming the diamonds.

FAULTS, EARTHQUAKES AND OUTGASSING

There are in fact 'cold' pathways where the gases coming up from great depths are subjected to less modification than in volcanic vents. These are the non-volcanic fault lines, which provide pathways through solid rather than liquid rock. Methane streaming along a fresh fault might initially be oxidized by the rock surfaces, but a long-lived stream would eventually exhaust all the available oxygen. After that, the oxygen fugacity would be dominated by that of the gas source region and the methane would remain largely unoxidized.

Major earthquakes provide the conditions whereby high pressure gases from great depth can suddenly gain access to the surface. Of course there is never anyone present prepared with sampling apparatus to observe the composition of such gases, but some inferences can still be made. Phenomena that can most readily be interpreted as due to gas eruptions have been reported from many or even most large earthquakes (Appendix III in Ref. 13). Flames shooting out of the ground have been seen in many parts of the world during earthquakes, and have on occasion been reported on a smaller scale prior to earthquakes. Methane and hydrogen are the only gases that are likely to provide fuel for such flames. Hydrogen is often present in volcanic eruptions, together with small amounts of methane, and flames are observed there also. Explosive noises often reported in connection with seismic activity may also indicate the action of high pressure gas venting.[14,15]

Methane is also the principal substance erupting from most of the world's mud volcanoes (non-magmatic sedimentary structures built up by erupting gases), and in those cases self-ignition and combustion is common.

The earthquake process itself could not occur at great depths without the presence of some fluid to maintain porosity in the rocks against the crushing lithostatic overburden pressure. It is only through the presence of such a high pressure fluid that an incipient crack can even be held open long enough to allow sudden slippage to occur. Without such a fluid the compressional friction across the crack is too high to allow a sudden brittle fracture to propagate. The resistance to plastic flow would be less than the resistance to brittle fracture, and one would have gradual deformation rather than a seismic shock. This would already be the case for earthquakes originating at a depth of ten kilometers, yet earthquakes are known with focal depths down to 700 km where the rocks are very hot as well as highly pressured and therefore mechanically viscous rather than brittle.

The pore fluids that can be considered most likely to be responsible for the embrittlement of such deep rocks are methane and carbon dioxide in various proportions (and water vapor in the shallower cases). The ascent of these gases in the course of terrestrial outgassing processes may well trigger earthquakes by weakening rocks that are already under shear stress. The various precursory phenomena that have been recognized prior to earthquakes can then be interpreted as arising from the escape to the surface of some of these gases, indicating that the rocks below have now been invaded by a fresh mass of gas, that their maximum shear strength has therefore been greatly diminished, and that if a fracture were to occur it would not immediately heal but rather would cause crack propagation due to the presence of high pressure fluids and therefore result in an earthquake.

DERIVATION OF HYDROCARBON DEPOSITS

If methane and its dissociation product hydrogen have in fact been coming up towards the surface over most of geologic time, and if this has been responsible for supplying the bulk of the surface carbon, then of course the conventional ideas regarding the derivation of hydrocarbon deposits must be re-evaluated. It is then no longer clear that biology is the only, or even the principal, agency for laying down such deposits. Much larger quantities of hydrocarbons will have streamed upwards from below than could ever have been moved down again from surface biological activity. Nevertheless a close and complex relationship between hydrocarbon deposits and biology is likely to exist, simply because of the numerous interactions involving any hydrocarbons in contact with the biosphere.

Organic material of biological origin is of course an important constituent in many sedimentary rocks, and we believe that biology plays an important role in the production of many hydrocarbon deposits. But we suggest that such biogenic materials (kerogen and dispersed unsaturated oily substances) are not the principal source for the bulk of the petroleum deposits but rather constitute a 'primer' for the accumulation of such deposits from abiogenic sources. It might work as follows.

Methane and hydrogen approaching the surface along deep fault lines will sometimes encounter sediments containing modest quantities of dispersed biogenic oils or kerogens. Some of the abiogenic gas may then become trapped in these substances. Methane is soluble in many organic oily substances, especially under pressure, and hydrogen can directly react with unsaturated compounds. The fraction of these gases that is so arrested might then, in the course of time, add to the polymer structure of the organic oils and thus augment the amount. Temperature, pressure, catalytic agents in the rocks and microbial action may all play a part in these chemical transformations.

The resulting liquids will be much less viscous than the original organic deposits, and can be expected to spread through the interconnected porosity of the sedimentary rocks. If this results in a continuous layer of pore spaces so filled, then an increasing proportion of the ascending gas will be trapped; the more petroleum that has been generated the more efficient it becomes in trapping the gas. Very large oil fields may then result, even though only rather modest organic sediments originally existed in the region. The process would resemble mineralization, in which high grade ore is precipitated out of a long-lived stream of hydrothermal fluids.

