Thomas Gold

The Origin of Methane (and Oil) in the Crust of the Earth

Thomas Gold

Abstract

The deposits of hydrocarbons in the crust of the Earth have long been regarded by many investigators as deriving from materials incorporated in the mantle at the time of the Earth's formation. Outgassing processes, active in all geological epochs, then transported the liquids and gases liberated there into porous rocks of the crust. The alternative viewpoint, that biological debris was the source material for all crustal hydrocarbons, gained widespread acceptance when molecules of clearly biological origin were found to be present in most commercial crude oils.

Modern information re-directs attention to the theories of a non-biological, primeval origin. Among this information is the prominence of hydrocarbons—gases, liquids and solids—on many other bodies of the solar system, as well as in interstellar space. Advances in high-pressure thermodynamics have shown that the pressure-temperature regime of the Earth would allow hydrocarbon molecules to be formed and to survive between the surface and a depth of 100 to 300 km. Outgassing from such depth would bring up other gases present in trace amounts in the rocks, thus accounting for the well known association of hydrocarbons with helium. Recent discoveries of the widespread presence of bacterial life at depth point to this as the origin of the biological content of petroleum. The carbon budget of the crust requires an outgassing process to have been active throughout the geologic record, and information from planets and meteorites, as well as from mantle samples, would suggest that methane rather than CO_2 could be the major souce of surface carbon. Isotopic fractionation of methane in its migration through rocks is indicated by numerous observations, providing an alternative to biological processes that have been held responsible for such fractionation. Information from deep boreholes in granitic and volcanic rock of Sweden has given support to the theory of the migration of gas and oil from depth, to the occurrence of isotopic fractionation in migration, to an association with helium, and to the presence of microbiology below 4 km depth.

Introduction

The gas methane, CH_4, the principal component of natural gas, does not contain sufficient evidence in itself from which to deduce its origin on the Earth. There is some evidence from its isotopic composition, but interpretations of that are not unique. Information, however, exists in the mode of occurrence of natural gas reservoirs, in the geographic and geological relationships, in associated chemicals, and, above all, in the frequent association with other hydrocarbons, specifically crude petroleum and bituminous coal. Although there are numerous occurrences of natural gas without the heavier hydrocarbons, the association is generally so clear that one cannot contemplate an origin for the natural gas deposits independent of those of petroleum. We shall therefore first consider the origin of the whole set of hydrocarbons, including natural gas, and then discuss aspects that are specific to methane.

Debate about the Origin of Petroleum

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. (H.D.Hedberg, 1964)

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 bio-products have been added. (Sir Robert Robinson, President, Royal Society, 1963)

The capital fact to note is that petroleum was born in the depths of the Earth, and it is only there that we must seek its origin. (D. Mendeleev, 1877)

The origin of petroleum has been a subject of many intense and heated debates, ever since this black fluid was first discovered to be present in large quantities in the pore spaces of many rocks. Is it something brought in from space when the Earth was formed? Or is it a fluid concentrated from huge amounts of vegetation and animal remains that may have been buried in the sediments over hundreds of millions of years?

Arguments have been advanced for each viewpoint, and although they conflict with each other, each line of argument sounds strangely convincing. In favor of the biogenic origin of petroleum, the following four observations have been advanced:

(1) Petroleum contains groups of molecules which are clearly identified as the breakdown products of complex, but common, organic molecules that occur in plants, and that could not have been built up in a non-biological process.

(2) Petroleum frequently shows the phenomenon of optical activity, i.e. a rotation of the plane of polarization when polarized light is passed through it. This implies that molecules which can have either a right-handed or a left-handed symmetry are not equally represented, but that one symmetry is preferred. This is normally a characteristic of biological materials and absent in fluids of non-biological origin.

(3) Some petroleums show a clear preference for molecules with an odd number of carbon atoms over those with an even number. Such an odd-even effect can be understood as arising from the breakdown of a class of molecules that are common in biological substances, and may be difficult to account for in other ways.

(4) Petroleum is mostly found in sedimentary deposits and only rarely in the primary rocks of the crust below; even among the sediment, it favors those that are geologically young. In many cases such sediment appears to be rich in carbonaceous materials that were interpreted as of biological origin, and as source material for the petroleum deposit.

On the other side of the argument, in favor of an origin from deeply buried materials incorporated in the Earth when it formed, the following observations have been cited:

(1) Petroleum and methane are found frequently in geographic patterns of long lines or arcs, which are related more to deep-seated large-scale structural features of the crust, than to the smaller scale patchwork of the sedimentary deposits.

(2) Hydrocarbon-rich areas tend to be hydrocarbon-rich at many different levels, corresponding to quite different geological epochs, and extending down to the crystalline basement that underlies the sediment. An invasion of an area by hydrocarbon fluids from below could better account for this than the chance of successive deposition.

(3) Some petroleums from deeper and hotter levels lack almost completely the biological evidence . Optical activity and the odd-even carbon number effect are sometimes totally absent, and it would be difficult to suppose that such a thorough destruction of the biological molecules had occurred as would be required to account for this, yet leaving the bulk substance quite similar to other crude oils.

(4) Methane is found in many locations where a biogenic origin is improbable or where biological deposits seem inadequate: in great ocean rifts in the absence of any substantial sediments; in fissures in igneous and metamorphic rocks, even at great depth; in active volcanic regions, even where there is a minimum of sediments; and there are massive amounts of methane hydrates (methane-water ice combinations) in permafrost and ocean deposits, where it is doubtful that an adequate quantity and distribution of biological source material is present.

(5) The hydrocarbon deposits of a large area often show common chemical or isotopic features, quite independent of the varied composition or the geological ages of the formations in which they are found. Such chemical signatures may be seen in the abundance ratios of some minor constituents such as traces of certain metals that are carried in petroleum; or a common tendency may be seen in the ratio of isotopes of some elements, or in the abundance ratio of some of the different molecules that make up petroleum. Thus a chemical analysis of a sample of petroleum could often allow the general area of its origin to be identified, even though quite different formations in that area may be producing petroleum. For example a crude oil from anywhere in the Middle East can be distinguished from an oil originating in any part of South America, or from the oils of West Africa; almost any of the oils from California can be distinguished from that of other regions by the carbon isotope ratio.

(6) The regional association of hydrocarbons with the inert gas helium, and a higher level of natural helium seepage in petroleum-bearing regions, has no explanation in the theories of biological origin of peroleum.

Advocates of the Abiogenic Theory

Among the early advocates of a non-biological origin of petroleum was the great Russian chemist Mendeleev, the originator of the periodic table of the elements. His arguments, presented in a paper on the origin of petroleum (Mendeleev, 1877) are still valid today. He already knew of the large-scale patterns of hydrocarbon occurrence, but his information on the processes that shaped the Earth was not our present understanding, and made his explanations much more complex than would need to be the case now.

Sokoloff (1889) discussed the "cosmic origin of bitumina" (carbonaceous substances from petroleum to pitch and tar), and he related these to the meteorites, knowing then already about their hydrocarbon content. He stressed that oil and tar occur in basement rocks, such as in the gneiss of Sweden. He could find no relationship to the fossil content of rocks, and he stressed that porosity was the sole circumstance which relates to the accumulation of bituminous substances.

Vernadsky (1933) gave reasons why he considered that with increased pressure and deceased oxygen availability with depth, hydrocarbons would be stable and largely replace carbon dioxide as the chief carbon-bearing fluid.

Kudryavtsev (1959) the most prominent and strongest advocate of the abiogenic theory in modern times, argued that no petroleum resembling the chemical composition of natural crudes has ever been made from genuine plant material in the laboratory, and in conditions resembling those in nature. He gave many examples of of substantial and sometimes commercial quantities of petroleum being found in crystalline or metamorphic basements, or in sediments directly overlying those. He cited cases in Kansas, California, Western Venezuela and Morocco. He pointed out that oil pools in sedimentary strata are often related to fractures in the basement directly below. The Lost Soldier Field in Wyoming has oil pools, he stated, at every horizon of the geological section, from the Cambrian sandstone overlying the basement to the upper Cretaceous deposits. A flow of oil was also obtained from the basement itself.

Hydrocarbon gases, he noted, are not rare in igneous and metamorphic rocks of the Canadian Shield. Petroleum in Precambrian gneiss is encountered in wells on the eastern shore of Lake Baikal. He stressed that petroleum is present, in large or small quantity, but in all horizons below any petroleum accumulation, apparently totally independent of the varied conditions of formation of these horizons. This statement has since become known as "Kudryavtsev's Rule" and many examples of it have been noted in different parts of the world. Commercial accumulations are simply found where permeable zones are overlaid by impermeable ones, he concluded.

Kudryavtsev introduced a number of other relevant considerations into the argument. Columns of flames have been seen during the eruptions of some volcanoes, sometimes reaching 500 meters in height, such as during the eruption of Merapi in Sumatra in 1932. (We since know of several other instances.) The eruptions of mud-volcanoes have liberated such quantities of methane, that even the most prolific gasfield underneath should have been exhausted long ago. Also the quantities of mud deposited in some cases would have required eruptions of much more gas than is known in any gasfield anywhere. The water coming up in some instances carries such substances as iodine, bromine and boron that could not have been derived from local sediments, and that exceed the concentrations in seawater one hundred fold. Mud volcanoes are often associated with lava volcanoes, and the typical relationship is that where they are close, the mud volcanoes emit incombustible gases, while the ones further away emit methane. He knew of the occurrence of oil in basement rocks of the Kola Peninsula, and of the surface seeps of oil in the Siljan Ring formation of Central Sweden (which we shall discuss later). He noted that the enormous quantities of hydrocarbons in the Athabasca tar sands in Canada would have required vast amounts of source rocks for their generation in the conventional discussion, when in fact no source rocks have been found.

Beskrovny and Tikhomirov (1968) noted, as did Anders, Hayatsu and Studier (1973), that of the many possible isomers of petroleum molecules, the particular sub-set found in natural petroleum is also the one singled out in artificial oil production from hydrogen and carbon rather than from biological substances.

Profir'ev (1974) argued that so-called source rocks have no identification that proves their hydrocarbons to be primarily biogenic. He also discounted the hypothesis, often advanced, that the transport and deposition of oil from supposed source rocks to the final reservoir was accomplished by solution in gas: the quantities of gas that would be required would exceed

by orders of magnitude the quantities that could be derived from the supposed source materials.

Levin (1958) concerned himself with the formation process of the Earth, claiming that the class of meteorites called carbonaceous chondrites, a low-temperature condensate that was probably responsible for bringing in solids that contained water, could have brought to the forming Earth several times larger quantities of carbonaceous materials than all the ocean water.

Kravtsov (1975) presented much observational material. He showed that the natural seepage of methane in many areas was far more than could be supplied by any kind of gasfield known. If the volcanic gases of the Kurile Islands, for example, are typical of the gases emitted over the time-span of the volcanic activity there, the amount of methane emitted would far exceed the conventional estimate of the present-day total world reserves. He also gave many examples of "Kudryavtsev's Rule."

Kropotkin and Valyaev (1976, 1984) and Kropotkin (1985) developed many aspects of the theory of deep-seated, inorganic origin of hydrocarbons. They concluded that petroleum deposits were formed where pressure conditions permitted the condensation of heavier hydrocarbons, transferred from great depth by rapidly rising streams of compressed gases. In volcanic regions, they noted, decomposition of hydrocarbons would be favored, resulting in the formation of carbon dioxide and water, while in "cool" regions hydrocarbons would be preserved, and could accumulate in alluvial cover and highly fractured beds, depending on the presence of adequate reservoirs and covers. According to these authors "vertical migration of hydrocarbons from levels far below formations rich in biogenic organic matter, which have been considered the source material for the oil, can be demonstrated in a majority of deposits." Kropotkin also presented numerous examples where Kudryavtsev's Rule is satisfied in a striking way.

There were several voices also outside Russia (or the Soviet Union), who argued for a non-biogenic origin. Most notable among them was Sir Robert Robinson (1963, 1966) who, like Mendeleev, can be considered among the most distinguished chemists of his day. He studied the chemical make-up of natural petroleums in great detail, and concluded that they were mostly far too hydrogen-rich to be a likely product of the decay of plant debris. Olefins, the unsaturated hydrocarbons, would have been expected to predominate by far in any material that was derived in that way.

