

## Review

# Abiogenic Origin of Hydrocarbons: An Historical Overview

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**Abstract:** The two theories of abiogenic formation of hydrocarbons, the Russian-Ukrainian theory of deep, abiotic petroleum origins and Thomas Gold's deep gas theory, have been considered in some detail. Whilst the Russian-Ukrainian theory was portrayed as being scientifically rigorous in contrast to the biogenic theory which was thought to be littered with invalid assumptions, this applies only to the formation of the higher hydrocarbons from methane in the upper mantle. In most other aspects, in particular the influence of the oxidation state of the mantle on the abundance of methane, this rigour is lacking especially when judged against modern criteria as opposed to the level of understanding in the 1950s to 1980s when this theory was at its peak. Thomas Gold's theory involves degassing of methane from the mantle and the formation of higher hydrocarbons from methane in the upper layers of the Earth's crust. However, formation of higher hydrocarbons in the upper layers of the Earth's crust occurs only as a result of Fischer-Tropsch-type reactions in the presence of hydrogen gas but is otherwise not possible on thermodynamic grounds. This theory is therefore invalid. Both theories have been overtaken by the increasingly sophisticated understanding of the modes of formation of hydrocarbon deposits in nature.

**Keywords:** abiogenic hydrocarbons, Russian-Ukrainian theory, Thomas Gold

The overwhelming preponderance of geological evidence compels the conclusion that crude oil and natural petroleum gas have no intrinsic connection with biological matter originating near the surface of the Earth. They are primordial materials which have been erupted from great depths. Academician Professor Vladimir B. Porfir'ev, senior petroleum exploration geologist for the U.S.S.R., at the All-Union Conference on Petroleum and Petroleum Geology, Moscow, 1956.

I have gone to the best geologists and the best petroleum researchers, and I can give you the authoritative answer: no one knows. Edward Teller on how living matter is converted into petroleum (Teller, 1979).

## 1. Introduction

There are two main theories dealing with the abiogenic formation of hydrocarbons in commercial quantities. The first is what may be called the Soviet or, as it has more recently been designated, the Russian-Ukrainian theory of deep, abiotic petroleum origins (Kenney, undated a). On this theory, petroleum is considered to be a primordial material which was erupted at the surface of the Earth and is therefore not a fossil fuel. According to its proponents, this theory is based upon rigorous scientific analysis as well as upon extensive geological observation and is consistent with the laws of physics and chemistry. Its principal tenet is that the generation of hydrocarbons must conform to the general laws of chemical thermodynamics (Kenney undated a).

According to Kenney (undated a), the Soviet Union was thought to have very limited petroleum reserves in

the aftermath of the Second World War and was essentially denied access to the major oil fields of the world. To overcome this problem, a Manhattan-type project was initiated in 1947 in order to determine the origins of petroleum and how petroleum reserves are generated in order to establish the most effective strategies for petroleum exploration. This led to the development of a new, innovative theory of petroleum science within five years which was said to have had major successes in the exploration of oil reservoirs in the former Soviet Union. The principal aspects of this theory were presented at the All-Union Petroleum Geology Congress in 1951 by N. A. Kudryavtsev (Kudryavtsev, 1951). As a result, this theory was at its most influential during the cold war and the vast majority of the results were published in Russian. This theory is therefore poorly known in the west. However, this explanation is contrary to the facts. The great oil fields of the Volga-Urals region, the northern Urals and western Siberia were discovered during and

after the Great Patriotic War (early 1940s to middle 1950s). These fields were found not as a result of the theories of the N. A. Kudryavtsev and V. P. Porfir'ev which were too abstract and geologically too vague to be of practical use but as a result of clear empirical relationships which gave "the final word to the borehole". On this basis, the Soviet theory of deep, abiotic petroleum origins was never the driving force in the discovery of the major oil fields in the Soviet Union as its proponents claim.

The second theory was developed by Thomas Gold from 1979 to 1998. By way of background, Professor Gold was born in Vienna in 1920 and educated at Cambridge where he obtained his Ph.D. and was a close colleague of Fred Hoyle with whom he had previously worked on radar during the war (Bondi, 2004). He was Professor of Astronomy at Cornell University and Director of the Cornell Center for Radiophysics and Space Research for 20 years. His deep gas theory is controversial for a number of reasons, the principal one being the strong suggestion that Professor Gold, a fluent reader of Russian, took the ideas of Soviet scientists and used them as the basis for his own theory without any attribution or acknowledgement, although he did cite Russian literature in some of his papers (Gold, 1985, 1987). This assertion has been elaborated at length in a letter from Professor V. A. Krayushkin of the Institute of Geological Sciences in Kiev dated 4 January, 1990 (Kenney, undated b). In particular, it is claimed that Professor Gold deliberately modified the Russian-Ukrainian theory in order to conceal its provenance and thereby introduced significant errors into the theory (Kenney, undated b).

In considering these allegations, however, it should be born in mind that Professor Gold was a distinguished scientist in his own right as shown by his election as a Fellow of the Royal Society of London. Furthermore, as an astrophysicist, Professor Gold was well aware that carbon is the fourth most abundant element in the universe and is present predominantly in the form of hydrocarbons. In the solar system, for example, Gold (1985, 1987) recognized that the greatest quantity of hydrocarbons is present in the massive outer planets and their satellites with huge amounts of methane present in the extensive atmospheres of Jupiter, Saturn, Uranus and Neptune. It was therefore logical for him to write that no special mechanism for the generation of hydrocarbons on the Earth needs to be invoked (Gold, 1993).

Although it seems more than probable that Professor Gold was influenced by the work of Russian and Ukrainian scientists, especially in his early papers, the approach, examples and theoretical basis adopted in his publications differ in many respects from those presented by the Russian-Ukrainian school at that time. Whilst Gold was undoubtedly cavalier in citing the Russian literature, it should be remembered that only one major

paper had been published in English on the Russian-Ukrainian theory by a Soviet scientist prior to the 27th International Geological Congress in Moscow in 1984 (Porfir'ev, 1974) and that this did not really coincide with Gold's interests. In addition, the idea that a scientist of Gold's calibre would deliberately modify a theory by introducing significant errors and thereby present a flawed theory in order to conceal its provenance seems implausible. In my opinion, it is more likely that Professor Gold's interest in the abiogenic formation of hydrocarbons was seeded 30 years before at Cambridge under the influence of the charismatic Fred Hoyle (see later). Gold was also responsible for bringing Carl Sagan to Cornell in 1968 and could hardly fail to have been influenced by him.

Because Professor Gold's results were published in English, his theory is much better known in the west than the Russian-Ukrainian theory. In view of the significant differences in the two theories, Professor Gold's theory is presented separately from the Russian-Ukrainian theory.