If the conditions for the direct polymerization of methane into petroleum are not met, it may still occur that deep-source methane (in chemical equilibrium with its changing environment during migration through regions of different oxygen fugacity, temperature, and pressure) will give rise to carbon monoxide and hydrogen. The interaction between these latter two gases to produce heavy hydrocarbons (in the Fischer-Tropsch reaction) is known to be very efficient.

The process of re-forming hydrocarbon molecules from thermally dissociated methane may be considered as a third possibility. This is known to result in a significant yield of heavier hydrocarbon molecules,[16] with the precise distribution among them depending on the detailed local circumstances of temperature, pressure, and catalytic agents. It is quite possible that all these processes contribute to the formation of petroleum.

The accumulation of a petroleum deposit would then require only that a long-lived stream of deep gas encounter an environment conducive to *in situ* polymerization (including a suitable structural trap). We would no longer require the proximity of some massive 'source rock' rich in biogenic sediments, and we could dispense with the severe problems of long distance migration from such sources.

Riviere[17] seems to have been the first to suggest, in 1858, such a duplex origin for petroleum deposits, in which the deep-source hydrocarbon gases, as well as biology, must have played a part. McDermott[18] independently discovered the idea and, realizing some of its important implications, he wrote:

> 'Evidence strongly suggests that oil and gas fields result from the polymerization of the migrating hydrocarbon gases. Two sources of such gases have been measured, namely, vegetable matter that is being devolatilized and the basement rocks . . . In view of the evidence for the prevalence of hydrocarbon gases leaking through the earth, and especially in view of the fact that the great interior of the earth may be a source of such hydrocarbons. . ., perhaps more attention should be paid to "cap rocks" over porous reservoirs than to "source rocks".'

McDermott also suggested that the biological indicators found in some oils (such as optical activity) might simply be residual from the biogenic materials that are present in the confining sedimentary rock.

Sylvester-Bradley[7,19,20] pointed out that 'virtually no sediments of suitable facies are known in which chemofossils do not occur' and that, in any event, the active bacteria known to exist in all crude oils could account for such biological contaminants. He identified many occurrences of petroleum found in circumstances precluding a biological contribution, and concluded that the important question was not the existence of abiogenic petroleum but rather how significant a contribution it makes.

It should be pointed out that a number of Soviet geochemists and petroleum geologists have independently arrived at a similar point of view, and in many particulars their discussion has developed along the same lines as ours. One of the most penetrating analyses of the subject yet published is that of Kropotkin and Valiaev.[21]

The duplex origin theory is supported by a detailed study of the chemistry of petroleum as well as by geological evidence. The distinguished British biochemist Sir Robert Robinson[22,23] examined the evidence and wrote that:

> 'Actually it cannot be too strongly emphasized that petroleum does not present the composition picture expected of 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 bio-products have been added.'

Consider, for example, the striking enrichment of hydrogen in petroleum relative to its supposed biological source material.[24,25] As Robinson put it,[23] 'the absence of olefins and other easily reducible substances strongly suggests that the oils have been subjected to powerful hydrogenating conditions'.

Petroleum itself is fluid and consists largely of saturated hydrocarbons. Kerogen, the substance of biological origin in the sediments that is supposed to be the source of all the petroleum and natural gas is hydrogen-poor, by comparison, containing aromatic and other unsaturated compounds. A substantial hydrogen enrichment would have to occur before material derived from the finely dispersed particles of kerogen could be mobilized and made to flow to produce a continuous petroleum reservoir. Where could the excess hydrogen (two or three hydrogen atoms added to every carbon atom in the kerogen) have come from? The prevalent viewpoint is that it comes from the thermal cracking of kerogen. The cracked-off components are then thought to assemble to form the methane and the hydrogen-rich molecules of petroleum.

In our view, the outgassing of deep methane is a major source of all surface carbon, and therefore this primary stream is a much larger source of the needed hydrogen-rich fluids than any of the secondary products (kerogen) considered in the biogenic theory. The chemical processes required in either case are quite similar, and it is only on quantitative grounds that the case can be argued. So long as the quantitative requirements for the formation of petroleum in actual circumstances (rather than in laboratory experiments) cannot be established, this uncertainty will persist.