Sylvester-Bradley (1964, 1972) discussed that the meteorites have hydrocarbons, and that hydrocarbons on the Earth derived in major part from such material. He proposed that hydrocarbons streaming up through the crust from great depth would have provided energy sources for simple forms of life. He knew about the biological materials in petroleum, but, like Robert Robinson, he thought that they were due to contaminating additions from microbiology in such locations.

Before discussing further the possible origins of hydrocarbons on the Earth, it is necessary to discuss the present state of knowledge of the formation process of the Earth and the planetary system, and the materials that contributed to the formation.

The Formation Process of the Earth

The Earth is a body with a most complex history. None of its sister planets display signs of the processes that appear to have been the major ones to shape this planet of ours. On all the other solid bodies of the Solar System the effects of impact cratering can be seen very clearly. Craters spanning a range of size from a few kilometers to several thousand can be clearly recognized. Impacts of solid objects upon all the planetary bodies in the process of their formation must have been a common occurrence.

Strangely, on our Earth similar cratering events can only be seen, if at all, in a very subdued form. We see arcs of circles appearing in the midst of a topography shaped by other effects. It seems reasonable to interpret such circular features as the remains of impacts, now deeply buried but affecting the outer crust at a later stage in some way that makes the buried impacts recognizable again. One has to suppose that other events occurred here that obscured most of the evidence of this early bombardment.

Nevertheless, it is now quite clear that the Earth, like the other solid planetary bodies, also formed by the accretion of solid objects, probably largely in the form of small grains, but interspersed with occasional major pieces. It appears that then a partial melting took place, causing materials of lower density to make their way to the surface, while presumably melts of high density sank down towards the center. The heat for this melting was the result of radioactivity contained in the material,

as well as just the heat resulting from compression. Once partial melting occurred, two other sources of heat came into play: firstly the gravitational energy that is released as materials can move and sort themselves out according to density. Secondly there is the chemical energy that results from all the chemical reactions that can then take place, either between different liquids or between liquids and solids. The original diverse materials accreted as cold objects would certainly not have been chemically equilibrated with each other, but would be left in an uneven distribution by the chances of the impact events. After gaining mobility by melting, many chemical reactions would take place that would, on average, release energy and thus provide more heat, as well as giving rise to volatile substances.

Both these last two sources of energy have the interesting property that they make the heating unstable: where more heating has occurred and more melt produced, more of these actions can take place and therefore still more heat will be produced there. One may well speculate that the very uneven distribution of internal heat sources which we recognize at the surface, derives from such an instability. The circumpacific "belt of fire" is the most striking example, but there are also many other lanes characterized by high heat flow and volcanic activity. They are also characterized by the outflow of fluids, gases and liquids, that are thought to have a deep origin. Deposits of hydrocarbons frequently show a clear association with such patterns. (An example is shown in Figure 3.)

If the major volume of the Earth has never been molten, the mantle of the Earth underneath the crust must still contain the diversity of chemistry, the chemical energy sources and the sources of gases and liquids that would be the legacy of an accretion process from diverse and initially cold solids. Major impacts would have thrown up ring patterns of mountains, which, as on the Moon, would convert vertical patterns of chemical inhomogeneity into regional patterns. Many arcuate patterns on the Earth of present surface topography and of chemical features or of heat flow may be a consequence of this.

The Theory of the Biological Origin of Hydrocarbons on Earth

Oil, hydrocarbon gases and coal on the Earth were thought to have derived entirely from biological debris for the following reasons: One reason was the belief in earlier times that hydrocarbons were specifically organic substances: hence the name "organic carbon" for all forms of unoxidized carbon. The knowledge that hydrocarbons are abundant in the universe, and on many of the other planetary bodies of our solar system, was not available at that time. Now we know that carbon, the fourth most abundant element in the Universe after hydrogen, helium and oxygen, is almost certainly also the fourth most abundant in the planetary system; there it is predominantly in the form of hydrocarbons. The major planets Jupiter, Saturn, Uranus and Neptune, have large amounts of methane and other hydrocarbon gases in their atmospheres. Titan, a large satellite of Saturn, has methane and ethane in its atmosphere, and these gases form clouds and behave much like water does in the atmosphere of the Earth. Triton, a large satellite of Neptune, appears to have hydrocarbons mixed with water ices on its surface, as does the outermost planet known at this time, Pluto. A large fraction of all the asteroids show a surface reflectance closely resembling that of tar, and the comets have hydrocarbons among the gases they emit. The surface of the core of Comet Halley, recently observed by spacecraft, is most reasonably interpreted as one of tar. Complex, polycyclic hydrocarbon molecules, similar to those in natural petroleum have been observed to be a prominent component of interplanetary dust grains that currently enter the Earth's upper atmosphere (Clemett and others, 1993).

Hydrocarbons in our planetary system are certainly very abundant, and in all the extraterrestrial examples mentioned almost certainly not related to biology. Also hydrocarbons are prominent among the gases identified in the molecular clouds of the galaxy, and it is from such clouds that the solar system formed initially. The presence and great abundance of hydrocarbons is universal, and no special mechanism for their generation on the Earth needs to be invoked, unless one knew with certainty that they could not have survived the formation process here, although they did so on many of the other planetary bodies. (No evidence of hydrocarbons has yet been seen on Mars, Moon, Venus and Mercury. The atmosphere of Venus is too hot to have maintained gaseous or liquid hydrocarbons; the other three bodies lack an adequate protective atmosphere to have maintained them on their surfaces.)

In earlier times there was the belief that the Earth had formed as a hot, molten body. In that case no hydrocarbons or hydrogen would have survived against oxidation, nor would any of these substances have been maintained in the interior after solidification. With that belief, there seemed no other possibility of accounting for the hydrocarbons embedded in the crust than by the outgassing of carbon in the form of CO_2, produced by materials that could have survived in a hot Earth, and subsequent photosynthesis by plants that converted this CO_2 into unoxidized carbon compounds. This consideration is irrelevant now that we know that a cold formation process assembled the Earth and that hydrocarbons could have been

maintained, and could be here for the same reasons as they are on the other planetary bodies.

The common existence of molecules of clearly biological origin in most petroleum and bituminous coal is no longer an argument for a biological origin of hydrocarbons, now that we know of the wide reach of microbiology in the crust (Jannasch, 1983; Yayanos, 1986; Gold, 1992). Before this had been identified, the possibility of widespread biological contamination at depth had not been considered. Now, especially after the discovery of the volcanic vents on the ocean floors and the profuse chemosynthetic life that exists there, the outlook is different. It is now seen as not only possible, but very likely, that microbiology is common in the crust down to depths of between 5 and 10 kilometers, a level below which the temperature will reach values too high for any microbial life we know, thought to be between 110 and 150 $^\circ$C. This deep microbial life uses as its energy source the various chemical imbalances that the outgassing process creates as gases and liquids stream up through rocks with which they have never been chemically equilibrated. Knowing now of the occurrences of such deep microbial life, it seems likely that no location that could support such life has been kept sterile from it for the long periods of geologic time. Hydrocarbons, together with oxygen donors such as sulfates or metal (principally iron) oxides, substances that are common in the rocks or water, would provide a usable energy source for microorganisms. Hydrocarbon deposits would therefore acquire biological debris in the course of time. The molecules which are commonly regarded as proof of the biological origin of petroleum and of bituminous coal have all been found to be also produced by subsurface bacteria; indeed some of them can only be produced by bacteria (Ourisson and others, 1984). Pristane, phytane, steranes, hopanes are unquestionably of biological origin, but do not certify the biological origin of either petroleum, coal, kerogen or whatever other deposits in which they are seen. With the photosynthetic theory of their origin, they seemed to certify that these materials were all once at the surface. But this is no longer a valid inference. Many other conclusions in geology were based on this, and should also be reconsidered now.

Origin of the Carbon on the Earth

The surface and surface sediment on the Earth contain approximately one hundred times as much carbon as would have been derived from the grinding up of the basement rocks that contributed to the sediment. The surface is enormously enriched in carbon, and this needs an explanation.

The carbon we have on the surface or in the sediment of the Earth is estimated to be 4/5 in the form of carbonate rocks, and 1/5 in unoxidized form, frequently referred to as "organic." (The word "organic" given then to all unoxidized carbon, is of course now a misleading misnomer.) The quantities are large: if expressed as the mass of the element carbon per square centimeter of total Earth surface area, the estimate is about 20 kilograms. (I will be referring to this quantity again later.)

During formation of the Earth by the accumulation of cold solids, very little gaseous material was incorporated. The knowledge of this comes from the extremely low level of the non-radiogenic noble gases in the atmosphere of the Earth. Among those, only helium could have escaped into space, and only xenon could have been significantly removed by absorption into rocks. Neon, argon, krypton would have been maintained as an atmospheric component. The noble gas proportions in the Sun and in space are known. Any acquisition of such a mix of gases in the formation process would not have been able to selectively exclude noble gases that have no significant chemical interactions. One is forced to conclude that the acquisition of gases, or substances that would be gaseous at the pressures and temperatures that ruled in the region of formation of the Earth, was limited to the small value implied by the low noble gas values. The carbon supply the Earth received initially could not have been in the form of hydrocarbon gases, high volatility hydrocarbon liquids, or CO or CO_2.

Could meteoritic infall of carbon at later times be held responsible for the surface carbon excess? Such a massive infall would have left much other evidence in the geologic record, and this is absent. The only alternative is that carbon came up from the interior as a liquid or gas, just as is also true for the water of the oceans (approximately 300 kg/cm^2) the nitrogen of the atmosphere (1 kg/cm^2 approximately) and the (largely radiogenic) argon of the atmosphere.

Perhaps one might consider the possibility that the Earth once had a massive atmosphere of carbon dioxide that evolved early on, from materials that could have survived the formation process, and that these then became converted in into the carbon deposits we now have; but that also does not seem an acceptable explanation, for in that case we should see incomparably more very early carbonate rocks than the amounts laid down later. This is not what the geologic record shows. What it does show is a reasonably continuous process of laying down carbonate rocks; no epoch having enormously more per unit time, nor enormously less. If outgassing from depth is responsible, then one has to discuss what the source material

in the Earth might have been, what liquids or gases might have come from them, and what their fate would have been as they made their way up through the crust.

The meteorites represent some samples of leftover material from the formation of the planets. While they may not be representative of the quantities of the different types that made up the Earth, they appear to represent at least samples of all the major components. Only one type, the carbonaceous chondrites, contain significant amounts of carbon, and they contain it mainly in unoxidized form, a substantial fraction in the form of solid, heavy hydrocarbons. This material, when heated under pressure as it would be in the interior of the Earth, would indeed release hydrocarbon fluids, leaving behind deposits of solid carbon.

The quantitative information on carbonaceous chondrites is difficult to evaluate. They are much more friable than most other meteorites, and therefore survive the fall through the atmosphere less often than the others. Carbonaceous chondrites also are destroyed by erosion on the ground much more rapidly. The result must be that far fewer than the original proportion are ever discovered. They may well represent even now the largest quantity of meteoritic material still available for collection by the Earth; the infall of interplanetary dust to which I have referred, contains similar carbonaceous material.

By contrast, carbonates, which would be a source material for CO_2, exist in meteoritic materials only in very small concentrations, so that an origin of the carbon from an initial CO_2 source seems unlikely. If the carbonaceous chondrite material is the principal source of the surface carbon we have, then the initial material that could be mobilized in the Earth at elevated temperatures and pressure would be a mix of carbon and hydrogen. What would be the fate of such a mix? Would it all be oxidized with oxygen from the rocks, as some chemical equilibrium calculations have suggested? Evidently not, for we have clear evidence that unoxidized carbon exists at depths between 150 km and 300 km in the diamonds. We know they come from there, because it is only in this depth range that the pressures would be adequate for their formation. Diamonds are known to have high-pressure inclusions that contain CH_4 and heavier hydrocarbons, as well as CO_2 and nitrogen (Melton and Giardini, 1974). The presence of at least centimeter-sized pieces of very pure carbon implies that carbon-bearing fluids exist there, and that they must be able to move through pore-spaces at that depth, so that a dissociation process may deposit selectively the pure carbon; a process akin to mineralization processes as we know them at shallower levels. The fluid responsible cannot be CO_2, since this has a higher dissociation temperature than the hydrocarbons that co-exist in the diamonds; it must therefore have been a hydrocarbon that laid down the diamonds.