## 2. The Russian-Ukrainian Theory

Amongst early Russian proponents of the inorganic origin of hydrocarbon formation were Mendeleev (1877) who assumed that hydrocarbons were generated within the Earth by interaction of water with iron carbide and Vernadsky (1933) who concluded that, with increasing depth in the Earth's crust, the oxygen content would decrease to zero and the content of hydrogen would increase leading to the formation of hydrocarbons at depth.

More than a thousand papers on the Russian-Ukrainian theory have been published in Russian (Kenney, undated b) but only a handful in English. This makes an assessment of this theory by non-Russian speakers very difficult because very few papers have been translated dealing with the processes involved in petroleum formation and migration at specific locations. It is therefore not easy to get a feel for how the Russian-Ukrainian theory was used to find commercial hydrocarbon deposits. However, two papers by key protagonists of the biogenic and abiogenic theories can be considered to compare the different attitudes of western and Russian petroleum geologists at a critical juncture.

In his paper, H. D. Hedberg (1969) offered an almost encyclopaedic examination of the inorganic origin of petroleum with many examples from the nineteenth century. Unfortunately, the views of geologists from the U.S.S.R. made up only the last two pages of this paper and these consisted only of a translation of comments by N. A. Eremenko which were essentially a rebuttal of the inorganic theory as described by a number of leading scientists such as N. A. Kudryavtsev, V. B. Porfir'ev and others at the 1958 All-Union Conference on the Problem of

the Origin of the Petroleum held in Moscow. Eremenko's main conclusion was that, while it is theoretically possible to prove the formation of hydrocarbons by inorganic means, the question remained unproved as to whether oil, a very complex system of organic compounds, could be formed from these hydrocarbons. Although this is fair comment, this statement can not be taken to represent the views of the leading proponents of the inorganic theory at the 1958 conference. It is clear therefore that Hedberg's paper did not give a fair hearing to the Russian-Ukrainian theory, the leading theory on the abiogenic formation of hydrocarbons at that time, because of the impossibility of translating a large body of information from Russian.

However, V. B. Porfir'ev (1974) was able to present an overview of this theory in the American Association of Petroleum Geologists Bulletin. This paper was divided into two sections. The first dealt with the limitations of the organic theory. In this, the author made a number of critical comments. In particular, he took exception to the idea of source rocks for the formation of hydrocarbons but based this on the assumption that these source rocks can contain as little as a few thousands of a percent of organic matter, thereby including all sedimentary rocks. Similarly, he dismissed the idea of migration of petroleum from the source area to the reservoir but assumed that the organic matter must be first converted to a gas by metamorphism or migrate as "micropetroleum". These comments were, of course, made before modern theories on the migration of fluids in the Earth's crust became known (e.g. Fyfe et al., 1978). The author also questioned whether compounds such as porphyrins could be considered to be indicators of an organic origin of petroleum since these compounds had already been found in meteorites and synthesized abiogenically. Similarly, optical activity in some crude oil compounds was not considered to be an indicator of biogenic origin because optically active hydrocarbons had previously been synthesized from optically inactive precursors at relatively low temperatures (130°C). There was also serious doubt about whether the processes of petroleum formation are permanent and have taken place from the Proterozoic to the present. This would imply a great age for some petroleum deposits indicating that petroleum is extraordinarily stable and can preserve all its properties for hundreds of millions of years. The assumption that oil accumulations in crystalline and metamorphic basement rocks could be the result of secondary migration of oil from nearby sedimentary rocks was also firmly rejected. In particular, it was thought that the forces controlling the migration of hydrocarbons were limited with the possible exception of endogenic energy.

Porfir'ev (1974) then presented his case for the inorganic theory. The author began by emphasizing the link of the inorganic theory to the mantle but pointed out that this linkage is conditional because it is not possible to study

the mantle directly. Nonetheless, he proposed that the original compounds for the formation of the petroleum hydrocarbons under mantle conditions could be CO<sub>2</sub> and H<sub>2</sub>, CO and H<sub>2</sub>O and CO<sub>2</sub> and H<sub>2</sub>O. It was claimed that methane, naphthene and aromatic hydrocarbons similar to those found in natural oil (but in different ratios) had been obtained synthetically from CO<sub>2</sub> and H<sub>2</sub> and CO<sub>2</sub> and H<sub>2</sub>O. However, as will be shown later, it is not possible to produce hydrocarbons from either CO and H<sub>2</sub>O or CO<sub>2</sub> and H<sub>2</sub>O under mantle conditions on thermodynamic grounds. The most convincing evidence for the inorganic theory was considered to be the occurrence of commercial quantities of oil in crystalline and metamorphic basement rocks as outlined by Kudryavtsev (1959). The main problem was the mode of transport of the hydrocarbons from the source rock to the reservoir. The solution to this problem was the proposed migration of mineralizing fluids and hydrocarbons from the upper mantle to the Earth's surface along deep faults. Within Russia, many giant ore deposits and diamondiferous provinces are considered to be controlled by mantle-derived magmatic products which are most abundant in zones of high permeability of the Earth's crust and are located mainly at the junctions of rifts, grabens and faults (Anon, 2002). Such zones could also serve for the migration of hydrocarbons. Examples of deep faults bordering platform grabens include the Limagne graben in France, the Baykal and Barguzin grabens in Siberia, the Dnieper-Donets graben in the Ukraine, the Rhine graben in West Germany, the Suez in Egypt, the Dead Sea in Jordan, the Reconcavo in Brazil, the Fusin in China and many others. According to Porfir'ev (1974), the genetic connection of gas and oil deposits with the deep fault zones is so clear and well known that documentation was not required! However, this leaves the questions of exactly which hydrocarbons were formed in the upper mantle, what transformations were required to convert these precursor hydrocarbons into oil and gas, how this oil ultimately became incorporated in reservoirs located in crystalline, or perhaps more pertinently, in sedimentary rocks and the exact relation between the reservoirs and the deep faults feeding them.