In addition to chemical composition, the regional distribution of petroleum also appears to be consistent with a duplex origin. Major hydrocarbon deposits tend to form in regions where there has been a stream of deep source gases active over a significant period of geological time. This would then favor the production of regional patterns of such deposits corresponding to major underlying fault lines. Many of the commercial hydrocarbon deposits in fact show such a relationship with zones of past and present seismic activity. Lines of hydrocarbon deposits are often found to run parallel to lines of tectonic activity, including volcanic arcs. This suggests to us the possibility that the spatially correlated occurrence of seismicity, volcanic activity, and some oil and gas deposits, are separate manifestations of a common underlying phenomenon—the upward migration of deep gases. Such a fluid will have mobility greater than that of any other component of the upper mantle; depending on the geological conditions encountered, it can act to embrittle rock and thereby permit earthquakes, it can destabilize magma chambers to trigger volcanic eruptions (in which events any methane present will be mostly oxidized prior to venting), and it can simply accumulate in deep reservoirs.

Hydrocarbon seeps or deposits are found in the vicinity of many volcanic zones: examples are seen in Mexico, the Caribbean islands, Venezuela, the Aleutians, Kamchatka and the Kurile Islands, New Zealand, and the Philippines. The most striking case is in Indonesia, where the oilfields run nearly the entire length of the volcanic belt into the geologically different province of Burma (Fig. 2). It appears that very large-scale underlying patterns are responsible for the distribution of such deposits, rather than the much more localized patchwork that would describe the distribution of source sediments rich in biogenic deposits.

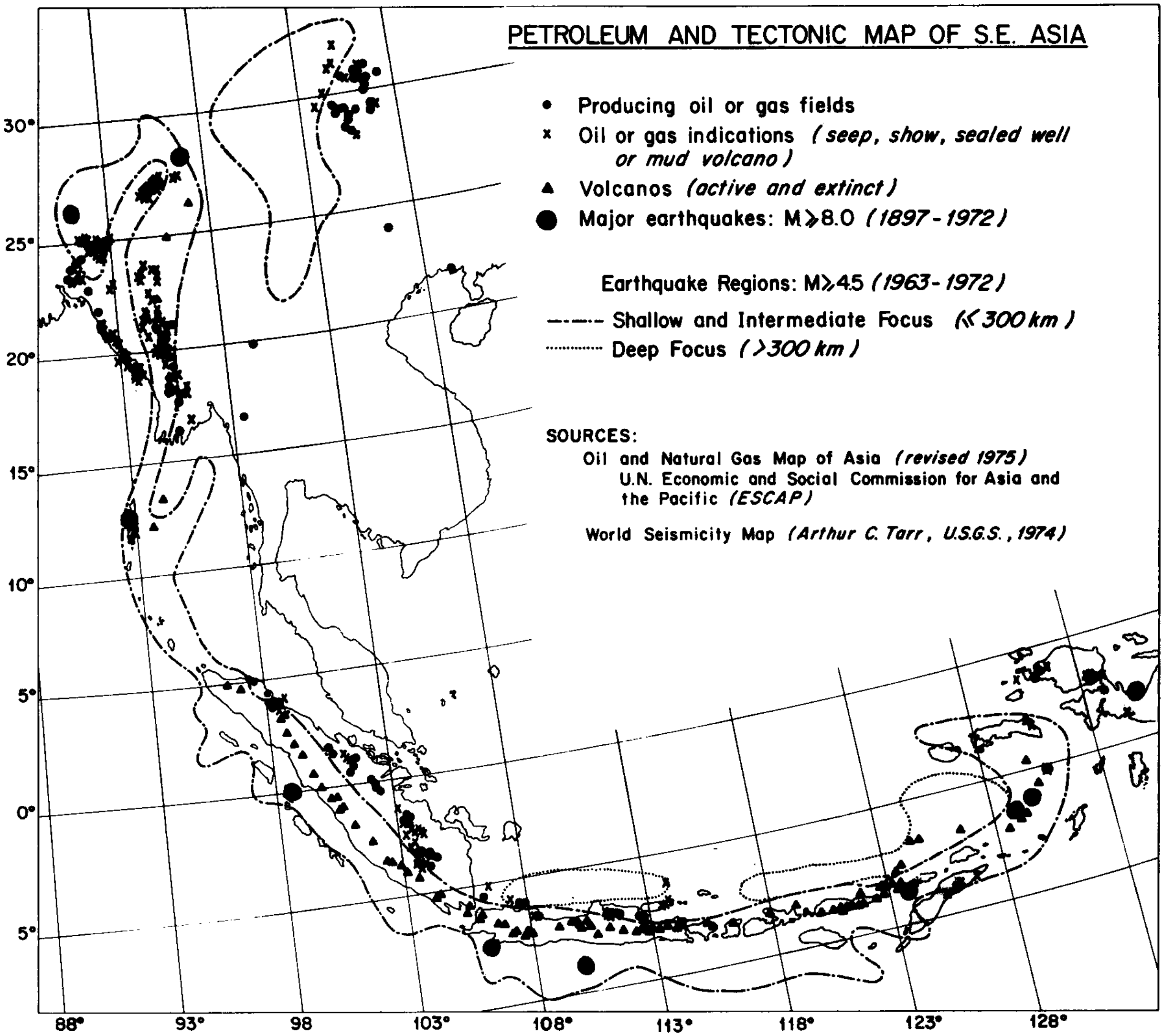

Fig. 2. The correlation between earthquakes, volcanoes, and hydrocarbon deposits in Southeast Asia.