Diamonds will only survive a transport to the low pressure at the surface, if it is accompanied by rapid cooling; if they are taken through a slow cooling process they will turn to graphite, the equilibrium form of carbon at low pressure. Diamond is a metastable form of carbon at the low surface pressure, but the temperature is too low for a relaxation to the stable form. Indeed, diamonds are found predominately in the vicinity of sites of explosive gas eruptions, diamond pipes, where rapid gas expansion caused quick cooling. There is also evidence for pure carbon transported up from depth at a slow rate: pseudomorphs of diamonds. Spaces showing the octahedral symmetry of diamond have been found filled with graphite, in mantle rocks that have come to the surface in Morocco (Pearson and others, 1989). These rocks came up presumably in a slow ascent, and contained a dense array of octahedral spaces filled with graphite, clearly fitting the interpretation as pseudomorphs of diamond. This discovery suggests that a very high density of diamonds exists at least in some locations in the mantle, and that their rarity on the surface is to be attributed to the rarity of the explosive events that could bring them up sufficiently quickly. It is noteworthy that hydrocarbons are found in diamond pipes together with the diamonds, suggesting that the gases involved in the explosive events were not oxidizing (Kravtsov and others, 1976; 1981).

The Surface Carbon Budget

The deposition of carbonate rocks has been an ongoing process throughout the times of the geologic record. Most, but not all of this carbonate has been an oceanic deposit, deriving the necessary CO_2 from the atmospheric-oceanic CO_2 store. The amount that is at present in this store is, however, only a very small fraction of the amount required to lay down the carbonates present in the geologic record. The atmospheric-oceanic reservoir holds at present only about 0.01 kg of carbon per cm^2 of the Earth's surface area. If we take the figure quoted, of about 20 kg of carbon per cm^2 laid down over the time of the identified geologic record, there must have been a supply renewing the atmospheric-oceanic CO_2 gradually, but by an amount 2,000 times the present content. This amount of carbon, if calculated as a continuous and steady outgassing rate and initially all coming up as methane, would translate into a one meter deep layer of methane (at STP) being created all over

the Earth every 2,700 years. If the rate is regionally variable so that, for example, one tenth of the area produces nine tenths of the amount, then in the gas-prone areas one meter STP methane would come up every 300 years. If natural gas fields are filled from outgassing methane, such a supply rate would be much more than adequate in the timespans available to create all the known fields.

If the supply of carbon from below ceased, the present rate of laying down carbon would deplete the atmosphere-ocean reservoir in something on the order of 500,000 years, a very short fraction of geologic time. Outgassing of carbon in some form must have been a continuous process; it is not likely that humans evolved just in the last period, just before the death of all plant life. We must therefore inquire what quantities of carbon would have been available at deep levels, in what form this was, and in what manner this resupply of the atmospheric-oceanic CO_2 reservoir could have taken place. It is also clear that one cannot discuss the man-made additions to the atmospheric carbon gases without regard to the large and surely variable natural carbon emission that has taken place throughout geologic time.

The resupply of carbon must be from juvenile sources. Recycling of sediments cannot account for it, both for reasons of the quantities involved and for reasons of the isotopic composition. If the repeated subduction of carbonate rocks occurred on the necessary massive scale, it would seem that old carbonates should have disappeared almost completely. This is not the case. The isotopic information, to which we shall return later, also would say that in a process of continuous recycling the proportion of ^{13}C would continuously increase in the atmosphere, and hence the younger carbonates should be isotopically heavier than the old ones; this also is not the case. Marine carbonates of all ages back to the Archaean show the same narrow range of the carbon isotopic ratio (Schidlowski and others, 1975, see also Figure 4).

How much carbonaceous chondrite material would have been required to provide the supply of the surface carbon? Let us make a simple calculation for this. Suppose that in the depth range between 100 and 300 kilometers we have a patchwork in which the carbonaceous chondrite material comprises 20 percent on an average. In this material, carbon amounts to 5 percent. This means, on an average, each square centimeter column through the 200 kilometer layer would contain 1 percent of carbon (5% of 20%), which would translate into 660 kilograms per square centimeter. If one-thirtieth of this had been mobilized and reached the outer crust, it would suffice to account for all the carbon of the carbonate sediments and the sediments of unoxidized carbon. Of course the proportion of carbonaceous chondrite type of material may have been very much larger, and the producing layer much thicker. The fraction that needs to have been mobilized would then be much smaller. All one can really say at this stage is that there is no quantitative problem. Volatile-rich material of sufficient quantity to have supplied the water of the oceans, as discussed by Levin (1958), could quite easily have supplied the quantity of hydrocarbons for all the surface carbon.

As we have seen, the primary source material in the Earth that would send up a carbon-bearing fluid is likely to be a hydrocarbon mix, not a substance that would produce CO_2 in the first place. On the way up, however, some unknown fraction would come on pathways held open by magma, where these fluids would largely be oxidized to CO_2 and water. On other pathways, created by pressure fracturing in solid rock, the direct oxidation will be minimal and these fluids may arrive at the surface as methane and other hydrocarbon gases or liquids. However, even in the solid rock a substantial proportion is frequently oxidized at shallow levels, as is indicated by the common presence in oil and gas-rich regions, of carbonate cements. These cements derive from metal oxides initially present in the rocks, and CO_2 derived apparently from the oxidation of methane with some oxygen supplied from the rocks; the carbon isotope ratio of these pore-filling cements is not compatible with a derivation from atmospheric CO_2, and their distribution fills the pores in a vertical column, suggesting an origin from ascending fluids. This oxidation is probably due to the action of microorganisms that obtain oxygen from components of the rock, and it is then limited to the outer levels of the crust where the temperature is in the range in which microbial activity can take place. It can be presumed quite reasonably that only a fraction of the CO_2 so produced will in fact remain in the ground as carbonate, and a substantial fraction, quite possibly the major amount, will escape into the atmosphere.

A supply of hydrocarbons at depth may thus provide CO_2 into the atmospheric-oceanic reservoir in three different ways. One is through volcanic pathways and oxidation with oxygen supplied by the magma; another is by ascent of hydrocarbons through solid rocks and oxidation at shallow levels, most likely by bacterial action, with subsequent escape of CO_2 to the atmosphere; a third process will be the escape of methane and other hydrocarbons into the atmosphere, where, in the

presence of atmospheric oxygen, they would reside on average 10 years before oxidation to CO_2. What fraction of carbon resupply comes by each of these pathways is still not known directly, but some limits can be placed by considerations of the maintenance of the atmospheric oxygen level within the bounds suggested by the geologic record, and possibly by some other more direct measurements.

Methane in the atmosphere is present at about 1.7 ppm by volume. Much or most of this represents a cycling of atmospheric carbon through biological processes, but the quantitative estimates of the magnitudes and speeds of these processes are not sufficiently precise to determine whether the observed concentration is the one to be expected. One may therefore inquire whether a contribution to this methane directly from outgassing sources is a possibility. Fortunately there is a clear possibility of distinguishing biologically recycled methane from juvenile methane: the radiocarbon (^{14}C) proportion of the biological contribution should be the same as that of atmospheric CO_2, since such recycling would almost all take place in a short time compared with the half-life of radiocarbon (5,700 years). Thus carbon from deep sources would be free from radiocarbon. A measurement of the fraction of radiocarbon in atmospheric methane can therefore supply the information. Several such measurements have been attempted, but there are difficulties and uncertainties connected with the sampling method and with the measurement itself. The latest measurements have given values of approximately 32% of non-radiocarbon bearing atmospheric methane (Lowe and others, 1988). Would such values be compatible with a supply of carbon from juvenile sources?

We may take, for a simple calculation, methane at 1.7 ppm (vol) and a lifetime of about 10 years against oxidation. Let us suppose that 30% of this is juvenile, and see how this compares with the requirements of the terrestrial carbon budget. The measurements quoted would give an amount of juvenile carbon at present in CH_4 in the air of 2×10^{-7} kg carbon/cm^2. If this were replenished on a ten year timescale, the lifetime of atmospheric methane, the average supply per year would have to be 2×10^{-8} kg/cm^2 year. To lay down the carbon deposits of 20 kg/cm^2 entirely from this source would therefore take 1 billion years, a figure compatible with the geologic record. While this cannot be taken to be a confirmation of the results that have been reported, nor of the proportion of the juvenile supply of CH_4, it does demonstrate that such measurements are worth doing, and that a substantial fraction of the atmospheric methane may in fact be juvenile. If it is, one must suspect that such a contribution would have large time variations, as have all other tectonic processes, and that therefore much higher or much lower values could be registered at the present time, or at any one time, than the long-term average value. The time variations of atmospheric CH_4 reported from ice cores should be seen in the light of these considerations.

Thermodynamics of Outgassing

With the carbonaceous chondrite type of material as the prime source of the surface carbon, the question arises as to the fate of this material under heat and pressure, and in the conditions it would encounter as buoyancy forces drove some of it it towards the surface.

This problem has been tackled by thermodynamicists, most thoroughly by Chekaliuk (1976). His conclusion was that at sufficient pressure, such as that at a depth of 200 km or so, a mix of hydrocarbon molecules would be the equilibrium configuration, despite a temperature which would be far in excess of the dissociation temperature for these molecules (Figure 1). The pressure would provide these molecules with some stability, although any one molecule may indeed have sufficient internal energy to fall apart at the elevated temperature. At high pressures the assembly as a whole does not have enough energy to generate the increased volume that the dissociated molecules would demand. Fragments will instantly be reformed in such a way as to satisfy the volumetric constraint. No molecule has permanent stability, but a statistical assembly of hydrocarbon molecules will represent an average equilibrium. The detailed mix of molecules will depend on pressure and temperature, and on the carbon - hydrogen ratio present. Other atoms that may be present also, such as oxygen and nitrogen, will form a variety of complex molecules with the carbon and hydrogen. Metal atoms that may be present in the surroundings will form a range of organo-metallic molecules in these circumstances.

Even with the knowledge that the diamonds and their high-pressure inclusions have provided, it has been argued that hydrocarbons could not come from these deep levels, because they could not survive at temperatures that are reached in the crust at a depth below 20 kilometers (Hunt, 1975); but these discussions in the petroleum literature have not included the effects of pressure.
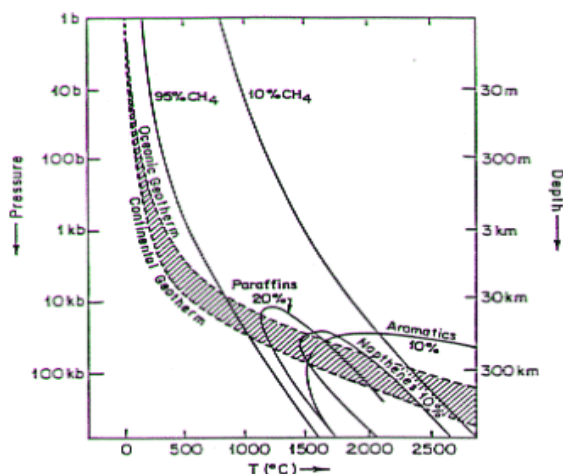
Figure 1. Stability of hydrocarbons at temperatures and pressures in the Earth (from Chekaliuk, 1976). Pressure-temperature regime of Earth is indicated by the shaded region. Thermodynamic calculations indicate domains in which various hydrocarbon molecules are stable. The lines marked Paraffins, Naphthenes, and Aromatics enclose domains in which a mix of hydrocarbon molecules would be set up from hydrogen and carbon, and on crossing outward from these domains the percentages indicated would be retained. Methane is essentially stable to the left of the line marked 95 percent, and 10 percent would still be retained on crossing to the right of the line so marked (that is, 90 percent would dissociate into hydrogen and carbon). According to these calculations, most of the petroleum components would be present in equilibrium of a carbon-hydrogen mix at a depth between 100 and 300 km, and methane streaming up could bring a significant fraction of these petroleum components toward the surface. b, bar; kb, kilobar; km, kilometer; m, meter; T, temperature.