Porfir'ev (1974) also made the point that, in the inorganic theory, the designation of the age of an oil as, for example, "Cambrian", "Devonian", "Permian" or "Cretaceous" does not imply that this is the actual age of the deposit because more recently formed oil could have migrated into an older reservoir. He then went on to conclude that all the oil fields on the Earth were formed by vertical migration of the oil between the early Miocene and late Quaternary without presenting any clear evidence to support this statement. However, a clinching argument against the organic theory was considered to be the occurrence of giant and supergiant oil fields such as the Ghawar oil field in Saudi Arabia (11 billion tonnes) and the solid-

petroleum-bitumen accumulations and asphalts located in basal Palaeozoic beds in the southern Fergana area of Soviet Central Asia (30 billion tonnes). In the case of the asphalts, it was assumed the deposits must have been converted into a gaseous or aqueous solution in order to be transferred to the reservoir. According to Porfir'ev (1974), this clearly demonstrated the role of inorganic petroleum migration from the mantle along deep faults as the only way to form these giant deposits. However, it should be emphasized that many of the arguments on both sides of this discussion could not be answered unequivocally at that time because the necessary scientific methods had not yet been developed to answer them. For example, the question of source rocks could not be properly considered until the development of gas chromatography/mass spectrometry (GC/MS) in the 1980's. As a result, much of the discussion at that time was tangential. Neither side could answer the questions posed by the other side unambiguously.

Nonetheless, Porfir'ev (1974) did raise some key questions concerning the inorganic origin of hydrocarbons. In particular, he cited work showing the occurrence of hydrocarbon gases ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ ) and reduced bitumens in alkaline mafic and ultramafic rocks in some intrusive masses in the Kola Peninsula, the Russian platform, the Urals and Siberia. In some cases, the geological conditions of the hydrocarbon gases and the presence of endogenic minerals in the cavities showed that these gases formed by inorganic processes during cooling of the intrusive bodies. Bitumens enclosed in intrusive rocks from the Khibiny massif on the Kola Peninsula were considered to be unmetamorphosed because they contained the most unstable paraffin hydrocarbons and could only have been formed during the cooling period of the massif at temperatures in the range 600-150°C. In California, oil shows were found associated with serpentinites. The presence of such complex molecules as isoprenoid hydrocarbons, porphyrins and amino acids in carbonaceous chondritic meteorites was also taken as unambiguous evidence of the abiogenic formation of complex "organic" compounds. Of particular importance here is the extremely perceptive comment by Kropotkin et al. (1971) that 'everything that is known about the compositions of ultrabasic rocks, meteorites, comets and planets suggests that sharply reducing conditions are present in the Earth's deep layers. The reducing agents present, such as free hydrogen, metallic iron-nickel, and primary hydrocarbons, determine the character of the physical medium which is most important to the formation of hydrocarbon mixtures'. This is the nub of the abiogenic theory. A key point is the role of hydrogen generated by the Fischer-Tropsch reaction in the formation of abiogenic hydrocarbons (Holm and Charlou, 2001). However, the error in this statement, as we shall see later, lies in the fact that the upper mantle is

too oxidizing to permit methane to be the dominant form of carbon there. It is for this reason that commercial-grade petroleum deposits could not have formed abiogenically.

The role of outgassing of hydrocarbons from the mantle along deep faults was also emphasized by Kropotkin and Valyaev (1984) and Kropotkin (1985). In particular, these authors took up Vernadsky's (1933) idea of a deep origin of hydrogen which had been confirmed by the demonstration of hydrogen seepages associated with helium of mantle origin along deep faults in Iceland, the East Pacific Rise and elsewhere. According to these authors, the high content of hydrogen in petroleum indicated that these compounds must have formed under strongly reducing conditions. It was also emphasized that hydrocarbons and hydrogen predominate in the gas in fluid inclusions which are dissipated in alkaline, basic and ultrabasic igneous rocks including kimberlites. The role of free hydrogen in the abiogenic formation of hydrocarbons has subsequently been emphasized by a number of authors (Bezmen, 1992; Apps and van der Kamp, 1993; Marakhushev, 2000). Many examples were quoted in support the role of mantle degassing in the formation of hydrocarbon deposits including the Kola Peninsula, the Russian platform and the Siberian craton. The authors also emphasized the importance of Kudryavtsev's rule which states that, if oil or gas is present in any horizon of a succession, then some amounts of hydrocarbons should also be discovered in all underlying units, even if only as tracks of migration along the cracks or fissures in rocks (Kudryavtsev, 1973). This regularity was taken to mean that the crystalline basement is the source of petroleum in the sedimentary cover and was taken as conclusive evidence for the abiogenic theory. For example, the main oil deposits in the Volga-Ural region were discovered below the "domanik" beds of the Upper Devonian series rich in biogenic organic matter. The petroleum deposits are associated mainly with the varied sedimentary beds deposited under oxidizing conditions. The sediments rest on the Precambrian crystalline basement, with some oil beds lying almost on the basement surface.

Of particular importance are several papers coauthored by J. F. Kenney which give a modern interpretation of the abiogenic theory (Kenney, 1996; Kenney et al., 2001a, b, 2002; Krayushkin et al., 2001). Perhaps, the most significant conclusion is that methane is the only hydrocarbon stable at STP. Formation of normal alkanes from methane is thermodynamically favourable only at pressures >30 kbar and temperatures >700°C which correspond to a depth of ~100 km below the Earth's surface (equivalent to the depth of the upper mantle) (Kenney et al., 2002). As a result, higher hydrocarbons such as found in natural petroleum at the Earth's surface are metastable. By contrast, formation of higher hydrocarbons from oxidized organic molecules such as carbohydrates ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is not thermo-

dynamically favourable under any conditions (Kenney et al., 2002). These data demonstrate that it is possible to convert methane into a complex mixture of higher alkanes and alkenes at high pressures and temperatures but not carbohydrates, the fundamental building block of plants. The rigorous thermodynamic analysis presented by Kenney et al. (2002) forms the basis of the abiogenic theory.

The success of the abiogenic theory can be seen by the fact that more than 80 oil and gas fields in the Caspian district have been explored and developed in crystalline basement rock on the basis of this theory (Kenney, 1996). According to this author, exploration in the western Siberian cratonic rift sedimentary basin has led to the development of 90 petroleum fields of which 80 produce either partly or entirely from the crystalline basement. Fifty commercial oil and gas fields have also been developed in a 100 × 600 km strip of the northern flank of the Dneiper-Donets Basin. However, it should be emphasized that 15 of the fields in the Dneiper-Donets Basin exploit both Carboniferous sediments and lower crystalline basement rocks but only 2 exploit the crystalline basement exclusively (Krayushkin et al., 2001). Deep drilling has also been carried out in Azerbaijan, Tatarstan and Siberia to test the potential oil and gas reservoirs in the crystalline basement (Kenney, 1996). According to Kenney (1996) and Odell (2000, 2003, 2004), these considerations lead to an important corollary, namely that hydrocarbons are essentially a renewable resource and that there is no more reason to expect a future shortage of petroleum than that of, say, mid-oceanic ridge basalt. Nonetheless, in spite of the recent efforts of J. F. Kenney and his colleagues, the Russian-Ukrainian theory of deep, abiotic petroleum origins remains poorly known in the west.