Although the origin of coal is widely believed to be completely understood, we think that it, too, has frequently (but not always) a relationship to ascending methane. In circumstances where free hydrogen is allowed to escape rapidly, and where temperature, microbial and catalytic actions favor the dissociation of methane, carbon will be shed from the gaseous stream. This may account for the fact that many fossils in coal are found to be highly enriched in carbon relative to the original plant matter; some fossils are so infused that the interior of every cell is filled with carbon. Occasionally a well preserved fossil can be found embedded in an otherwise homogenous matrix of coal. In such cases, it seems unlikely that it was other plants of the same kind and period, suffering the same treatment, that resulted in the homogenous coal seam.

There are many areas where a strong regional correlation exists between gas, oil, and coal deposits of different ages. Often, there is no clear correlation with biogenic source sediments, but rather the controlling features appear to lie in the deep tectonic structure.[26] Such spatial correlations are found in Iran, Venezuela and Columbia, Alaska, the Appalachians, Wyoming, and large areas in Siberia.

In addition to regional correlations, there are also vertical correlations: the same region may show particularly rich deposits of coal, oil, and gas, all vertically stacked, but spanning very long periods of geological time. In Indonesia there are regular sequences of oil and coal vertically stacked above one another. The San Juan Basin of New Mexico is a particularly good example (Fig. 3); gas and oil in large amounts are found in deep Mississippian sediments more than 300 million years old, above which are multiple coal seams of Cretaceous age (about 100 million years old). The biogenic theory is hard pressed to explain why the same small spot should have been repeatedly favored for the production of rich organic sediments at totally different epochs, when local topography, climate, and all other surface conditions had changed completely. However, one can understand on the basis of long-lived deep methane seeps that the augmentation process would have been at work at all levels, and with different results depending on the detailed local conditions.

In some instances the process of accumulation of hydrocarbon deposits from an ascending stream of methane may start without the advantage of a biogenic primer, and indeed there are many cases of hydrocarbon deposits in the igneous rocks of the basement far from any sedimentary 'source rocks'.[27–29] Basement rocks are generally avoided in oil exploration because they are thought to possess neither the organic source materials for production nor the porosity necessary for accumulation of petroleum. But neither of these objections ought to be considered as universally applicable.

First, some crystalline rocks may in fact constitute potential hydrocarbon sources. Hoefs[30] pointed out that 'reduced carbon is more or less evenly distributed in all types of igneous rocks and minerals with a rather constant concentration range around 200 ppm'. Freund *et al.*[31] found experimentally that supposedly 'pure' crystals of MgO and CaO actually contain dissolved atomic carbon and hydrogen which upon heating give rise to a wide variety of hydrocarbons. According to Freund (personal communication, 1981), average basalts yield about 100 ppm of hydrocarbons.

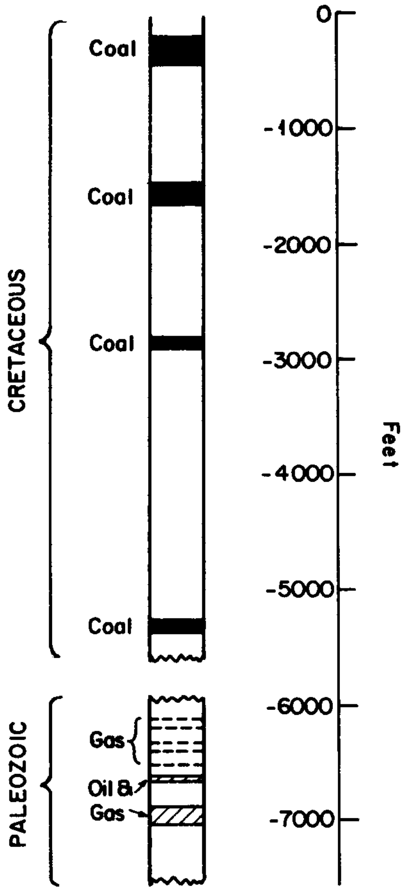

Fig. 3. The vertical stacking of coal, oil, and gas in the Hogback Field of the San Juan Basin in northwest New Mexico (compiled from Refs 54, 55). The hydrocarbon deposits in this one region are in sediments with ages spanning more than 200 million years.