The statistical mix of hydrocarbon molecules expected from a carbonaceous chondrite source material, being less dense than the surrounding rock, would have buoyancy forces driving it towards the surface. If present in a locality in sufficient concentration, the fluid will fracture the solid rock, and ascend in such fracture porosity. (Molecular diffusion in rock over large distances is too slow a process to be of any significance, even on the long time-scales of geology.) In that upward travel, the temperature and the pressure would be decreasing, and the various molecules would reach levels where the temperature was low enough for them to achieve stability. Each one of these molecules would then cease the "musical chairs" game, and become effectively permanent. If there is a high ratio of hydrogen to carbon in the stream, saturated hydrocarbons would become a major component, and, with sufficient hydrogen, methane, the most stable of all the hydrocarbon molecules, may become by far the dominant component. At depth methane will behave chemically like a liquid, and it will dissolve the heavier hydrocarbons that may be present, and therefore greatly reduce the viscosity of the entire fluid.

The continuing upward stream would acquire more and more of such unchangeable molecules, and the final product that may be caught in the reservoirs we tap for oil and gas, is the end product of this process. The detailed chemistry of the oils in each region then represents this final phase of the oil molecules on their way up, and that chemistry will be determined by the pressure-temperature regime the flow has experienced, the initial hydrogen-carbon ratio of the mix, and possibly surface catalytic actions and contributions from the rocks through which the flow has gone.

At shallow levels and low pressures, methane, now a gas, will separate out from the heavier components, leaving those as fluids of higher viscosity, and therefore much more subject to retention in reservoir rocks: the quantities of methane that would need to have been in the stream to facilitate the transport of oils, would be many times larger than that of the oils, but because of the great mobility of methane gas, most of it would fail to be retained in the ground at shallow levels.

Horizontal and Vertical Patterns of Hydrocarbon Fields

Everyone now thinks of Arabia, the Persian Gulf, Iran and Iraq as being the oil region of the world. It is indeed one connected large patch that is oil-rich, stretching for 2,700 km from the mountains of Eastern Turkey down through the Tigris Valley of Iraq and through the Zagros Mountains of Iran into the Persian Gulf, into Saudi Arabia and further south into Oman (Figure 2). There is no feature that the geology or the topography of this entire large region has in common, and that

would give any hint why it would all be oil and gas rich. The various oil deposits are in different types of rock, in rocks of quite different ages, and they are overlaid by quite different caprocks. They are in a topography of folded mountains in Turkey and the high Zagros mountains of Iran, in the river valley of the Tigris in Iraq, in the Persian Gulf itself, in the flat plains of Arabia and in the mountainous regions of Oman. It cannot have been a matter of chance that this connected region had so prolific a supply of oil and gas, but resulting from totally different circumstances in different parts of the region. These hydrocarbon-bearing formations represent times so different from each other that there would have been no similarity in the climate or in the types of vegetation that existed there during deposition, just as there is no similarity in the reservoir rocks or in the caprocks of the different regions now. Yet it is a striking fact that the detailed chemistry of these oils is similar over the whole of this large region (Kent and Warman, 1972). Surely this is an example of the need to invoke a larger scale phenomenon for the cause of the oil supply than any scale we can see in the geology of the outer crust.

Figure 2. Oil fields of the Middle East, showing continuous region from Turkey to Oman. The dots represent individual fields, and the size of each dot indicates the magnitude of the field.

The island arc of Indonesia, of which Java and Sumatra are the main components, belongs to a much larger pattern of an arc, that stretches from the western tip of New Guinea through these Indonesian islands into the Indian Ocean, through the Andaman Islands up into the Irrawaddi valley of Burma, and on into the high mountains of Southern China, over a total length of 6,000 km (Figure 3). That it is one connected arc all the way cannot be doubted because the frequency of earthquakes along the whole of this arc is hundreds of times greater than outside. Along the whole of this arc petroleum is very abundant. But at one end this arc is made up of volcanic islands; at the other end, in Burma and China, it is in continental material with folded mountains. Again there are great age differences and differences in every aspect of the geology in which the oilfields exist; but here we have a unifying feature, namely the belt of earthquakes and volcanoes which stretches over this entire length, and which points to causes in the deeper crust or in the mantle.

Many other examples can be quoted and they all point to the same conclusion: oil-rich regions seem to be defined by much larger-scale patterns than those we see in the surface geology or topography of the region.
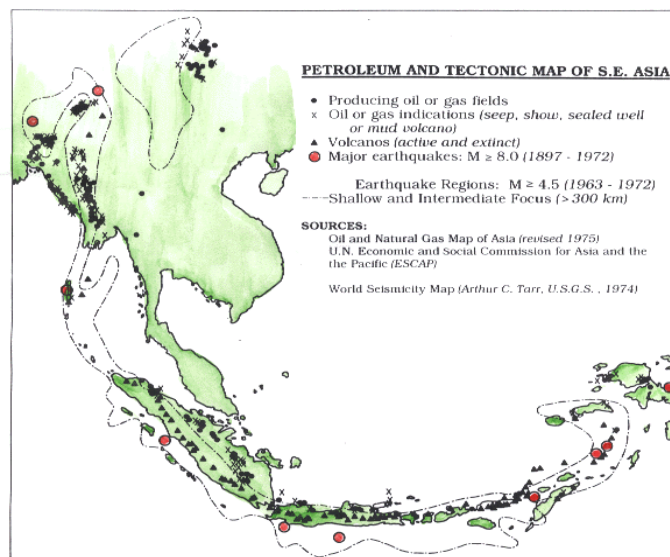
Figure 3. Petroleum and tectonic map of Southeast Asia. The map shows the belt of hydrocarbon occurrence paralleling the volcanic and earthquake belt from New Guinea, through the southern islands of Indonesia, Java, and Sumatra, through the Andaman Islands and on into the Irrawaddy valley of Burma and the mountains of southern China. Data compiled from World Seismicity Map (Tarr, 1974) and from the Oil and Natural Gas Map of Asia (revised 1975), published by the United Nations Economic and Social Commission for Asia and the Pacific (ESCAP). M, earthquake magnitude.

Another global observation of similar significance is the vertical stacking of hydrocarbons deposits, Kudryavtsev's Rule: "Any region in which hydrocarbons are found at one level will be seen to have hydrocarbons in large or small quantities, but at all levels down to and into the basement rock." The most common sequence is to find gas at the deepest levels, oil above, sometimes more gas above the oil, and coal at the shallowest. If one examines gas, oil and coal maps of different parts of the globe, one finds this rule repeated very frequently. It holds in most of the Middle East: many oil wells in Iran have penetrated through large coal deposits. Deep underneath the oil of the Gulf States, large gas fields have been discovered. Almost all the oil wells of Java and Sumatra have drilled through coal, and even the deep gas of Oklahoma is often underneath coal. What we are seeing is principally a succession of hydrocarbons with diminishing hydrogen content as one goes from the deepest to the shallowest. One presumes that bacterial action, which attacks the hydrogen rich hydrocarbons first, has been largely responsible for the progressive hydrogen depletion of upwelling hydrocarbons. For coal, the situation is more complex because biology can be involved in another way also. In a hydrocarbon outgassing area, the ground water is held strongly anoxic because hydrocarbon oxidizing bacteria are abundant there, and quickly remove atmospheric oxygen carried in that water. The result is that the normal processes of fermentation of plant material, which would turn the carbon back to the atmospheric CO_2, will be interrupted. Hydrocarbon outgassing areas tend to become swamps filled with the insoluble carbon of plant material. What plant fossils there are in bituminous coal (frequently there are none) are often themselves filled with the same homogeneous coal as that which surrounds them, suggesting a carbon source different from the fossilized plant material itself. It would not seem possible that plant material was converted into the homogeneous coal, and yet that a fraction survived as fossils with a precise maintenance of detail; and that this was then filled by the homogeneous coal derived from similar material.

The huge gas deposits in the form of methane hydrates in the oceans may not have an adequate explanation in terms of the plant debris of the ocean mud. There is often little organic mud and its gaseous products would not have migrated downwards. Yet it has been said by the Russian investigators (Makogan, 1988) that, so far as they could see, in every location on the ocean floor and in the permafrost of the North where the temperature-pressure situation would make methane hydrates stable, they are found. As the deeper ocean regions are being investigated for hydrates, the inadequacy of a biological source material for them may become even more obvious, since the biological deposits there tend to be much smaller than in the continental shelf regions that have been the principal targets so far.

Every deep hole that has been drilled into the crystalline basement, by several Soviet deep drilling programs, by the German on-going deep drilling efforts, by the deep drilling into the Swedish granite, has shown the presence of hydrocarbons at depth. While the quantities vary regionally, the indications we now have would point to a ubiquitous presence of some

amounts at deep levels everywhere. Even small amounts of methane or of hydrogen at the deeper levels in the rocks show that equilibration between the oxygen fugacity of the rocks and of the fluids has not taken place, since in chemical equilibrium these fluids could not be present. The explanation for this is that only a small fraction of the volume of the rocks could equilibrate by diffusive processes with the fluid streaming through pores; the pore fluids determine the oxygen levels in these cracks, the rest of the rock takes no part in this. Chemical equilibrium calculations are meaningful only in situations where the rocks and the fluids are much more tightly intermixed, such as in gases streaming through molten rocks. There each moving gas bubble keeps meeting new rock material to provide oxygen, and in these circumstances most carbon reaches the surface in oxidized form as CO_2. In solid rock there is a mixture of various proportions of methane and CO_2, frequently with methane as the major quantity.

Since methane hydrate formation is a very efficient means of retaining any upward streaming methane, even regions with low rates of methane emission would still build up hydrates in the long course of time. CO_2 hydrates could exist also, but very little of this has so far been found, presumably because the cool, non-volcanic regions produce mainly methane, and the hot regions do not lay down hydrates. If plant debris were responsible, CO_2 would be a major component of the gases produced, and CO_2 hydrates should be common.

If hydrocarbon outgassing is in fact a major source of the surface carbon excess, then one must of course consider whether it is also a major source of all the carbonaceous deposits that are found in the crust. The frequent compliance with Kudryavtsev's Rule would have no explanation for any other mode of deposition.

It has often been argued that oil deposits are in the vicinity of "source-rocks", rocks that contain carbonaceous materials which have been assumed to come from biological deposits. Most commonly these rocks are shales, and their hydrocarbon content often shows a close chemical match to that of the oil pool in the vicinity. This has been taken to verify the source-rock concept; but it would only do so if these shales were generally particularly rich in discerible fossils. This is not the case, and there is no reason for attributing their hydrocarbon content to anything other than a supply from the same source as that of the neighboring oil. The so called "source-rocks" can be regarded as a further demonstration of Kudryavtsev's Rule.

Interpretations Based on the Carbon Stable Isotopes

Carbon has two stable isotopes; [12]C (6 protons, 6 neutrons) and [13]C (6 protons, 7 neutrons). The natural carbon on the Earth contains predominantly [12]C , and ^{13}C is mixed in at a level of approximately 1 percent. This mixing ratio must have been determined in the nuclear processes in the stars that cooked up the elements and eventually supplied them to form the planets. There are no processes that could occur on the planets that would be able to change this ratio greatly. Only small variations can be produced, not by any effects on the nuclei themselves, but only by processes that show a slight preference and select in favor of either the light or the heavy isotope.

The study of the distribution of the carbon isotopes in relation to petroleum and natural gas has a very extensive literature. We shall discuss here only one aspect of it: can isotope measurements determine whether a hydrocarbon compound was derived from biological material or whether it is primordial? Because many petroleum geologists have considered that such a distinction can be made, and that petroleum and natural gas appear on that basis to be usually of biological origin, it is clear that we must address this aspect here.

