

Chapter 4

BIOGENIC AND ABIOGENIC PETROLEUM

© M. Ragheb
2/23/2019

4.1 INTRODUCTION

The presence of heat generated from the process of radioactive decay in the Earth's crust and mantle in addition to the high pressures, could be related to the postulated formation of abiogenic or inorganic hydrocarbons.

At the 2.5 miles depth of the Mponeng world deepest gold mine in the Witwatersrand gold belt in South Africa, a bacterium called "Desulforudis audaxviator" exists independent from photosynthesis, using energy from natural radioactivity to create food. It is speculated that similar bacteria may exist on other planets.

The power generation in the Earth's is presently attributed to the uranium isotopes U^{238} , U^{235} , and U^{234} , in addition to Thorium²³², and Potassium⁴⁰ with a half-life of 1.28 billion years. In the past, Aluminum²⁶ with a half-life of 0.7 million years and Palladium¹⁰⁷ with a half-life of 6 million years have contributed to the heat generation.

The terrestrial power generation is thought to amount to 3.2×10^{13} Watts appearing in the form of thermal conduction in the rocks of which just 3×10^{11} Watts appears as convection in volcanoes and hot springs. This is small compared with the solar power radiation impinging on Earth of 1.73×10^{17} Watts, but nevertheless, it is significant in magnitude.

Two schools of thought exist about the origin of petroleum: a Western school suggesting that its origin is biogenic resulting from the decay of organic biological matter and stored in sedimentary basins near the Earth's surface, and an Ukrainian-Russian school proposing that it is abiogenic with an inorganic origin deep within the Earth's crust dating back to the time of formation of the Earth. The first suggestion implies a finite resource, whereas the second implies an almost unlimited one. Each school dismisses the other one, leading to interesting discussions and discourses.

An argument for the possible existence of abiogenic petroleum is that the deepest fossil ever found has been at about 16,000 feet below sea level, yet petroleum can be extracted from wells drilled down to 30,000 feet and more. The argument is advanced that if a fossil was once a living matter, it had to be on the surface. If it did turn into petroleum, at or near the surface, and since petroleum has a lower density than water it would be expected to rise on top of water not go under it. The counter-argument is that these deep deposits may have resulted from crustal movements or were buried by bolide impacts.

Vladimir Kutcherov, Professor at the Royal Institute of Technology in Sweden and the Russian State University of Oil and Gas, suggested that the April 2010 petroleum spill that flooded the Gulf Coast shores of the USA: "... could go on for years and years ... many years." Vladimir Kutcherov is a leading advocate of the theory of abiogenic deep origin of petroleum. He suggests drilling may have occurred into what he refers to as a "migration channel;" a deep fault on which hydrocarbons generated in the depths of the Earth migrate to the crust and are accumulated in rocks.

This is likened to the giant Ghawar petroleum field in Saudi Arabia. Ghawar, the world's most prolific petroleum field has been productive for a 70-year span. According to the abiotic theory, Ghawar, like all elephant and giant petroleum and gas deposits, is located on a migration channel similar to that in the petroleum-rich Gulf of Mexico. Along this line of reasoning, Haiti is identified as having potentially hydrocarbon deposits, as has neighboring Cuba. Vladimir Kutcherov estimates that the entire Gulf of Mexico is one of the planet's most abundant accessible locations to extract petroleum and gas.

The Permian mass extinction, 251 million years ago is attributed to the release by seismic activity of an undersea methane bubble. Gregory Ryskin from North-Western University associates the Late Paleocene Thermal Maximum (LPTM) mass extinction, 55 million years ago, which lasted for about 100,000 years, to the release of sub-ocean CH₄, H₂S gases and benzene vapors. The seismic eruption of such bubbles may have been associated with an atmospheric shock wave and a marine tsunami.

It must be admitted that the biogenic origin of petroleum is a mainstream theory adopted by the majority of petroleum reservoir engineers, geologists and scientists. It is supported by field observations, laboratory experiments and basin models used to explain known economic occurrences of natural gas, crude petroleum and asphalt. The abiogenic origin theory has a small number of vocal advocates, yet it would have significant implications if they were proven correct.

As a contribution to the ongoing debate about the abiogenic and biogenic origins of petroleum, the underlying arguments from both sides' point of view are considered.

4.2 PETROLEUM RESOURCES

The International Monetary Fund (IMF) projected that global demand for petroleum by 2030 would reach 139 million barrels a day, a 65 percent increase. Alaska's Prudhoe Bay field, the largest field in North America had its reserves estimated at 12.5 Giga barrels (Gb) in 1977, but were reported as 9 Gb to comply with stock exchange rules concerning reporting about reserve bases.

To enhance production in the Prudhoe Bay field, various secondary recovery techniques, such as gas injection followed by horizontal drilling, were started in 1982. This did not prevent its peaking and decline in production starting in 1988. Gas injection did stop the decline for a year, but then the decline became steeper. The field will barely produce the original 1977 estimate. Technology did not add to the reserve estimate. As reported by Colin J. Campbell, the world has produced almost half of its conventional petroleum reserves, and it has already discovered or found about 90 percent of what existed there.