Methane and other hydrocarbons are in fact found occluded in many basement rocks. Alkaline igneous rocks from the Kola Peninsula[32] and Greenland[33] show methane in occluded pores. (In the more oxygen-rich surroundings of acidic rocks methane would have been oxidized when the rock was still liquid.) Methane and hydrogen have also been found occluded in diamonds[34] and in other mantle rocks.[35]

Although reduced carbon as found in igneous rocks is generally in too dispersed a state to permit its mobilization and concentration in commercial deposits, nevertheless its very presence suggests that enormous quantities of abiogenic hydrocarbons are to be found in the mantle.

As for the objection that basement rocks lack the porosity required for reservoir accumulation, there are many examples to the contrary;[36] basement rocks are often crushed by faults and cracks, and the porosity thereby created is sometimes filled with commercial deposits of petroleum. Donofrio[37] has shown that the thousands of ancient buried meteoroidal impact basins in the Earth's crust contain enormous volumes of porosity due to shattering, that some of these impact features are in fact productive of petroleum, and that 'The explanation for the "non-productive" reputation of basement may not lie in the nature of the rock, but results from the routine practice of not drilling into it'.

Methane has been found associated with some of the great global rift systems. When igneous alkaline rocks from the East African Rift[38] and basalts from the Mid-Atlantic Ridge[39] are pulverized, a small quantity of gas is liberated, of which hydrogen and methane are major constituents. Higher hydrocarbons are also present. The waters above such crustal rifts are also found to contain anomalous concentrations of abiogenic methane, most clearly in the case of the East Pacific Rise;[40] methane is also found in the deep Red Sea brines.[41]

Perhaps the most striking example is that of Lake Kivu, which lies in the East African Rift valley; its deep waters contain some 2 Tcf of dissolved methane, the largest methane anomaly for any lake in the world. It also contains an even larger quantity of dissolved CO_2. Attempts to account for the CH_4 anomaly with a biogenic source[42,43] have not been particularly convincing. The entire region consists of young volcanic rocks and the bottom sediments in Lake Kivu are not extraordinary. (The neighboring Lake Tanganyika, also occupying the rift, possesses much deeper sediments but has no such methane anomaly.)

But there is another unique feature of Lake Kivu: it is contained by a natural dam consisting of active volcanoes. This led Burke[44] to suggest that the dissolved CH_4 was of volcanic origin, but the idea was generally rejected because CH_4 was not detected in the hot gases of Nyiragongo, the closest of the volcanoes. Recently, however, Gerlach[45] showed that the Nyiragongo gases, if cooled to 300°C in the presence of the same alkaline rocks, would re-equilibrate with a high CH_4 composition (up to 70%). This makes a magmatic source for the Lake Kivu methane more likely.

It is made even more likely by Harmon Craig's recent discovery (personal communication, 1981) that the waters of Lake Kivu contain an anomalously large amount of helium-3, a trace gas generally regarded as the most reliable indicator of a mantle contribution.[46] Unlike the more common isotope ^{4}He—which results from the decay of uranium and thorium—the rare isotope ^{3}He has no adequate terrestrial progenitors that could have become chemically concentrated. Therefore if ^{3}He emerges anywhere in unusually large amounts, one can assume that it was "washed out" from a large internal volume by other more abundant gases which carried it up through vents. In the case of Lake Kivu, the carrier gases are presumably mantle CO_2 and CH_4.

Throughout the world, excess ^{3}He is found in the gases and waters associated with tectonic plate boundaries and deep faults. Only more recently have investigators begun to look for CH_4 in the same places; not only is it being found, but in several instances the isotopic signature of its carbon is consistent with a deep origin as well.[47,48]

CARBON ISOTOPES AS INDICATORS OF ORIGIN

No discussion of the origin of hydrocarbons can be presented without referring to the carbon isotope information. The bulk of terrestrial carbon contains the isotopes ^{12}C and ^{13}C in the approximate ratio of 99:1. This ratio, when investigated with high precision, is seen to have some small but significant variations among carbon samples from different sources. For example, biological carbon is somewhat deficient in the heavy carbon isotope relative to the oxidized carbon in atmospheric CO_2. This is because the process of photosynthesis preferentially selects against ^{13}C. The largest carbon isotope effects are observed in methane, and when isotopically very light methane is found (i.e. CH_4 deficient in ^{13}C by several per cent) it is generally thought that this proves its biological origin. This has become a cornerstone of the discussion, and therefore needs careful scrutiny.