A selection process that enriches one or other isotope is usually referred to as a process of "fractionation." The resulting fractionated material is referred to as isotopically light or isotopically heavy, depending on the ratio of the lighter to the heavier isotope. Measurements of the slight variations in the carbon isotope ratio in different samples is usually not done in absolute terms, but by comparison with a norm, and the small departures from this norm are then the quantities noted. The norm that has been selected for this purpose is a marine carbonate rock called Pee Dee Belemnite, or PDB, and this norm has a carbon isotope value that is about in the middle of the distribution of all the marine carbonates. The measurements are then quoted as the departure of the ^{13}C content of the sample from that of the norm, and the figure is usually given in parts per thousand (permil) and referred to as the $d^{13}C$ value of the sample.

Unoxidized carbon in plants derives from atmospheric carbon dioxide by the process of photosynthesis. In this process the

light isotope is slightly favored. As a result this carbon is slightly depleted in ^{13}C relative to atmospheric carbon dioxide, and the effect is larger than that occurring in any other single nonbiological chemical process recognized in nature. When it was found that most of the deposits of unoxidized carbon, like petroleum, methane, coal and kerogen, show also a marked depletion of ^{13}C, it was considered that this confirmed their biological origin. d^{13}C for plant organic carbon is generally in the range of -8 to -35 permil (PDB standard). The atmospheric carbon dioxide from which that carbon derived is at -6 per mil, showing the possibility of a large fractionation effect. Marine carbonates laid down from atmospheric carbon dioxide dissolved in ocean water have d^{13}C values ranging from about +5 to -5 permil (average 0) and thus evidently a fractionation averaging 6 permil occurs in favor of the heavy isotope during that process.

In the production of methane from plant debris a further fractionation takes place that again favors the light isotope, and plant-derived methane is therefore isotopically even lighter and its d^{13}C plots at -50 to -80 permil. In the literature we now find that some arbitrary division has generally been assumed, so that carbon with d^{13}C values lighter than -30 permil is regarded as of biological origin, while heavier carbon is taken to be from some other source.

There is no clear division in the actual data. Carbonaceous materials have d^{13}C values spanning the range from +20 to -110 permil on the Earth, and they span an even larger range in the carbonaceous meteorites. There is no natural dividing point in the data and the choice of a particular figure in this continuous distribution, for making the distinction between organic and inorganic origin seems very arbitrary. The question is of course what other fractionation processes can select in favor of the light isotope.
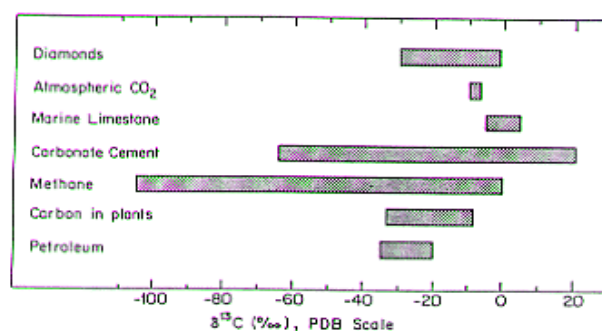

Figure 4. Distribution of ratio (expressed as d^{13}C) of the stable isotopes ^{13}C and ^{12}C in different terrestrial materials. Methane and carbonate cements span a much larger range of these isotope ratios than all other forms of terrestrial carbon. PDB, Peedee belemnite.

A look at the distribution of the carbon isotope ratio in different natural forms of carbon gives immediately a strong suggestion (Figure 4). Just methane, the only carbon-bearing molecule that is light enough to suffer significant isotopic fraction, shows the largest spread of values. The atmospheric carbon dioxide from which marine carbonates have been deposited throughout geological time seems to have had a remarkably constant isotopic ratio, so that d^{13}C values for nearly all these carbonates fall into the range of -5 to +5 permil. d^{13}C in petroleum has a fairly narrow range, from -20 to -38 permil. Carbonate (calcite) cements in the rocks have d^{13}C values spanning the second widest range. This fact by itself would suggest that the carbonate cements are generally produced from methane, and their shift of between 20 and 40 permil heavier than the range for methane suggests that a fractionation occurs when methane is oxidized in the ground and then combined with calcium oxide to produce the carbonate cement. Everything in the data points to such a process. These cements are found in great quantity overlying gas and oil fields. They are usually isotopically lighter than marine carbonates, the lightest among them as light as -65 permil. Where methane and carbonate cements are found in the same location the methane is usually isotopically lighter than the carbonate by between 20 to 60 permil. The overall isotopic distribution of methane and carbonate cements show a similar shift.
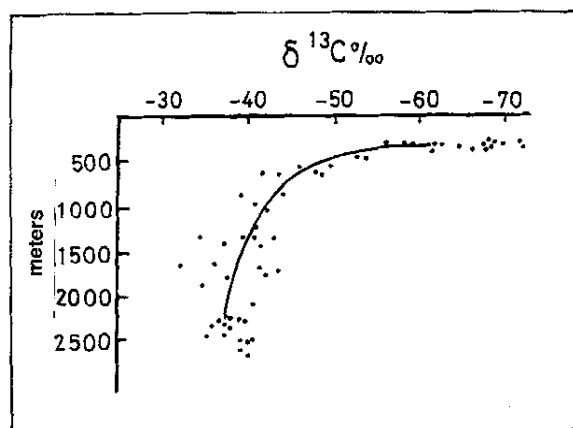
Figure 5. Carbon isotope ratios (expressed as $d^{13}C$) of methane plotted against depth of occurrence (from Galimov, 1969). Although there is much variability in this relationship, it is almost always true that where methane is found at different levels in the same area, the methane is isotopically lighter (contains less ^{13}C) the shallower the level.

Galimov (1969), a major contributor to the carbon isotope investigations, saw that in any vertical column methane tends to be isotopically lighter, the shallower the level. This appears to be true irrespective of the type or age of the formation from which the sample was taken.(Figure 5). It is most unlikely that in all those cases methane from two different sources mixed in such a fashion. A much better explanation is that a progressive fractionation of the methane had taken place in its upward migration. Some of this methane appears to be lost to oxidation, ending up as carbon dioxide (Figure 6), and a fraction of that in turn as calcite cements. This oxidation process seems to prefer the heavy isotope and so the remaining methane gets isotopically lighter on the way up. At each level the calcite thus derives from the already fractionated methane and so it also will become lighter, tracking the methane but always remaining heavier than the methane at that same level.
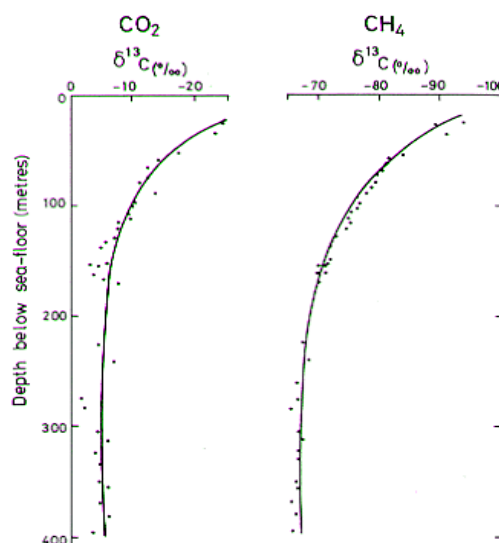

Figure 6. Comparison of the carbon isotope ratios (expressed as $d^{13}C$) of methane and coexisting carbon dioxide in ocean-floor sediments (from Galimov and Kvenvolden, 1983). The carbon isotope ratios of the two gases seem to follow the same depth dependence, but with the CO_2 always isotopically heavier than the methane. This is the pattern to be expected if progressive fractionation were happening, with the CO_2 produced (probably by bacterial oxidation) from methane moving upward through the crust. Both the methane and the CO_2 produced would become isotopically lighter on the way up, but the CO_2 would be heavier by a constant amount than the methane from which it was derived. (This is not the interpretation given by the authors of the article.)

Progressive fractionation is an important process because it can drive the remaining material to a very much greater

fractionation than could be done by any single chemical step. It is of course the technique used for commercial isotope separation, where extremely large fractionation factors are required. In our case two effects work in the same sense, helping to create the result. One is the tendency for the oxide to bind slightly more tightly with the heavier carbon isotope (in CO_2), and in equilibrium conditions at a low temperature the heavy isotope will therefore be enriched in the oxide and depleted in the remaining methane. The other effect is the diffusion speed, which for methane with the heavier isotope and a mass number of 17, will be 3 percent slower than for the light methane with a mass number of 16. This means that in any circumstance where methane is diffusing through a barrier to fill a reservoir, the light isotope methane will enter initially with a 30 per mil enrichment. If this reservoir were to fill another, the light isotope enrichment would augment. Differential removal by oxydation, by different solubilities in water, by different adsorption on solids, by bacterial attack, will all affect the final result of a slow percolation of methane through diverse strata of rock. Since in any such progressive fractionation the final effect can be arbitrarily large, one cannot conclude that a large fractionation implies that of a single step process, namely the one that occurs in plants.

The constancy of the isotopic ratio of marine carbonates spanning all ages deserves further comment. If at any time between the Archean and the present a large change had taken place in the amount of plant debris that was buried, and if this plant debris was, as is usual, isotopically light, then more of the light isotope would have been taken out of the atmospheric-oceanic carbon dioxide reservoir. The remaining CO_2 in that reservoir would have been driven to a slightly heavier composition. If as much as one-fifth of the buried carbon was in the form of such plant debris, then the shift in the remaining atmospheric carbon and the resulting shift in the carbonates laid down from it should have been readily observable. When land vegetation suddenly proliferated in Silurian times, for example, one might well think that twice as much unoxidized plant material was buried as before this event. Why is there no change in the isotopic ratio of marine carbonates in that epoch? An explanation that the primordial supply suffered a change in the isotopic ratio just sufficient to compensate is improbable. A more likely explanation is that the quantity of biological debris that is buried is a much smaller fraction than the one usually assumed. The reason for this may be that the identification of much of the buried carbonaceous material as plant debris is not correct and that a large proportion of this material derived directly from hydrocarbons ascending from the mantle. The extra contribution made by the time-variable burial of plant debris may then be so small an effect that it does not show in the isotopic ratio of the carbonates. Of course if all the dispersed kerogen and the oil shales, which have been regarded as source material for oil pools, were derived from the primary hydrocarbons, then this discrepancy would disappear. It is worth noting that the amount of carbon that would have been contained in certifiable fossils is a very small quantity by comparison.

The remarkable constancy of isotope values of marine carbonates also affects the question mentioned earlier, of the amount of carbon that may be coming up as a result of the heating of subducted sediment. In such a process some or all of the carbonates may be dissociated and the CO_2 may come to the surface. Much of the unoxidized carbon that is in the same sediment, whether it derives from plants or from a primordial hydrocarbon supply, is known to be isotopically much lighter. Of that, only a fraction would be turned into liquids or gases, limited by the availability of hydrogen; the remainder would eventually turn into elemental carbon--graphite or anthracite--and in that form it would be insoluble and stable, and would not be returned to the atmosphere. A process of multiple recycling of sedimentary carbon would therefore always take away more of the light isotope than of the heavy, and this would drive the atmospheric-oceanic CO_2 to a heavier isotope value. Recycling of sediments cannot account for a significant fraction of the resupply of atmospheric CO_2 over geologic time.

The Helium Association with Petroleum

On the basis of hydrocarbon outgassing from great depth, we understand immediately why various trace elements, especially helium, should be so commonly associated with deposits of oil and gas. The long pathway through pressure created fracture porosity in the rocks will, of course, sweep up whatever helium was available in those pores. Helium is generated in the rocks by the radioactive decay of uranium and thorium, but at too low a concentration to create a fracture porosity or hold it open. Its transport is therefore dependent entirely on a carrier gas, such as the more abundant hydrocarbons may provide. Helium is not only strongly associated with hydrocarbon deposits, it has even been noted to be particularly enriched in gas-oil reservoirs, more so than in dry gas reservoirs (Nikonov, 1973). It is also particularly enriched in reservoirs having a high nitrogen content. Any chemical or biological cause for the enrichment can be ruled out for the chemically inert helium. Only variations in the concentrations of the parent radioactive elements, and variations in the the length of pathway through the rocks from which the helium has been swept, can come under consideration for an explanation of the great regional

differences of the observed helium concentration. Where large variations have to be explained, such as by a factor of 100 or more from one location to another, the lenth of pathway through which the carrier gas has swept is likely to have been the dominant effect. If carrier gases from a depth of 300 km are involved in one case, while only gases from the depth of sediment are involved in another, then this variant will outweigh any likely variation in the concentration of the radioactive elements. The helium concentration in a gas is then mainly an indication of the depth from which this gas has come. With this explanation one would conclude that nitrogen frequently derives from the deepest levels of any of the volatiles, and oil from the next deepest; dry methane sometimes from shallower levels still, but all from levels far deeper than the sediment. Helium enrichment is not found in sediment in the absence of larger amounts of hydrocarbons or nitrogen, and ten percent helium in methane-nitrogen gases is the highest concentration that has been found. Yet if helium could flow without a carrier gas, there should be many locations where amounts of helium had accumulated that were similar to the amounts of helium in some gas-fields, but now, in the absence of methane or nitrogen, they would be pure helium fields. Such fields would have been discovered, and would be very valuable. Their absence thus certifies the carrier gas concept for helium transport.