### 3. Thomas Gold's Theory

The deep gas theory of Thomas Gold evolved over time. In his early papers, Gold was mainly concerned with the role of major earthquakes in facilitating the migration of gases, and in particular methane, from the deep Earth (Gold, 1979, 1984, 1987; Gold and Soter, 1980, 1984/85). If an earthquake was large enough to fracture the ground up to the Earth's surface, it was assumed that it would open up an escape route for gas and that this could generate some of the peculiar phenomena accompanying major earthquakes such as flames shooting from the ground, "earthquake lights" and sulphurous air. In particular, Gold and Soter (1980) prepared a map of the world showing the correlation between major oil and gas regions and areas of present and past seismicity from which it was apparent that many of the known hydrocarbon reservoirs, including those in Alaska, Texas, the Caribbean, Mexico, Venezuela, the Persian

Gulf, the Urals, Siberia, and Southeast Asia, lie on deformation belts. This association of oil and gas fields with earthquake-prone regions suggested that deep faults may play a role in the continuous migration of methane and other gases to the Earth's surface and therefore in the generation of these oil and gas fields.

Subsequently, Gold (1985, 1993) examined two regions in more detail. In both the Middle East and in the arc stretching from Indonesia thorough the Andaman Islands into the Irrawaddy Valley of Burma and into the high mountains of southern China, petroleum is very abundant but there is no similarity in geology or topography of these regions on a local scale. This suggested that these oil-rich regions are defined by much larger scale patterns than are seen in the surface geology and topography and pointed to the role of deep faults in controlling the locations of these oil and gas fields, especially along the arc from Indonesia to southern China where the frequency of earthquakes is hundreds of times higher than away from the arc. The association of helium with hydrocarbons in oil and gas fields was also taken as strong evidence for a deep source of the hydrocarbons (Gold and Held, 1987; Gold, 1993).

In these papers, it was assumed that mantle methane was injected into the Earth's crust in areas of crustal weakness such as lithospheric plate boundaries, ancient suture zones and meteor impact sites. Under conditions of slow upward migration and cooling, some of the methane was assumed to polymerize to form higher hydrocarbons and crude oil (Jenden et al., 1993). Although Gold (1985, 1987, 1999) was aware that methane can be converted to higher hydrocarbons in the mantle based on the experimental observations of Chekaliuk (1976), he nonetheless considered methane to be the principal hydrocarbon entering the Earth's crust from below. This led Gold (1993) to make the fundamental assumption that mantle-derived methane is converted to higher hydrocarbons in the upper layers of the Earth's crust. In addition, Gold et al. (1986) proposed that methane may be a transporting agent for hydrocarbons to the Earth's crust based on the experimental observation that ethyl benzene and ethyl toluene can form on reaction of benzene and toluene with methane at 1000 atm and 150-250°C in the presence of montmorillonite, a natural clay catalyst. However, this is not a major aspect of the deep gas theory.

More controversial was the drilling of the Siljan Ring, a 360 Ma old impact crater with a diameter of 45 km, in central Sweden (Gold, 1987, 1991, 1993). This project was undertaken at the initiative of Thomas Gold (Gold, 1993) as a commercial venture to explore for abiogenic gas of mantle origin (Castaño, 1993). Two holes were drilled, one 6.7 km deep and the other 6.5 km deep. J. F. Kenney was the drilling manager for this pro-

ject. However, despite the great expense of this project, it yielded only 80 barrels of oil of doubtful provenance.

Within the Gravberg-1 well, dolerite sills intrude the granitic host rock. Gases in the dolerite were abundant, rich in methane (200-1,000 ppm) and lacked unsaturated hydrocarbons whereas gases in the granite were poor in methane (10-80 ppm) but contained much higher proportions of ethane and propane and their unsaturated analogues (Castaño, 1993). The gases in the dolerite were considered to be abiogenic but the origin of the gases in the granites was more problematic. It was thought that the alkenes in these samples might have formed as a result of a Fisher-Tropsch reaction between CO<sub>2</sub> and H<sub>2</sub> catalyzed by magnetite in the granite (Castaño, 1993). If so, this could explain the occurrence of the "black gunk" which formed at a depth of about 5.5 to 6.7 km in the hole after the drill string had been stuck there for several days and consisted of 90 % fine-grained magnetite suspended in a light oil of alkanes in the range C8 to C16 (Aldhous, 1991; Gold, 1993; Kenney, 1999). This would undermine the assertion of these authors that this material was of mantle origin. Based on his extensive studies at this site, Castaño (1993) concluded that there was no convincing evidence for a dominant mantle source of hydrocarbons at Siljan nor any realistic prospects for the development of a commercial gas field at this site.

Nonetheless, the discovery of this "black gunk" led Gold (1992) to speculate that formation of this material was bacterially mediated. This conclusion was based, in part, on the fact that several strains of thermophilic bacteria were cultured from this material. The upper limit of temperature at which these bacteria could survive was taken to be 110-150°C corresponding to a depth in the Earth's crust of 5 to 10 km (Gold, 1992). This temperature is somewhat above the known tolerance range of bacterial life but not unreasonably so (Holland and Baross, 2003). Ourisson et al. (1984) had previously identified hopanoids which are the remains of cell walls of bacteria in several hundred samples of oil, coal and kerogen and demonstrated that these compounds are ubiquitous in sedimentary rocks. Based on the concentrations of these compounds in sedimentary rocks, these authors concluded that hopanoids are the most common compounds on the Earth with a total abundance of 10<sup>13</sup>-10<sup>14</sup> t compared to 10<sup>12</sup> t for the total mass of organisms living at or near the surface of the Earth. This led to the idea that some of the compounds used as biomarkers in petroleum such as pristane and phytane may not, in fact, be derived from chlorophyll as is commonly thought but rather from the breakdown of bacterial residues. It was the occurrence of this huge potential bacterial biomass in the subsurface of the Earth that led Gold (1992) to define the 'deep, hot biosphere' in which the energy required to support this bacterial life was thought to be derived from

fluids rich in hydrogen and methane migrating upwards from deeper levels in the Earth. Subsequently, these ideas were refined in Gold's (1999) book on this topic.

However, Drury (2000) cast doubt on Gold's assertion that the deep biota outweigh the surface biomass. In Gold's defence, it should be stated that his 1992 paper was published prior to Fyfe's (1996) landmark paper on the deep biosphere and that this conclusion is supported by recent estimates of the subsurface biomass of prokaryotic bacteria of 3-5 × 10<sup>17</sup> g of C which is equivalent to 60 to 100 % of the carbon present in the global plant biomass (Whitman et al., 1998; Head et al., 2003). Nonetheless, the relative roles of bacteria in mediating in the formation of petroleum, in degrading the initially formed petroleum to heavy oil and in supplying biomarkers to hydrocarbon deposits are still not fully understood, although it is well known that slow anaerobic processes dominate in the deep subsurface environment (Head et al., 2003) suggesting that degradation dominates over mediation. Peters (1999) also found many frustrating inconsistencies in his review of Gold's (1999) book. More recently, Laherrere (2004) has made a detailed critique of Gold's claims for the formation of abiotic oil and pointed out many inconsistencies and inaccuracies in this work.