It is probably true that in a single step process a larger isotope selection effect can take place in biology than is likely in non-biologically-mediated reactions. But with methane the process may be due to cumulative and not merely to single-step processes. Because methane is a light molecule, the difference in the total mass between $^{12}CH_4$ and $^{13}CH_4$ is significant for many processes. The diffusion speed of the heavier molecule is about 3% slower than that of the lighter, and this allows a cumulative selection to take place, as we shall see.

First let us consider the case in which methane is steadily diffusing through the ground towards the surface in such a way that none of it is lost from the stream. In such a steady diffusive flow, as many molecules of each type will arrive at the surface per unit time as are supplied into the column below. We must be careful, however, to distinguish between two different ways of measuring the isotopic ratio: one is the ratio in the flux, that is in the number of molecules of each type crossing any horizontal surface per unit time; the other is the ratio of the number densities for the two species existing within any given volume of the diffusion column. Since the heavy methane molecules have a diffusion velocity 3% slower than the light molecules, the number density ratio of $^{13}CH_4/^{12}CH_4$ must always be 3% higher than the flux density ratio.

This by itself does not lead to any isotopic selection gradient within the column. If, however, there is a process that continuously removes some of the gas during its upward diffusion, then a progressive isotope selection can occur. We believe that a substantial fraction of the slowly diffusing methane is generally lost by oxidation to CO_2, chiefly in the uppermost few kilometers. The oxidation process itself may select the heavy isotope, and in any case it is taking place in circumstances where the number density of the heavy isotope is enhanced by 3% compared with the ratio observed in the flux. If this results in a selection which slightly favors ^{13}C in the oxide, then the remaining stream of methane will become progressively depleted in $^{13}CH_4$. The importance of this process lies in the fact that it is cumulative; at each level the isotopic selection effect starts out with an isotopic ratio of methane that has already been affected by selection in all lower levels. As the diminishing supply of upward migrating methane becomes depleted in ^{13}C, so does the CO_2 which is derived from it. Although the isotopic selection in any one step may be small, the cumulative effect on the methane surviving to the top of the column may be very large. This process, a kind of 'Rayleigh distillation', is analogous to the commercial separation of isotopes in a gas diffusion column; it is inefficient on a small scale, but the Earth provides a column many kilometers in length which can effect a substantial isotope separation.

Two observations are consistent with this interpretation. Galimov[49] found a progressive enrichment of ^{13}C in methane at increasing depths, irrespective of the age or past history of the confining sediments. And there is now evidence for the oxidation of substantial quantities of upward migrating methane, in the form of carbonate deposits with anomalously light isotopic values (relative to normal carbonates) found in sediments above hydrocarbon deposits.[50–52] These carbonates are clearly formed locally, since they occur directly over underlying oil and gas fields; they are almost certainly deposited from carbon dioxide which in turn derived from the oxidation of ascending methane. Their carbon isotope ratio is intermediate between that of the ascending methane and that of ordinary marine carbonates.

PRACTICAL CONSEQUENCES

What is the practical importance of knowing the ultimate source of the carbon fuels? Will we find more as a result? Or is the conventional search strategy sufficient to find these fuels, whatever their origin?

It is still important to locate traps in porous rock, and that has been the principal target all along. But there are some important new elements. First, one should search for gas irrespective of any biological content of the regional sediments. The presence or absence in so-called 'source rocks' of biogenic materials may be irrelevant in the quest for gas deposits. Second, there is reason to believe that the deeper levels will in general contain more gas. Only a small fraction of the sediments have been probed to depths of 5 km or more, and there the success rate for gas has been surprisingly high. This can be attributed to good judgment, good luck, or to an intrinsically higher incidence of gas at these levels. If the third alternative is correct, one can anticipate