Some information can be gained from a study of the isotopic composition of the helium. Helium has two stable isotopes, helium-4 and helium-3. Most of the helium found on Earth is helium-4, the result of the radioactive decay of uranium and thorium. In the atmosphere helium is present at a concentration of 5.24 ppm by volume. The helium-3 isotope, which is much less abundant, is present in the atmosphere at about 1.4 parts of helium-3 to a million parts of helium-4. In the surface of the Sun and in the Solar Wind one observes a ratio of helium-3 to helium-4 of 3×10^{-4}, or about 200 times higher than the ratio in our atmosphere.

The primordial helium that was incorporated in the Earth as a small impurity in the rock grains must have been more similar to the solar composition and thus much richer in helium-3 than any present day terrestrial helium. But the total quantity that was brought in by the grains was small and so the continuous production of helium-4 from the radioactive decay became the major contributor to helium in all locations on the Earth.

While a small proportion of helium-3 can also be produced by radioactivity in an interaction involving uranium and lithium, this is not thought to be a major contribution to the Earth's helium-3. The lithium production of helium-3 in the most ideal circumstances, where lithium and uranium are in close association, could be as high as to give $^{3}He/^{4}He$ ratios of 1.2×10^{-5}, or ten times the ratio in the atmosphere (Morrison and Pine, 1955). But this would occur only in some rare minerals, and the average production in the crust of the Earth of helium-3 has been estimated as at least a hundred times lower. This means that in any location where we find a helium-3 to helium-4 ratio of more than one-tenth the atmospheric value, it is probably due to a contribution of some primordial helium. In those cases we then know that we are dealing with a gas that has at least a component that must have come from deep rocks, since the crust in its formation process would have largely outgassed, and primordial helium would not have been maintained there.

However, we cannot assume the converse. Where the proportion of helium-3 is low, the gas may well have come from mantle depths also, since in a mantle that was never all liquid, the gas content could never have become a uniform mix, nor could it have remained a uniform mix if the rates of outgassing were different in different regions.

Where a carrier gas has washed through pore spaces that it has created, it will have transported the mix of primordial and radiogenic helium that happens to have been there. If such a flow has been going on for a long time, then the primordial component will have been depleted, while the continuously produced radiogenic component will still be present. The heliun-3 proportion will have suffered a dilution throughout the existence of this flow. Pore spaces that have been flushed for a long time would have low helium-3 values, but there would be no reason to assume that such gases derived from a smaller depth. While the presence of a high helium-3 value is indicative of young pathways from mantle depths, helium with low helium-3 values does not give a firm indication of its depth of origin. Great concentrations of any helium, however, suggest that sweeping by a carrier gas on long pathways has been responsible, and this in itself is an indication of a deep origin.

The partial pressure at which helium is found, whether as a collection under a caprock or anywhere else, may also serve as in indication of its depth of origin. As an inert gas, it cannot have had its partial pressure increased from that of its point of origin by any chemical action. In any flow, its partial pressure must always decrease; only the (unlikely) circumstance a mechanical pumping action could ever cause an increase. Helium must have derived generally from a location where the radioactive decay could produce the partial pressure at which it is found, or a yet higher one. This is an important

consideration in estimating whether helium in a location could come from the radioactivity of the surrounding rocks or whether it has come from greater depths. For this calculation one has to take into consideration not only the local concentration of uranium and thorium, but the helium porosity that the rock has (the volume of pore spaces large enough to be occupied by the helium atom, which includes many imperfections in the rock crystals, and will therefore represent a larger volume than the porosity presented to a gas of larger molecular size). At deeper levels, where the rocks are subjected to a high lithostatic pressure, the helium porosity will be small, and a given radioactive concentration will send the resulting helium into smaller volumes, and therefore set up correspondingly higher partial pressures. This consideration shows that in many locations, even where natural gas has a comparatively high helium content, the local rock cannot have supplied it. It explains why helium measurements at or near the surface seem to be successful in finding hydrocarbons underneath (Roberts, 1980), but rarely successful as a means of prospecting for uranium deposits.

Regional patterns of helium abundance have been observed in which the helium concentration and the helium partial pressure are far higher than the sediments could have produced in their entire age (Pierce and others, 1964), but where the patterns of gas composition (ratios of components) stretch horizontally over distances very large compared with any particular gasfield of the region. The helium must certainly have come from below the sediment, and it must have arrived there already in regionally well-defined mixing ratios with methane and initrogen, so that the different fields of the region could all be filled with the same or a closely similar mix. Only a mix that had entered the sediment and its individual gas fields from below could achieve that (Gold and Held, 1987).

Relation of Outgassing of Hydrocarbons to Atmospheric Oxygen

The problem of the maintenance of the atmospheric oxygen levels within the bounds suggested by the geologic record has not yet been solved satisfactorily, but it is clearly closely related to the carbon supply. Photosynthesis in the plants produces free oxygen by the dissociation of water. If none of the products of photosynthesis escaped from the circulation of atmosphere and biosphere, if fermentation returned all the content of carbon and hydrogen in plant debris back to the atmosphere as carbon dioxide and water (the form in which it was taken up by the plants), then there would be no net gain or loss of atmospheric oxygen. If some hydrogen were to escape, however, as hydrogen does escape from the upper atmosphere into space, or if it were laid down in hydrides or other hydrogen compounds in the sediment, then for every two hydrogen atoms so removed, there would be one oxygen atom that would constitute a net addition to the atmosphere.

If all the fresh carbon supply that the atmosphere receives came in as CO_2, and if all the carbon laid down in the sediment were in the form of carbonate rocks (i.e. CaO from rocks combinig with CO_2 to make $Ca\ CO_3$), then also this process would neither add nor subtract from the atmospheric oxygen. If, however, as is generally thought, about one-fifth of the carbon that is laid down is in the form of plant debris, then there would be constantly a large addition to the atmospheric oxygen. For each carbon atom that is so buried there would be at most one oxygen atom and at most two hydrogen atoms (polysaccharides like cellulose are $(C_6H_{10}O_5)_x$). Every carbon atom that came up in the form of CO_2 provides two oxygen atoms, while the burial of that carbon atom would bury only one oxygen atom and take away possibly as many as two hydrogen atoms that had derived from the dissociation of water and would not now be available to reform a water molecule with its photosynthetically liberated oxygen atom. Thus, for every carbon atom laid down as biological debris, approximately two oxygen atoms would be liberated. For the figures given, of 20 kg/cm^2 of total carbon laid down, one-fifth in biological materials, the total amount of oxygen left over to join the atmosphere would be 10.6 kg/cm^2 of O_2. That is more than 50 times the present atmospheric oxygen content. All carbon being supplied as CO_2, and one-fifth laid down in plant debris, the rest as carbonate rocks, does not seem a possible scenario over long periods of geologic time.

If a fraction of the juvenile carbon was supplied as CH_4, that would diminish the oxygen excess, as both the carbonates and the organic carbon would lay down some oxygen, and the left-over hydrogen would form water, using up more atmospheric oxygen. Of course this could make the balance towards no gain or loss of atmospheric oxygen. But to maintain the atmospheric oxygen level within the bounds given by the geologic record, the supply of carbon as methane and as CO_2, and the laying down of carbon in the sediment would have to be balanced very precisely, since both involve such large quantities of oxygen compared to the atmospheric oxygen content. One could not attribute such constancy nor the chance of just producing the balance, to tectonically controlled events over long periods of time. Some powerful stabilizing effect would have to be at work.

What are the limits on the excursions of atmospheric oxygen content that the geologic record can provide? In all the times that forests have existed, oxygen levels cannot have been higher than the present by more than a few percent, for we are now not far from that concentration at which fires would make it impossible for forests and many other major land plants to survive. In earlier times, before the emergence of large land plants in the Silurian, there may have been periods of higher oxygen values, and such periods have been suggested to account for the oxidation states of iron in some ancient sediments. The other limit, that of low oxygen values, can only be estimated from the oxygen requirements of animals both in seawater and on land, and from the oxidation state of some sediments. Again this limit cannot be set very far below the present values for all the periods back to the Cambrian, in which oxygen-breathing fishes have existed. Before these epochs the limits may have been wider.

What could be the stabilizing influences that are at work? The laying down of inorganic sediments may have a stabilizing effect, as these sediments can become more highly oxidized than the basement rocks from which they derived. A large amount of sulfur may be present now in a more highly oxidized state than that in which it came to the surface. Another stabilizing effect may be the escape of hydrogen from the Earth into space. In the presence of smaller atmospheric oxygen values, more hydrogen liberated by photosynthesis could diffuse into the outer atmosphere without being caught by oxidation, thereby leaving more oxygen behind. It is doubtful, however, that such large quantities of oxygen could have been liberated or absorbed in these processes as would be required, or that the stabilizing effect could have the required strength to keep the atmospheric oxygen levels within the narow bounds.

Perhaps the strongest stabilizing effect would be the control that the atmospheric oxygen concentration must have on the amount of plant debris that will be buried before being re-oxidized. Higher oxygen levels in the air, and hence in groundwater, will diminish the areas of swamps and of anoxic lakes, ponds and seas, the locations in which plant material would escape the fermentation processes that would turn the carbon back to CO_2, thereby taking away atmospheric oxygen.

Conversely, low oxygen would favor anoxic deposition, leaving more oxygen behind. Possibly this effect could be sufficiently powerful. However with the imprecise knowledge of the amounts of plant material buried in different epochs, with the strong possibility that deposits of organic carbon are in significant part due to upwelling hydrocarbons and not all to plant debris, and with the inexact knowledge of the ratio of oxidized to unoxidized carbon in the primary carbon supply to the surface, no firm judgment can yet be made.

The Mechanics of the Ascent of Fluids through the Crust

There are two principal methods of ascent towards the surface of fluids that are liberated in the mantle and that are of lesser density than that of the rock, and hence buoyant relative to it. One is the ascent in volcanic regions, where magma, with its density closely similar to that of the surrounding rock, can hold open vertical pathways down to depths of a hundred kilometers or more. Any other fluids that can pressure fracture the rock and make their way through cracks into such lava channels can then move upward by buoyancy forces, and quickly reach the surface. Hydrogen and hydrocarbons would, as we have said, be largely oxidized in bubbling through magma, but the extent of this oxidation would of course depend on the relative proportions of hydrocarbons and magma at any time. There are strong indications that small amounts of gases coming out of volcanoes at quiet times are largely oxidized, while in violent eruptions the unoxidized gases--hydrogen and methane--are prominent. On many occasions flames have been reported during major eruptions, and have been seen as quite distinct from the ejection of hot material. During the episodes of the Krakatoa eruption below the sea surface, a large region of flames above the water were observed, in this case of course in the complete absence of any confusing sprays of lava. But even at quiet times some volcanoes emit enough combustible gases to burn above the lava lake. This has been observed in the Hawaiian volcanoes and also in volcanoes of the African Rift. Volcanic eruptions in Java have delivered ashes containing several percent of unoxidized carbon.