In spite of Gold's prescient observations on the deep biosphere, there remains some confusion regarding his terminology. In their deep-earth-gas hypothesis, Gold and Soter (1980) are referring to methane derived from the deep Earth, presumably meaning the mantle. In his discussion of the deep, hot biosphere, on the other hand, Gold (1992, 1999) is referring to the upper 5 to 10 km of the Earth crust. Deep therefore has two distinct meanings in this theory depending on context.

However, there is a fundamental flaw in Thomas Gold's theory of abiogenic petroleum formation. As previously pointed out, methane can only be converted to higher hydrocarbons at pressures >30 kbar corresponding to a depth of ~100 km below the Earth's surface. The proposed reaction of methane to produce higher hydrocarbons above this depth and, in particular, in the upper layers of the Earth's crust is therefore not consistent with the second law of thermodynamics. Furthermore, bacteria can not catalyze thermodynamically unfavourable reactions. Gold's deep gas theory in which hydrocarbons are supposedly formed from methane in the upper layers of the Earth's crust is therefore invalid.

#### 4. Other Contributors

In addition to the two main theories for the abiogenic formation of hydrocarbons, there are a number of less well-known contributors to this theory. In particular, A.

A. Giardini and C. E. Melton devised a method for calculating the amount of juvenile hydrocarbons migrating from the mantle in the last 700 Ma. Their calculations were based on an initial observation that gaseous inclusions in diamonds contain, in decreasing order of abundance, water, hydrogen, carbon dioxide, methane, carbon monoxide, nitrogen, argon, ethylene, ethyl alcohol, butane and oxygen (Melton and Giardini, 1974). These authors also determined the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in an 8.65 ct. diamond from Africa to be  $-35.2\text{‰}$  which is in the range specified for natural petroleum (more negative than  $-18\text{‰}$ ; Giardini and Melton, 1982). On this basis, they concluded that some carbonaceous material which is considered to be biogenic in origin may, in fact, be abiogenic (Giardini and Melton, 1981, 1982).

Based on the average amount of petroleum-type compounds in 3.1 Ga old diamonds from Arkansas ( $33\mu\text{g g}^{-1}$ ), these authors then estimated the amounts of such compounds in the uppermost 400 km of the mantle to be  $2 \times 10^{15}$  t (Giardini and Melton, 1981). In order to calculate the transport of hydrocarbons from the mantle to the atmosphere, Giardini and Melton (1983) used hydrogen as a proxy for the hydrocarbons on the basis that all hydrogen can, in principle, be converted into hydrocarbons by Fischer-Tropsch-type reactions. Taking the oldest known petroleum deposits to be 700 Ma and assuming that the transport constant of hydrocarbons from the mantle to the atmosphere is the same as for  $\text{N}_2$  ( $6.5 \times 10^{10} \text{ yr}^{-1}$ ), Giardini and Melton (1983) estimated that  $18.9 \times 10^{12}$  t of juvenile petroleum had migrated from the mantle to the Earth's surface over the last 700 Ma. This amount is two orders of magnitude more than the present global reserves of petroleum ( $143 \times 10^9$  t; Glasby, in press). However, this latter figure is a serious underestimate of the total global oil inventory since biodegraded oils occurring in heavy oil and tar sands make up 50 % of the world's oil inventory and the Venezuela and Athabasca Tar Sands alone contain  $2.8 \times 10^{11}$  t of oil (Head et al., 2003).

Assuming that this juvenile petroleum was transported to the Earth's surface by lithospheric faults with a total length of 240,000 km and an average width of 0.01 km, the amount of juvenile petroleum transported along these faults was then calculated to be  $93 \times 10^6$  t  $\text{km}^{-2} \text{ Ma}^{-1}$ . This compares with an average accumulation rate of petroleum in 78 giant oil fields of  $0.15 \times 10^6$  t  $\text{km}^{-2} \text{ Ma}^{-1}$ . On this basis, Giardini and Melton (1983) concluded that formation of these giant oil fields required on average only 0.2 % of the average outflow of juvenile petroleum precursors. This led the authors to conclude that the juvenile petroleum model easily accounts for all known petroleum accumulations. However, these are clearly only order of magnitude calculations and may be substantially in error, particularly in the extrapolation of the concentrations of

hydrocarbons in fluid inclusions in a few diamonds to the entire upper mantle and to a gross underestimation in the total global oil inventory.

In Britain, there were several prominent proponents of the abiogenic theory of hydrocarbon formation in the 1950's and 60's. In particular, Sir Fred Hoyle, one of the leading British astronomers of his day, championed the idea of chondritic material as the source of carbon in petroleum. According to Hoyle (1955), the presence of hydrocarbons in the bodies which formed the Earth would have resulted in the interior of the Earth containing vastly more oil than ever could have been produced by "decaying fish" which he described as a "strange theory that has been in vogue for many years". Based on the assumption that the oil deposits were squeezed out of the interior of the Earth, he concluded that the amount of oil still present at great depths in the Earth vastly exceeds the comparatively tiny quantities that man has been able to recover so far and considered the possibility of ever gaining access to these vast supplies "an entertaining speculation". However, these comments were only an aside to his main interests. Subsequently, Hoyle became an advocate of the panspermia theory which he argued that life on Earth was seeded from outer space (Hoyle 1999). Indeed, he became a leading authority on organic molecules in interstellar space (<http://www.panspermia.org>). It seems more than probable that Hoyle's ideas had a significant influence on his young contemporary at Cambridge, Thomas Gold.

Sir Robert Robinson, one of Britain's leading synthetic organic chemists at this time, also noted that the composition of petroleum does not match that expected of modified biogenic products and that the constituents of ancient crude oils fit equally well with a primordial hydrocarbon mixture to which bio-products have been added (Robinson, 1963, 1966). He therefore proposed a duplex origin of petroleum in which biogenic processes were dominant in the formation of younger oil but were virtually absent in the formation of older crude oil. However, this argument takes no account of the bacterial degradation of oil over time (Head et al., 2003). Furthermore, it overlooks the fact that petroleum is not formed directly from plant material but from type II kerogens which are derived from the low-temperature diagenetic alteration of planktonic organisms (see later).