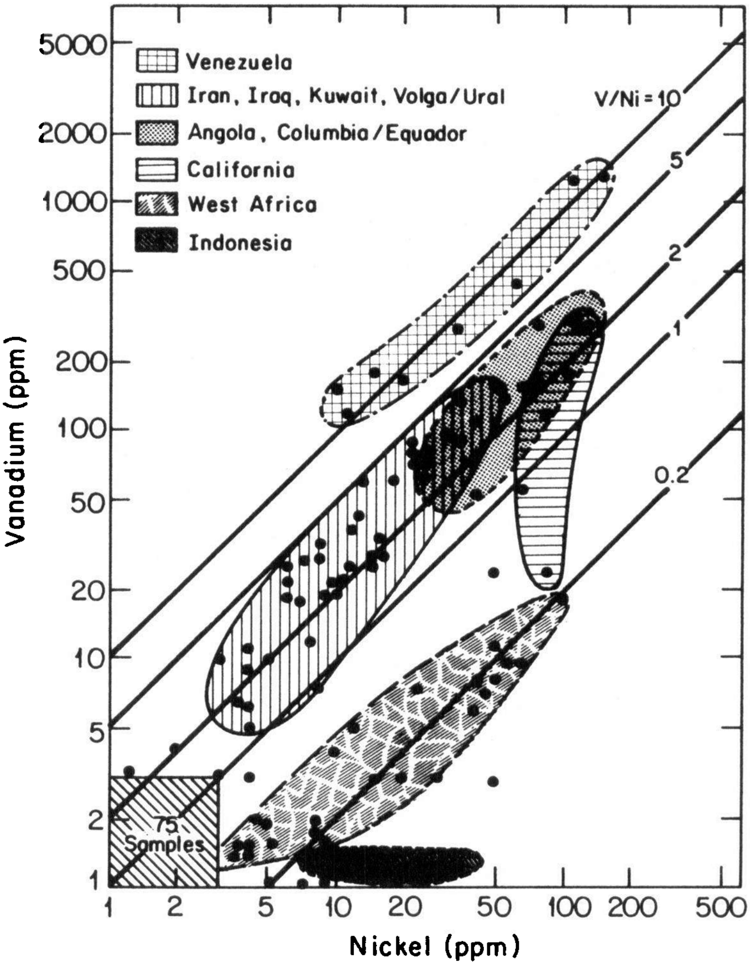

Fig. 4. Vanadium and nickel content of 175 crude oils. The box at lower left contains 75 samples with low concentrations of both elements. Most of the other samples show a clear proportionality between the vanadium and nickel concentrations (diagonal lines indicate constant ratios). Adapted from Tissot and Welte.[53]

much more vigorous progress in deep drilling.

Criteria become important now that seemed irrelevant before. Deep underlying structures, indeed down to the base of the crust or even below that, will influence the patterns of gas seepage. Long-lived fault lines, including those associated with past volcanic activity, may be particularly significant. The slopes of very deep layers, or of the base of the crust itself, may guide upward migrating gases and concentrate them at the high spots. This may be relevant to the prevalence of petroleum deposits in the continental shelves.

Large-scale patterns in the deep structure have been identified, and seem to be related not only to the seepage patterns of hydrocarbons but to deposits of other minerals as well. Such relationships tended to be ignored when there seemed to be no rational explanation for them. Vanadium, nickel, mercury, and perhaps other elements as well show a regional correlation with hydrocarbon deposits.

Particularly striking is the observation that vanadium and nickel concentrations in petroleum tend to maintain a distinct ratio in deposits which are spread over enormous regions, as seen in Fig. 4, adapted from Tissot and Welte.[53] One cannot hope to explain this in terms of a biological concentration of such large quantities of these elements, always in the same ratio over thousands of kilometers. It is also difficult to account for it in terms of erosion into the sediments from local ore deposits. We suspect that ascending deep-source methane and other gases (essentially liquids at very high pressures) may bring up certain elements as organometallic compounds in solution, and concentrate them at shallower levels. The large-scale spatial coherence of trace element concentrations in the shallow deposits is then merely a reflection of chemical uniformities in the deep source structures. An understanding of such relationships may well provide an important prospecting tool.

If the quantities of hydrocarbon gases that have come up have been a major contributor to the terrestrial surface carbon supply, then one is concerned with very much larger quantities than in the case of an exclusively biological origin for petroleum. And if the supply has come up from below, rather than being laid down from above, the occurrence of gas at or near the lithostatic pressure of the rock overburden ought then to be a common feature at the deeper levels, rather than a peculiar anomaly. At those levels there is a much better chance of containment, because the overburden pressure usually seals off any routes of escape. At the same time the high-pressure gas can maintain an acceptable porosity and permeability in the domain it occupies. Sudden transitions to high gas pressure with increased porosity are indeed encountered in many of the deep wells.

It is perhaps ironic that so little is known about the origin of the hydrocarbon fuels upon which our industrial economy is based. We cannot afford to accept without question the prediction of a fuel shortage in the absence of serious applied research to investigate the basis of this prediction. A vigorous program of scientific investigation, including deep prospecting in the unknown regions, may show whether or not much larger quantities of gas are available than predicted by the conventional projections. If the results are positive, a large-scale conversion to gas for stationary energy requirements would be indicated, so as to conserve the liquid fuels for transportation as long as possible. After that, one could derive liquid fuels from methane.

RESPONSE TO SOME CRITICISMS BY DR. F. K. NORTH

In the accompanying paper,[3] Dr F. K. North has critically reviewed the Deep-Earth-Gas Hypothesis. He has raised a number of questions which we would like to address. In one paragraph, he asserts that 'the nearly universal association of gas with either oil or coal, with unmistakable organic fingerprints, and the depletion of the heavy isotope of carbon . . . leave no room for doubt . . . in the minds of either geologists or geochemists' that the bulk of natural gas in geologically young strata is biogenic; furthermore, he writes that Gold at first accepted this proposition but later reversed himself to claim that most gas is abiogenic, while conceding that some oil is biogenic, 'a necessary genuflection to the imperative of an organic contribution.' There are a number of inaccuracies here.