The other possible manner of ascent of fluids from the mantle is the build-up of sufficient fluid pressure to fracture the rock and create pathways (Gold and Soter, 1984, 1985). For such pathways to stay open, the pressure in the rock due to the overburden weight, and the fluid pressure in the pore spaces, have to be closely similar. Since rock is extremely weak in tension, a fluid pressure higher than the lithostatic value will quickly create more fractures. In compression rock is much stronger and pore spaces will only be crushed shut when the pore pressure deficit exceeds a certain value. If one considers fluids that are less dense than the rock, then any connected system of pore spaces filled with such fluids will have a smaller pressure gradient with depth than that of the surrounding rock. At the top of such a domain the pressure may be close to that in the rock (the lithostatic pressure). The bottom of such a domain will then have a deficit of pressure and since this cannot

exceed a value defined by the compressive strength of the rock, there will be a limit to the vertical height that such a domain can occupy (Figure 7). In the volcanic case, the dense lava with its pressure gradient closely similar to that of the surrounding rock, can keep open a channel to a depth of a hundred kilometers or more. In the case where the fluid is a hydrocarbon or water, and hence of of much lower density, it is only an interval of a few kilometers that can be held open; an interval whose height can be calculated from a knowledge of the compressive strength of the rock, and vertical pressure gradients in rock and fluid, given by their respective densities.
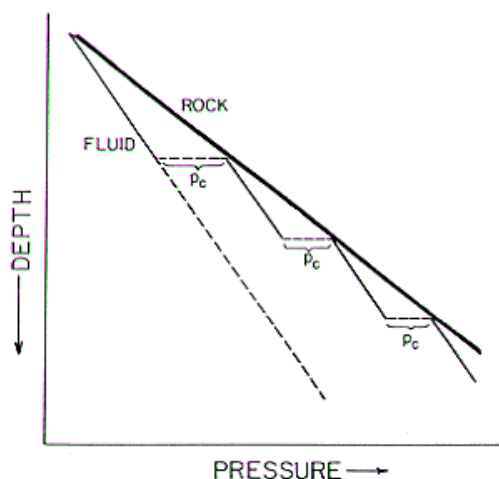

Figure 7. Schematic diagram showing pressure of rock due to overburden and pressure of fluid (less dense than the rock) in connected pore spaces. P_c denotes critical pressure difference (between rock pressure and fluid pressure) at which the rock compressive strength is inadequate to maintain pores. Dashed lines indicate fluid pressures that are physically unrealizable because of the limited compressive strength of the rock.

These limitations do not mean that gases or liquids are prevented from making their way up. If fluids are evolving as a consequence of an increase of temperature or of chemical reactions taking place at depth, they may create fracture porosity, and increase the pressure in such a domain of pore spaces. As more fractures are being created, the vertical height of the domain will increase. As soon as the height spanned exceeds the critical value, the rock at the bottom of the domain will crush shut. Such a domain may then be unstable and migrate upwards, driven by the force of buoyancy, much like a bubble of gas in a liquid makes its way up. Only here, in the presence of solid rock, it is not a round bubble but a region of rock with interspaced but connected pore spaces. Just as the bubble would split the liquid above it while the liquid below it would close again, so in this case it will happen with the rock. The rock itself does not move upwards, but the domain of pore spaces with its fluid makes its way up through the rock. Above strongly outgassing regions in the mantle one may have a frequent dispatch of pore space domains towards the surface.

Another mode of upward flow is also possible. If the generation of fluid is continuous, a set of adjoining, stationary pore space domains may be set up, and the flow may be in the form of a continuous or intermittent leakage from one to the next one above. The stability of such a flow will require that the pressure drop from the top of one domain to the base of the next will occur as a result of the flow through the low permeability of the dividing layer. (Figure 7.) However the flow occurs, it must always adopt a stepwise pressure profile, with domains in which the fluid pressure gradient has almost precisely the static value, given by the density of the fluid, divided from the next domain by a region in which the fluid pressure gradient has a much higher value. (If the mass of fluid is small compared to the mass of rock, as would mostly be the case, then the average pressure gradient over a large vertical interval must be the lithostatic one in both rock and fluid.) Such a flow can be compared with a flow of a river from the mountains, which creates a system of cataracts. Consider the potential energy in the flow: pressure in one case, height in the other. In the case of the river, almost all loss of height occurs at the cataracts, the flow between them being almost quiescent and level. Similarly, in the former case, almost all the drop in pressure would occur not continuously but in a few sharply defined locations.

If we look at this situation from the surface down we may find a system of connected pore spaces frequently filled with water, and we therefore define a pressure in the pore spaces that is called hydrostatic, and a pressure in the rock, called lithostatic. As the two pressure gradients with depth are dissimilar, a point must be reached where the rock will close. I have

referred to this as the "critical layer." Beneath that we can again have open pore spaces, but now only provided that they are filled with a fluid at a pressure exceeding the hydrostatic value that would be calculated for that depth, but not exceeding the lithostatic value. We may then have another domain of fluid-filled pores, but again only of a limited vertical height. The uppermost domain can be calculated to reach down to a depth of between 3 and 5 kilometers in soft rock, but possibly as much as 10 kilometers in hard rock. This is the domain in which most of the oil and gas exploitation has been done so far, but a comparatively small number of cases exist where the drill went through a sharp pressure transition, and where the secomd domain has been tapped.

It should be emphasized that such a critical layer is a necessity dictated by the finite compressive strength of rock. It is thus a caprock layer which must overlie any region in which outgassing is occurring. As the strength of the rock is of course regionally quite variable, this critical layer may be far from level. It may be of a complex shape with large variations in height, and there may even be locations where it doubles over on itself. The main thing is that it has to be a continuous sheet. This is not to say that there may not be other layers of caprock in an outgassing region where a material of low permeability was laid down, and presumably all shallow gasfields have required the presence of such a caprock. The importance of the critical layer is that an outgassing region will inevitably possess that type of caprock at a sufficiently deep level.

The critical layer, like other layers of caprock, will not have zero permeability and there will be some leakage through it, as we have discussed. In a long term steady state of a continuous upward flow, the leakage through the critical layer (and through all the similar layers at deeper levels) must occur at the mean supply rate. Nothing can change the flow rate of this upward stream: it is given by the production rate of the fluid below. All that any caprock or any critical layer can do is to increase the amount that is dammed up underneath it. The situation is similar to that of the flow of a river from the mountains to the sea, where, we may suppose, the rainfall producing the water all occurs up in the mountains. On the way down, the river will transport all the water that has been collected; and if the river is dammed up anywhere along its length, the steady state flow rate will not be changed. All that the dam will do is to create a lake on the upstream side of it, but finally the amount of water flowing over the dam will be exactly the same as that which would have flowed without the dam.

This is an important consideration from a practical point of view. One has observed that over natural gas producing regions the amount of methane and other hydrocarbons in the soil is greatly enhanced, sometimes by a factor of one hundred or more, and any attempts at deducing a flow rate to account for this gives such high rates of methane seepage as to appear incompatible with a supply coming only from a gasfield below. The technique of surface chemical prospecting, such as measuring the soil methane, has been described by some as necessarily in error, since it was not conceivable that the outflow rate could be so high that the gasfield would be exhausted in a few thousand years. But of course if there is a continuous gas supply from below, and at rates that are in no way in conflict with the limits we can place on such outgassing processes, then it will make good sense to observe the surface concentrations of hydrocarbon gases. It would also make good sense to extend this technique and introduce tracer gases in a well at some depth, and observe the time it takes for the tracer gases to appear in the surrounding soil. From this, and the knowledge of the porosity of the ground, an actual flow rate can be established, and so one could evaluate for any region how much methane per day or per year is seeping out.

Regions that have a high seepage rate will in general be favorable ones for finding good reservoirs, since for a given quality seal or caprock a larger quantity is likely to be dammed up underneath that seal. Surface gas prospecting has been certified over many known gasfields, the outstanding example being the Cement Field of Oklahoma. The technique is yet to be used on a large scale in the search for more gas.

In several regions of the U.S. drilling to 5 kilometers (15,000 ft.) or deeper has demonstrated the sharp pressure discontinuity to which I have referred. All of the deep gas in the Anadarko Basin is below this discontinuity and there all the deep gas seems to form essentially one reservoir. In Louisiana and neighboring areas of the Gulf Coast, the pressure discontinuity is a little shallower and the continuous sheet represented by it has been carefully mapped (Jones, 1980), with the information available from a large number of wells and the interpolation between them from seismic data. In Oklahoma there is, in some instances, a dramatic increase in the porosity after penetrating the critical layer. Porosities as high as 18 percent have been found below 20,000 feet in the carbonate rocks. It is clearly not possible to account for this by any process of enclosing a rock volume tightly, and then compressing it to achieve the gas pressure in the pores. Since that gas pressure is roughly twice that above the critical layer, one would have to contemplate an initial gas-filled porosity of 36 percent. This is not a value that has ever been seen. The conclusion must be, therefore, that the gas has entered from even

higher pressure regions deeper down, and that it has expanded pore spaces to these values. Investigations of the details of the fracture patterns in the rocks confirm such an explanation.

We may then describe how a flow of hydrocarbons from depth may take place. As we have discussed, a high proportion of saturated compounds would indicate that methane was a major component that dilutes the stream. But at shallow levels where the pressure is low, the heavier hydrocarbon molecules will be shed from the stream. The largest such effect will take place at the flow through the last pressure discontinuity on the way up, the shallowest critical layer. It is there that the oils are likely to be deposited, being now viscous and easily retained, while much or all of the gases can continue upwards and largely escape into the atmosphere. Oil deposits are concentrated laterally because major faults have facilitated their ascent and have caused a confluence towards them; and the oil deposits are concentrated vertically because of the sharp pressure changes in going from one pore-space domain to the next, at which oil and gas get separated.

Results in Sweden

The distinction between hydrocarbons derived from biological materials and hydrocarbons of primordial origin would be made most clearly by examining igneous or metamorphic rocks which could not have maintained either hydrocarbons or biogenic materials capable of producing them, before they froze to their present condition. If crude oil, methane and other hydrocarbon gases can be found in such locations, at depths that would exclude a seepage down from above, then this would demonstrate an origin from sources below.

Crude oil has been found and produced from crystalline and basement rocks in numerous locations, but mostly in places where a transport from neighboring sediments could be invoked as an explanation. The clearest example we have where a production from sedimentary materials can be excluded comes from two deep bore-holes in the granitic rock of central Sweden (Gold, 1991).

As we have noted, the granite and gneiss of Sweden has many signs of impregnation with hydrocarbons. Tar is frequently found during tunneling and mining operations as a substance filling cracks in the granite. Methane explosions and prominent shows of methane have been seen frequently. If hydrocarbons come from depth, one might judge that the large granitic block which makes up most of Sweden overlies an area of mantle that is particularly hydrocarbon rich, and one might think that the hydrocarbons of the Norwegian Trench or of the countries surrounding the Baltic signify an outflow from this area of the mantle. Fractures of the rock within Sweden may then have been conduits for hydrocarbons from the same source.

It is with this consideration in mind that I persuaded the Swedish Government to study the region of a giant meteoritic impact crater, the "Siljan Ring" in Central Sweden. An impact that left a circular formation 44 kilometers in diameter would undoubtedly have fractured the rock to great depth, and one might therefore have expected this to be a particularly favorable location for finding upwelling hydrocarbons.

It was quickly ascertained that just the area of the Siljan structure was quite anomalously rich in soil methane and other light hydrocarbons, that many ordinary water wells produced copious amounts of gas and that a number of stone quarries in the area had oil seeping out of the rocks and making oil pools in the ground. It is true that the stone quarries were in the sedimentary rock which fills a ring shaped depression, but those sediments are nowhere deeper than 300 meters. Oil seepage generated after 360 million years from such a small quantity of sediments seemed improbable. Aside from the ring shaped depression, the basement rock is very close to the surface in the whole area; there is barely enough soil for the trees to grow both inside and outside the Siljan Ring feature.