Following the lead of Russian proponents of the abiogenic theory, Sylvester-Bradley and King (1963) and Sylvester-Bradley (1964) described two types of heavy hydrocarbons which they considered to be abiogenic. The first was uraniferous pitchblende which is found in pegmatites, granites, gneisses and was thought to be formed by the polymerization of hydrocarbon gases by  $\alpha$ -particles emanating from uranium. The second type was so-called igneous hydrocarbons from a nepheline syenite complex in the Kola Peninsula where heavier bitumens

and all grades of oil including natural gas are found. In this case, it was believed that the hydrocarbons had formed by hydrogenation of dispersed carbon or carbon dioxide during crystallization of the magma. Ikorsky et al. (1999) subsequently reported the presence of CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>, He, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>, in decreasing order of abundance, in Proterozoic and Archean complexes in the Kola Peninsula during drilling of the Kola Superdeep Borehole. These authors concluded that these hydrocarbons are biogenic in origin and were derived from sedimentary rocks which had been metamorphosed to greenschist facies. However, this view is in contradiction to earlier studies which showed that these gases are present only in alkaline rocks of the Khibiny, Lovozero and Salmagory massifs of the Kola Peninsula (Porfir'ev, 1974) and is supported by the high H<sub>2</sub> content of this gas (20.6 % by volume in a representative gas sample; Ikorsky et al., 1999).

Sylvester-Bradley and King (1963) and Sylvester-Bradley (1964) also pointed out the frequent association of bitumen with cinnabar. This association was subsequently attributed to degassing of mercury and associate volatiles from the mantle (Ozerova et al., 1999). These findings led Sylvester-Bradley (1964) to conclude that oil is polygenetic but this poses the question of how much oil is biogenic and how much is derived from other sources and, perhaps more pertinently, other possible mechanisms for the abiogenic formation of oil.

## 5. Discussion

In the previous sections, the abiogenic theory of hydrocarbon has been outlined. As already stated, the proponents of this theory claim that it is based upon rigorous scientific reasoning, consistent with the laws of physics and chemistry, as well as upon extensive geological observation. The question is to what extent this is true. Certainly, the arguments presented by Kenney et al. (2002) do represent a rigorous interpretation of the thermodynamic data. However, the formation of higher hydrocarbons from methane in the upper mantle is only one link in the chain of petroleum formation.

Perhaps the clearest argument against the abiogenic theory is the oxidation state of the mantle. Whilst it is true that the mantle is the major reservoir for carbon on the Earth (Wood et al., 1996), it is equally true that the upper mantle is moderately oxidizing (Kadik, 2003). According to Wood et al. (1990), the mantle beneath active subduction zones is much more oxidizing than that beneath mid-ocean ridges. Although peridotites from mid-ocean ridges are reduced with an average  $f_{O_2}$  of  $-0.9$  log units relative to the FMQ (fayalite-magnetite-quartz) buffer, CO<sub>2</sub> and H<sub>2</sub>O are the major fluid species present even there (Wood et al., 1990). The

dominant forms of carbon in the upper mantle are diamonds and carbonate (Wood et al., 1996). Methane is considered to be only a minor constituent in fluid inclusions from upper mantle based on its paucity in fluid inclusions from upper mantle rocks (Roedder, 1984; Apps and van der Kamp, 1993). In contrast, large amounts of CO<sub>2</sub> appear to be degassing from the mantle (Javoy et al., 1982; Sano and Williams, 1996). Equally crucial is the observation of Apps and van der Kamp (1993) that the only mechanism by which volatile gases can be transferred from the mantle to the Earth's surface is through magma transport. Although Gold (1985, 1987) was aware that carbon was generally assumed to migrate from depth as CO<sub>2</sub>, he believed that, if the gases migrated through cracks in solid rock, oxidation of the methane would be limited.

Furthermore, on the basis of the abiogenic theory, it would be expected that abiogenic hydrocarbons would be located principally at convergent plate margins and along major fault zones (Gold and Soter, 1980). However, as shown by Klemme (1975), high geothermal gradients in clastic rock sequences located near plate boundaries enhance the formation, migration and entrapment of oil and gas. Glasby et al. (2004) have subsequently argued that it is these high geothermal gradients rather than proximity to faults which most probably accounts for the formation of the Niigata and Akita oil fields of northern Honshu, Japan, for example.

In addition, the abiogenic theory lays particular emphasis on the discovery of major oil and gas fields in crystalline basement rocks such as in the Caspian district, the western Siberian cratonic rift sedimentary basin and the northern flank of the Dnieper-Donets Basin which is considered to be incompatible with the biogenic theory (Porfir'ev, 1974; Kenney, 1996). However, this view does not take into account modern theories of fluid migration in the Earth's crust (Bredehoeft and Norton, 1990; Dahlberg, 1994; Lerch and Thomsen, 1994; Parnell, 1994) or of the permeability of crystalline rocks (Batchelor and Gutmanis, 2002). For example, Wang and Davies (2003) have shown that the permeability of rocks is a property that depends on scale with actual permeabilities orders of magnitude higher than those determined by direct measurements made on boreholes. Incorporation of hydrocarbons into crystalline rocks is therefore not uncommon and is a function of these enhanced permeabilities. According to Petford and McCaffrey (2002), some of these reservoirs are very prolific. Although most hydrocarbons associated with igneous rocks are derived from maturation of organic-rich sediments (Schutter, 2002), examples of the occurrence of abiogenically-derived hydrocarbons have been recorded in this type of rock.

The U.S. Geological Survey has recently undertaken a series of detailed studies of the petroleum geology and

resources of two of the areas mentioned above, the Middle and North Caspian Basins (Ulmishek, 2001a, b) and the Dnieper-Donets Basin (Ulmishek, 2001c). In the Middle Caspian Basin, source rocks were not positively identified but were thought to be alternating shales, carbonates and tuffs of upper Olenekian-Middle Triassic age (Ulmishek, 2001a). In the North Caspian Basin, the source rocks were thought to be basinal black shales of upper Palaeozoic age (Ulmishek, 2001b). In the Dnieper-Donets Basin, geological data indicated the presence of two principal source rocks, the Lower Carboniferous marine shales and Devonian siliceous shales and carbonates (Ulmishek, 2001c). In a large part of this basin, the source rocks occur at a great depth and have not yet been drilled. In spite of the incomplete knowledge of the source rocks in these three areas, petroleum formation was interpreted entirely and convincingly within the framework of conventional petroleum geology with no mention made of an abiogenic source of hydrocarbons. If the biogenic origin of these key deposits were to be confirmed, it would essentially mark the end of the Russian-Ukrainian theory of deep, abiotic petroleum origins as a viable theory.