In fact many of the world's gas deposits are not associated with either oil or coal. Many of the so-called 'organic fingerprints' (such as porphyrins and odd–even carbon number ratios) are found in meteorites or in laboratory syntheses, and others (such as optical activity) may well be contaminants from sediments or microbial metabolism. The depletion of ^{13}C in most methane deposits may be the result of Rayleigh fractionation rather than photosynthesis, as we have shown. There most decidedly is 'room for doubt' regarding an exclusively biogenic derivation of gas; many Soviet geologists and geochemists have expressed it. From his first publication on this subject, Gold[1] has consistently recognized that some oil and gas is of biological origin but at the same time proposed that most of it is not. The acceptance of a duplex origin theory is not 'a necessary genuflection' but a straightforward recognition of the evidence in all its complexity.

Later Dr North lists several gas-bearing basins, including the Anadarko-Amarillo basin, and asserts that 'none of these great accumulations is as deep as 4 km. . .' In fact, some of these sedimentary basins extend to greater depths, and the Anadarko, in which there has been the most extensive exploration below 4 km, is currently producing a high yield of gas from as deep as 8.7 km.

Dr North writes that we fail to explain 'why all the escape routes end up in sedimentary basins.'

The reason is that we do not believe it. There are many places where methane is flowing out of igneous rocks (*cf.* Ref. 27), and there is growing evidence that escape routes for methane include the great tectonic rifts, such as the East Pacific Rise and the East African Rift. The only thing special about sedimentary basins is that a stream of methane finding its way into one is able to inflate the finely distributed porosity there to produce the best kind of reservoir, both in terms of capacity and drilling expense.

We cannot agree with Dr North's assertion that 'there is no *abundant* gas production below 6 km', when we have accounts such as the following (from the trade journal *Drilling*, pp. 92 – 102, August 1981):

> 'The deepest producing well in the world, Chevron No. 1 Ledbetter in the Mills Ranch Field in Wheeler, Texas was completed in October 1977 in the Arbuckle formation below 26 000 ft [8.7 km]. Calculated open flow was 12.45 MMcfd from the Arbuckle . . . Some of the world's most prolific individual gas wells are found in the Texas portion of the Deep Basin. Phillips Petroleum Co.'s Bowers B-2-A in the Washita Creek field has produced more than 74 billion cu ft of gas from the Hunton formation below 20 000 ft [6.7 km].'

In the same article we read:

> 'The wildcat success ratio in the Oklahoma portion of the basin has been estimated around 60%. . . In areas like the Anadarko basin methane is pervasive in the sediment so that you never drill a dry hole, you only drill holes that produce gas at uneconomic rates. Therefore as the price increases, success ratios can be expected to increase concurrently.'

A success rate of 60% is much higher than occurs for shallow gas exploration, despite the fact that petroleum geologists have much more detailed information about the shallow structure.

Although Dr North regards the subject of abiogenic methane to be of considerable scientific interest, he regrets that we have taken it further and attempted to examine the possible consequences of the hypothesis, if it proves to be correct, in terms of the world energy situation. Our rather optimistic discussion in this respect is based not, as Dr North suggests, on some philosophical notion that the Earth will provide without limit (which we do not believe). It is based rather on the cosmochemical indications that enormous quantities of reduced carbon were deposited in the Earth during its formation, and on the mechanics of the migration if hydrocarbon gases actually originate from deep below.

The upward migration of a gas-filled 'pore space domain' in the region below the critical layer (at which porosity communicating with the surface is closed off by overburden pressure) cannot occur until the domain becomes interconnected over a sufficiently large vertical extent (probably of order several kilometers) that it is no longer stable in terms of pressure.[2] Any region below the critical layer can accumulate and hold quantities of trapped gases only up to the size at which this instability sets in. On this basis, it appears that very substantial pockets of gas below the critical layer will be the rule rather than the exception. No special process for pressurizing is implied, since the gases have in any case come from a domain of higher pressure. Any deep rock with a texture that permits fluid fracturing to produce finely divided and reasonably uniform porosity is a suitable candidate for drilling.

Dr North asks where our proposal for deep gas drilling should stand in the list of other gas-recovery priorities—including strip mining to get gas from shale and nuclear detonations to get it from tight sands. We would expect that the widespread availability of deep gas would make drilling for it far more economical, as well as far less destructive to the environment, than many of the alternative proposals.

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