As a result of the clear demonstration that the area was quite anomalous for its hydrocarbon content, it was decided to engage in a major drilling operation. Since 1986 two wells have been drilled: one to a depth of 6.7 kilometers, the other to a depth of 6.5 kilometers. Both holes showed the presence of methane and of other hydrocarbon gases, as well as of crude oil. While in the first hole (Gravberg I) diesel oil was used for a time as a component of the drilling mud, only water-based mud was used in the second hole (Stenberg 1), which is situated in the center of the ring, and is 12 km distant from the ring sediments, and also from Gravberg 1. Although the detailed chemical makeup of the oil found at deep levels in Gravberg was not the same as diesel oil, many considered nevertheless that the diesel drilling oil could be held responsible. Some 15 tons of oil were pumped up, oil that had hydrocarbon components and organo-metallic compounds that are frequently in natural crude oils, but were absent or present only in very much lower abundance in any of the drilling fluids. Some biological molecules, steranes, were found to be from the same set and in closely similar ratios as had been seen in the

surface seepage oils (Figure 8), and this strengthened the case that the two oils had a common origin. Steranes are thought to derive from sterol, a component of methane-oxidizing bacteria.
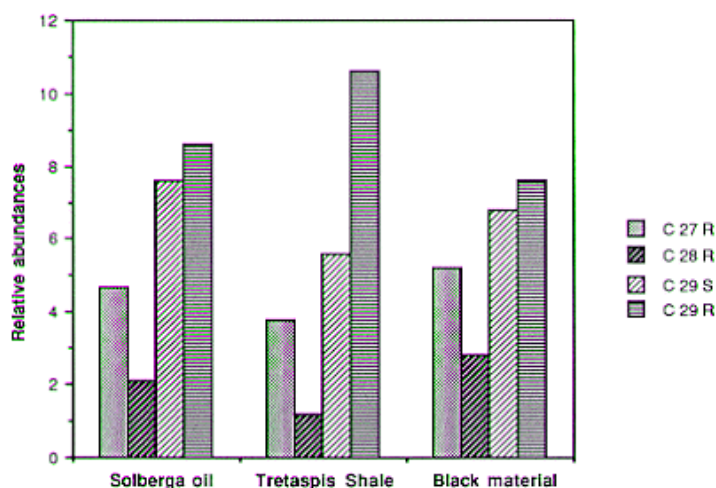

Figure 8. The four most prominent biomarker molecules, steranes, found in the oils of the Siljan region, Sweden. The steranes are present in similar proportions in surface-seep oil (Solberga quarry), local near-surface oil shale (Tretaspis Shale), and oil in black sludge obtained from 5.6 km depth in Gravberg 1 well. This similarity indicates a common origin of all three oils. The identity of the four sterane molecules is given in the usual notation by the number of carbon atoms and the right or left symmetry of the molecule.

In both holes the hydrocarbon content of the rocks increased with depth and in both holes high spots in methane (and in Gravberg 1 also in heavier hydrocarbons) were in the locations in which volcanic intrusive rock, dolerite, was present (Figure 9). (Heavier hydrocarbons were not measured during drilling in Gravberg 1).
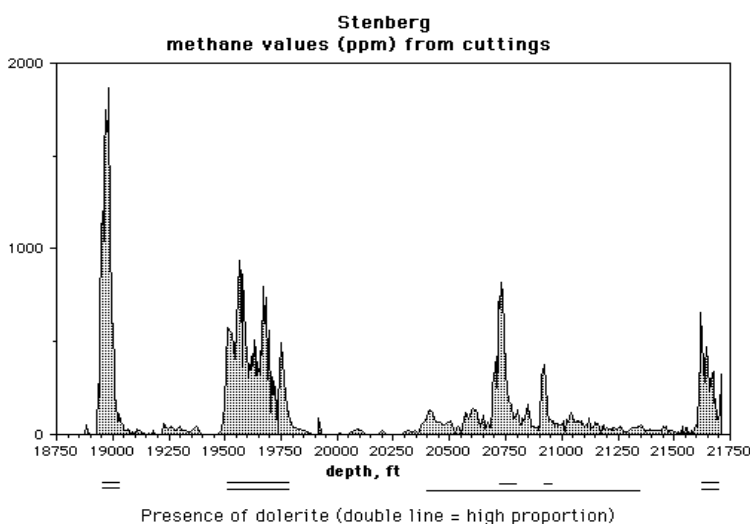

Figure 9. Stenberg 1 well, Sweden: Methane content of drill cuttings as function of depth. Presence of intrusive volcanic rock, dolerite, is marked below graph, showing correlation with high spots of methane readings. Heavier hydrocarbons were also measured, and were largely in step with methane.

The carbon isotope ratio of the methane became heavier with increasing depth, and in the dolerite zones and their immediate surroundings it was as heavy as between -12 to -15 per mil in the Gravberg hole, and -7.2 to-7.8 per mil in the Stenberg hole. In both holes the helium concentrations were frequently as high as several percent of the total gas present, and possibly exceeding the highest concentration seen in any well.

The investigations during the drilling of Stenberg I gave the clearest indication that a range of hydrocarbon gases and liquids

had indeed entered from deep levels. The content of hydrocarbon gases and liquids (aromatics) in the drilled out rock was carefully measured every five-foot interval during drilling. It showed very large increases in the dolerite and in the granite closely adjoining it (Figure 9). Since the dolerite has undoubtedly intruded from below, one has to conclude that the pathways which guided it up, or the pathways which it generated in the intrusion, are the pathways later used by the hydrocarbons. This relationship also confirms that contaminants introduced during drilling were not responsible for the observed hydrocarbon.

In both holes large amounts of a magnetite/oil sludge were discovered, the magnetite present as very small grains, mostly submicroscopic and highly concentrated in the sense that it formed more than 95 percent of the mineral content of the sludge. Twelve tons of this substance were pumped up from the Gravberg hole from a depth below 5.2 kilometers. It was suspected that the magnetite had been refined and concentrated by bacterial action, as has been seen in other oil-bearing regions at shallower levels (Sparks and others, 1990). Sample collection of liquids that entered the Gravberg wellbore below 5.2 kilometer depth was carried out by the Swedish State Bacteriological Laboratory in Stockholm and several strains of previously unknown thermophilic and anaerobic microorganisms were cultured from these samples (Szewzyk and others, 1993).

During the test procedure of the Stenberg well a gas cylinder was brought up containing free gas that would readily burn. Apart from a nitrogen contamination (due to nitrogen used to expel the drilling water), the gas consisted principally of methane with approximately 10 percent helium and 10 percent hydrogen. No continuous flow could be obtained, apparently due to the blocking effect of the entry of dense magnetite sludge into the wellbore.

The oil brought up with this sludge was investigated in detail by the Danish Geological Survey and considered to be a biodegraded crude oil. Chromatograms of it matched closely those obtained from the oil pumped up in Gravberg.

The scientific investigations carried out on products of the two holes have thus demonstrated that hydrocarbons are present deep in granitic rock in the complete absence or proximity of any sedimentary materials and in a distribution that leaves no reasonable doubt that they have come from deeper levels. The mix of the different hydrocarbon molecules, both of the gases and the oils, is quite a typical mix, as it is found in other oil and gas producing regions. The quantities of oil and gas that appear to be present in this 44 km diameter formation, tested in two distant locations, appear to be very large, as judged by the porosity measurements and the vertical intervals showing high concentrations. Production flow rates could not be achieved in either hole, apparently because in a confluent flow towards the wellbore, the sludge quickly concentrates and blocks the pores. The observed concentration of iron oxides in the rock is too low for the magnetite sludge to have been generated in the depth intervals in which it was found, and it must have been gathered and concentrated by a flow. We presume that this flow was that of the oil with which the magnetite is now associated. In that case, deeper levels than those that could be reached by the two boreholes (6.7 and 6.5 km) would tap into liquids and gases that contain smaller concentrations of magnetite, and would therefore cause less obstruction to a flow.

Conclusions

If the main supply of the commercial quantities of hydrocarbons, both gas and oil, is indeed derived from mantle depths and from materials that were incorporated in the Earth at its formation, then many points in petroleum geology and in other aspects of geology will have to be reconsidered. The quantity and locations of gas and oil that can be found, the method of prospecting for them, and the technology involved will all be affected.

It was thought previously that gas could only be found where there was a particularly impermeable caprock, tight enough to hold gas, above sediments rich in biological debris. Now one would judge that gas can be found wherever a seepage of gas can be found at the surface, and where there is an adequate porosity at some depth below. If a low permeability layer exists over a porous region, then this may have dammed up the flow sufficiently for production. But at deeper levels the critical layer will in any case provide a caprock. Thus in searching for gas, the requirement of a special caprock and the requirement of biological debris have both disappeared. The porosity requirement may be satisfied in many more locations than was previously thought, since beneath the critical layer the fluids coming from high pressures will frequently have created fracture porosity (as was clearly seen in Oklahoma).

If hydrocarbons have been a major source of all the carbon supplied to the surface, then of course the quantities that would be involved are orders of magnitude larger than was previously estimated. The shallow zone above the shallowest critical

layer, which is almost everywhere the only zone that has been the subject of oil and gas prospecting, will be seen to be the zone low in hydrocarbons, because they have largely escaped from these shallow levels. Oils, which became concentrated at shallow levels by the escape of the much more abundant gases, have been the chief object of the petroleum explorers. The deeper levels, which must be expected to have maintained the much more abundant gas, have not been explored at all outside of the United States, and in the U.S. the few areas that have been so explored have been found to be very productive.

Drilling to below 5 or 6 kilometers is still expensive and not much exploration to these levels will be done so long as the good prospects there are not recognized. But despite the expense of drilling, which would no doubt greatly decrease if more of it were done, the productivity from deep levels has frequently shown itself to be very high. Gas at depth below the critical layer tends to have a pressure approaching the lithostatic value, which may be on the order of 2,000 bar. The density is thus hundreds of times higher than it is in shallow wells, and may be as high as half the density of oils; therefore the content of gas in a given volume of pore spaces is hundreds of times greater than in shallow wells. The high pressure differentials into the well bore mean that very high flow rates can be obtained, even from rock which at shallower levels would be regarded as of insufficient permeability for production. The ultimate production from a given well is greater, because a greater pressure gradient drives gas to the wellbore, and the expansion of the gas will allow a large proportion of the initial gas in place to be produced. It is therefore by no means true that gas production from the deep horizons must be expensive, and many examples exist already that show that deep gas production can be quite competitive with shallow gas. The initial investment in an area will be higher, but so will be the returns.

Because deep gas does not have many of the special requirements for its accumulation that oil has, one may expect it to be in many more locations than oil. Many countries in all parts of the world will benefit from a more widely distributed fuel source.

Prospecting by the search for surface seepage of gas is a rational procedure, since large quantities of gas must constantly be escaping. Oil was found mainly by the attention that oil seeps drew to an area; gas seeps require instruments to be found, but, with more gas than oil coming up and escaping more readily, gas seeps are good indicators of the presence of gas underneath. The quality of available prospecting methods is a major economic item, especially for the deep horizons where exploratory drilling is expensive.

A flow of hydrocarbon fluids through the crust will have affected much of its chemical development. The concentration of many types of mineral deposits, especially of metal ores, has not had adequate explanations. The leaching out of particular components from the rocks requires fluids that can dissolve these components, and it requires large pressure differentials to drive these fluids through the pores of a sufficient quantity of rock to gain access to the materials. Hydrocarbons ascending from depth may provide these requirements. They will be present at a high temperature and pressure, where organo-metallic compounds can readily form. Such compounds are largely soluble in hydrocarbons, and may thus be transported upwards by them. These metals may include some that have quite inadequate solubilities to have been transported by aqueous fluids, but that can form organo-metallics. Silver, gold, and the platinum group are in that category, but many others may come under consideration for such processes. It is interesting to note that particularly gold has been found in many locations together with elemental carbon. Vanadium and nickel have shown a strong association with petroleum, both by the presence of compounds in the petroleum, and the deposition in or near oilfields. Several of the elements that would have a high vapor pressure at mantle temperatures have been found associated with hydrocarbons, not only helium but also mercury, and all the halides. A range of new processes will have to be investigated for the understanding of mineralization in the crust, and the search for hydrocarbons may become associated with the search for certain minerals. The microbiology in the ground which is fed by hydrocarbons may have contributed to highly selective processes; just as we saw concentrated magnetite in the boreholes in Sweden, apparently concentrated by microbial action, so perhaps all the large magnetite deposits of Sweden have a similar origin. Judging from the quantities of microbial material that have been identified in hydrocarbon regions (Ourisson and others, 1984), microbial processing may have been of major importance in the evolution of the crust.

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