Many articles have been published in the Russian journal, *Petroleum Geology*, on the geology of the Caspian, western Siberian and Dnieper-Donets oil fields and English abstracts posted on the internet (<http://www.geocities.com/internetgeology>). However, no reference has been made to the abiogenic theory of hydrocarbon formation in any of these articles. This would suggest that the abiogenic theory has much more limited support in Russia and the Ukraine now than in Soviet times, particularly with respect to the commercial exploration for oil and gas.

The abiogenic theory is, of course, bolstered by the occurrence of hydrocarbons which clearly have an abiogenic origin. For example, over 70 carbon-bearing radicals and ions and organic compounds have been identified in dense interstellar gas and dust clouds which have temperatures in the range 10-100°K (Lewis, 1995). In addition, complex organic compounds can be synthesized on very short time scales ( $10^3$  years) in the low-density circum-stellar environment during the late stages of stellar evolution (Kwok, 2004). Within the solar system, at least 80 organic compounds are known to occur in carbonaceous meteorites (Lewis, 1995). However, calculations suggest that far more organics would have been delivered to the surface of the Earth by interplanetary dust particles than from meteorites and that these organic compounds may have constituted, in part, the prebiotic organic molecules from which life on the Earth eventually emerged (Chyba and Sagan, 1992).

Serpentinization of ultramafic rocks near the crest of mid-ocean ridges may also lead to the formation of higher hydrocarbons containing between 16 and 29 carbon atoms

(Holm and Charlou, 2001). Abiogenic methane and hydrogen also occur in significant quantities in mines in the crystalline rocks of the Canadian and Fennoscandian shields (Apps and van der Kamp, 1993; Sherwood Lollar et al., 2002). These gases were thought to be generated by hydrolysis from meteoric waters circulating through fractures in mafic and graphitic igneous and metamorphic rocks. Up to  $30 \times 10^{11} \text{ m}^3$  ( $2 \times 10^6 \text{ t}$ ) of methane can be generated from a single giant quartz vein by this mechanism (Burruss, 1993). Although these processes may be important locally, Apps and van der Kamp (1993) concluded that commercial hydrocarbon deposits appear to be exclusively biogenic in origin except possibly in the case of deposits associated with serpentinization.

If petroleum hydrocarbons and natural gas are the result of degassing from the mantle, then it follows that the amounts of petroleum available could be orders of magnitude larger than presently estimated (Gold, 1985, 1986, 1987, 1993). The abiogenic theory therefore challenges present assumptions regarding the resource potential of hydrocarbons (Kenney, 1996). Evidence for the vertical migration of hydrocarbons or 'dynamic fluid injection' has been reported in the western Gulf of Mexico and is considered to occur worldwide (Whelan, 2000; Whelan et al., 2001). This view is supported by L. M. Cathles of Cornell University who views the Gulf as a giant hydrocarbon flow-through system which is currently active (Pinsker, 2003). However, a recent study in the northern Gulf of Mexico has shown that most of the large volume of gas venting there is biogenic or thermogenic in origin (Whelan et al., 2005). Gas washing of reservoir oils is believed to carry the most volatile components of the oil upwards and vent them into the overlying seawater. These observations do not support an abiogenic origin of gas in this area. In addition, Pfeiffer (2005) has concluded that refilling of the reservoir at Eugene Island in the Gulf of Mexico is minor based on production statistics and that production there is in decline. Pfeiffer (2005) therefore asked the rhetorical question 'Where is all the abiotic oil if it exists?' After considering a number of possibilities including the Siljan Ring, offshore Vietnam, Eugene Island in the Gulf of Mexico and the Dnieper-Donets Basin, he was unable to cite any example of the occurrence of abiotic oil in commercial quantities.

As previously noted, proponents of the abiogenic theory have put particular emphasis on disputing the validity of the biogenic theory (Porfir'ev, 1974). Kenney et al. (2001b), for example, have raised doubts about the possible use of biomarkers such as porphyrins, isoprenoids, pristane, phytane, cholestane, terpanes and chlorins to support a biogenic origin of petroleum. Pristane and phytane were considered to be simply branched alkanes of the isoprenoid class. Cholestane

and cholesterol were considered to have similar organic structures but cholestane is a highly reduced hydrocarbon whereas cholesterol is a highly oxidized organic molecule. The occurrence of porphyrins, isoprenoids, terpanes and chlorins in meteorites was taken as evidence to discredit the use of these molecules as biomarkers. However, the development of gas chromatography/mass spectrometry (GC/MS) in the 1980s vastly increased knowledge of the breakdown products of biomarkers and enabled much more precise correlations to be made between biomarkers in the source rocks and in petroleum reservoirs (Peters and Moldowan, 1993; Eglinton, 2004; Philp, 2004). Kenney et al. (2001b) also noted that petroleum contains Ni and V porphyrins which can not be derived from chlorophyll in which Mg is the centrally chelated metal. However, it is now well known that these porphyrins were formed not from chlorophyll but from marine organisms in which the porphyrins are chelated around Ni and V (Yen, 1975; Berner, 2003). This is consistent with the formation of petroleum hydrocarbons from marine shales.

A particularly contentious issue in this regard is whether higher hydrocarbons can be formed from oxidized organic molecules such as carbohydrates ( $C_6H_{12}O_6$ ) which are the dominant constituents of plants. As noted earlier, formation of higher hydrocarbons from oxidized organic molecules such as carbohydrates ( $C_6H_{12}O_6$ ) is not thermodynamically favourable under any conditions (Kenney et al., 2002). However, only 0.01-0.1 % of organic matter enters the biological carbon cycle (Schaefer, 1999). Petroleum is therefore not formed directly from plant material but mainly from type II kerogens which are derived from the low-temperature (<50°C) diagenesis of planktonic organisms and are rich in hydrogen and poor in oxygen (Tissot and Welte, 1984; Klemme and Ulmishek, 1991; Schaefer, 1999; Berner, 2003). This is consistent with the formation of petroleum hydrocarbons from marine shales.

In addition to biomarkers, the carbon and hydrogen isotopic ratios of methane can be used to characterize natural gases (Schoell, 1983; Jenden et al., 1993; Wiese and Kvenvolden, 1993). In particular, Jenden et al. (1993) showed a clear distinction between the  $\delta^{13}C$  values of abiogenic methane from submarine hydrothermal vents on the East Pacific Rise, fluid inclusions in alkaline igneous rocks from the Kola Peninsula, Russia, and the Zambales Ophiolite in the Philippines (-18 to -1 ‰) and those of 1699 commercial gases (more negative than -20 ‰). These data led these authors to conclude that less than 1 % of the methane in most oil and gas fields is abiogenic in origin. In a more detailed analysis, Sherwood Lollar et al. (2002) confirmed this conclusion based on a comparison between the carbon and hydrogen isotopic compositions of abiogenic methane and higher hydrocar-

bons in crystalline rocks from the Canadian Shield and the isotopic compositions of thermogenic hydrocarbons. This observation led these authors to rule out the presence of a globally significant abiogenic source of hydrocarbons. Hayes et al. (1990) also used carbon isotopic analysis of individual organic compounds to demonstrate that biomarkers such as porphyrins and geolipids are derived from biological precursor molecules. This approach enabled the isotopic compositions of individual compounds to be interpreted in terms of the biochemical processes taking place in ancient depositional environments. Jonathan Clarke, an Australian astrobiologist and geologist, has recently presented a checklist of 16 observations which must be explained by the abiotic hypothesis before it can be accepted (Bardi and Pfeiffer, 2005). Based on these criteria, it becomes difficult to support the abiotic origin of hydrocarbons.

In fact, 90 % of the world's original oil and gas reserves are located in six stratigraphic intervals during the Phanerozoic which include the Silurian (9 % of world reserves), Upper Devonian-Tournaisian (8 % of reserves), Pennsylvanian-Lower Permian (8 % of reserves), Upper Jurassic (25 % of reserves) Middle Cretaceous (29 % of reserves) and Oligocene (12.5% of reserves) (Klemme and Ulmishek, 1991). These data show that the majority of the world's oil and gas is very young with 50 % generated since the Oligocene. Burial of global organic carbon during this period corresponds closely to the deposition of major source rocks for oil and gas (Berner, 2003). However, these time intervals also appear to be closely related to the cyclic eruption of hot plumes from the lowermost mantle which leads to a correlation between eustatic sea-level highstands and the deposition of marine black shales (Sheridan, 1997). Of particular interest is the suggestion that the high global organic carbon burial during the middle Cretaceous was a consequence of the mid-Cretaceous superplume (Larson, 1991a) which created a greenhouse world without ice-caps, sea level a hundred metres and more higher than at present at times, extensive continental flooding, deposition of black shales and oil formation (Caldeira and Rampino, 1991; Larson, 1991b). However, this superplume was characterized by high emissions of  $CO_2$  rather than methane (Caldeira and Rampino, 1991). It seems more probable therefore that the formation of the major oil and gas reserves at that time was related to the deposition of suitable source rocks as a result of high carbon burial rates rather than to the degassing of methane from the mantle. According to Klemme (1994), the presence of a source rock is a requirement for all petroleum systems. The abiogenic theory, on the other hand, would lead us to expect that the formation of oil and gas is independent of source rock formation and therefore much more extensive in the Precambrian and Proterozoic than is the case.

Finally, it is worth emphasizing that only one of the 16 papers presented by Soviet scientists during the oil and gas session of the 27th International Geological Congress held in Moscow in 1984 specifically dealt with or mentioned the abiogenic theory of hydrocarbon formation (Kropotkin and Valyaev, 1984). Kudryavtsev's (1959) book on oil, gas and solid bitumen in igneous and metamorphic rocks was also subject to a withering review by Teodorovich (1962) in which the author's assumptions were questioned in great detail. Since N. A. Kudryavtsev was the first to formulate the abiogenic theory in 1951 (see earlier), this represents severe criticism indeed. These observations strongly suggest that support for the abiogenic theory within the Soviet Union may not have been as total as its proponents would like to suggest even at this high water mark.

## 6. Summary

The preceding sections have outlined the two principal theories of abiogenic formation of petroleum hydrocarbons. The Russian-Ukrainian theory of deep, abiotic petroleum origins was an attempt to formulate a scientifically rigorous theory of hydrocarbon formation which could play a major role in the exploration and exploitation of hydrocarbon deposits in the Soviet Union in the immediate post-war period. The theory is rigorous in its interpretation of the thermodynamic data for the conversion of methane to higher hydrocarbons at high temperatures and pressures. However, the formation of higher hydrocarbons from methane is only one step in the complex chain leading to the formation of commercial petroleum deposits and there are several major objections to this theory. First and foremost is the fact that the mantle is too oxidizing for methane to form there in abundance. Furthermore, most volatiles including methane are transported from the mantle to the Earth's crust in magma and not by faults as required by the theory. The occurrence of major oil and gas fields in crystalline basement rocks was also taken as confirmation of the abiogenic theory. However, this assumption predates modern theories of fluid migration in the Earth's crust. The theory also identified a number of mechanisms by which higher hydrocarbons can be formed abiogenically, of which serpentinization of ultramafic rocks does have the potential to produce commercial oil and gas fields. Proponents of the abiogenic theory have also emphasized perceived inadequacies of the biogenic theory for the formation of petroleum hydrocarbons.

However, at the time that the abiogenic theory was at its peak from the 1950s to the 1980s, it was not possible to assess the relative merits of these two theories objectively on the basis of the then existing scientific data and this only became possible with the development of

much more sophisticated techniques for the analysis of the organic constituents in petroleum such as GC/MS in the 1980s. As a result, a much more detailed understanding of the pathways of organic constituents from source rocks to petroleum was established which offered convincing evidence to support the biogenic theory. By contrast, the abiogenic theory made no real attempt to explain the formation of the very complex mixture of organic compounds which make up oil.

A major claim of the Russian-Ukrainian theory of abiogenic hydrocarbon formation is that it had major successes in the discovery of oil and gas deposits in crystalline basement rocks. However, it now appears that the great oil fields of the Volga-Urals region, the northern Urals and western Siberia were discovered not as a result of application of this theory as its proponents claim but by the use of conventional exploration methods which gave "the final word to the borehole". Furthermore, recent studies of the petroleum resources of the Dnieper-Donets Basin in the Ukraine by the U.S. Geological Survey have been interpreted entirely within the framework of conventional petroleum geology with no mention made of an abiogenic source of hydrocarbons. These failures of the Russian-Ukrainian theory in areas where it has claimed its greatest successes essentially bring its role as a viable theory on which to base exploration programmes for commercial hydrocarbon deposits to an end. As a matter of fact, this theory is now largely forgotten even in the Former Soviet Union and is virtually unknown in the west.

The deep gas theory of Thomas Gold is based on the assumption that deep faults play the dominant role in the continuous migration of methane and other gases to the Earth's surface and that this methane is then converted into oil and gas in the upper layers of the Earth's crust. However, this reaction is not thermodynamically favourable under these conditions and can not be facilitated by the presence of bacteria. In addition, deep drilling of the Siljan Ring did not offer any convincing evidence for a dominant mantle source for hydrocarbon formation there. This theory is therefore invalid.

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