The world consumes 22 Gb of petroleum a year but discovers only 6 Gb, that is only one barrel found for every four barrels that are consumed. The current depletion rate is about 2 percent per year. This creates serious concerns about the world existing petroleum reserves and the possibility of reaching global peak petroleum production.

In Europe in late 2000, the French fishermen blockaded the Channel Ports because their fuel costs had doubled, even though their fuel was already supplied to them tax-free. The discontent spread rapidly to the UK and other European countries. Schools were closed, hospitals had red alerts because staff and patients could not reach them, supermarkets started rationing bread, trade and industry were seriously interrupted, and

people lost confidence in their governments. An interruption in supply for just a few days created havoc demonstrating the deep dependence of modern society on petroleum as an energy source.

4.3 BIOGENIC AND ABIOGENIC PETROLEUM FORMATION

The dominant conventional petroleum biogenic or biotic formation theory suggests that petroleum and natural gas are biogenic in origin, as the product of the decomposition of biological organisms over geological times. The theory suggests that coal beds are the product of vegetative deposition and decomposition over millions of years, and that petroleum and natural gas are the result of the accumulation of marine organisms that died and drifted to the seafloor where they were buried by marine sediment. This is advanced as an explanation on why most large petroleum and natural gas deposits are found in regions that were once the mouths and deltas of ancient rivers and along prehistoric coastal reefs.

A corollary is that these sedimentary deposits are finite and depleting in nature, would get more expensive to extract, and that their production would reach a peak at some future time, declining as they get replaced by other sources of more available and hopefully cheaper energy.

Proponents of the theory of abiogenic or abiotic petroleum formation on the other hand, adhering to theories developed by several Ukrainian and Russian scientists, argue that hydrocarbons exist and are generated deep in the Earth's mantle, below its crust. The implication is that there could be vast deposits of petroleum and gas yet to be discovered miles below the Earth's crust, with a half-life of millions of years, assuring a practically unlimited supply. They dismiss the idea that petroleum is a finite resource of biological origin and that given enough time, the Earth's finite crustal petroleum and gas reservoirs get replenished through diffusion from the mantle's practically limitless source to the surface.

4.4 DECAY POWER OF POTASSIUM⁴⁰

The Earth's internal heat generation is 80 percent caused by radioactive decay, and 20 percent as residual heat from the process of planetary accretion.

If the total power generation in the earth is 3.2×10^{13} Watts, the amount attributed to radioactive decay is $3.2 \times 10^{13} \times 0.80 = 2.56 \times 10^{13}$ Watts.

From Table 1, the power production attributed to K^{40} would be:

$$\begin{aligned}
 P(t) &= 2.56 \times 10^{13} \times 0.15 \\
 &= 3.84 \times 10^{12} [Watts] \\
 &= 3.84 \times 10^{12} \left[\frac{Joules}{sec} \right] \times 3.15 \times 10^7 \left[\frac{sec}{year} \right] \\
 &= 1.21 \times 10^{20} \left[\frac{Joules}{year} \right]
 \end{aligned}$$

Table 1. Contribution of different isotopes to the internal heat generation in the Earth.

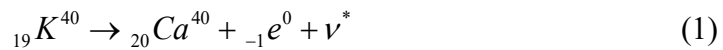
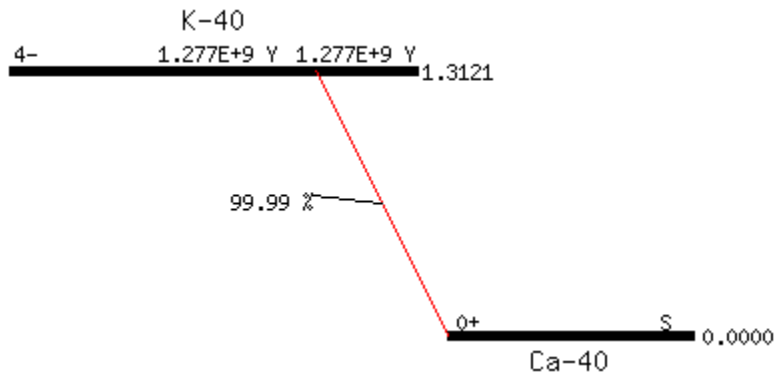
Isotope	Power Generation [Watt/kg of mantle]	Fraction of radioactive power production	Abundance [kg/kg of mantle]
Th ²³²	3.270 x 10 ⁻¹²	0.44	124.0 x 10 ⁻⁹
U ²³⁸	2.910 x 10 ⁻¹²	0.39	30.8 x 10 ⁻⁹
K ⁴⁰	1.080 x 10 ⁻¹²	0.15	36.9 x 10 ⁻⁹
U ²³⁵	0.125 x 10 ⁻¹²	0.02	0.22 x 10 ⁻⁹
Total	7.385 x 10 ⁻¹²	1.00	

A source of heat generation from radioactive decay in the Earth's crust is that of the Potassium ⁴⁰ isotope. The naturally occurring isotope of Potassium (K) is widely spread in the environment. In fact, the average concentration of K in the crustal rocks is 27 [g/kg] and in the oceans is 380 [mg/liter]. Potassium occurs in plants and animals and its concentration in humans is 1.7 [g/kg]. In human urine, potassium's concentration is 1.5 [g/liter].

Natural potassium has three isotopes in nature with different percent atomic abundances:

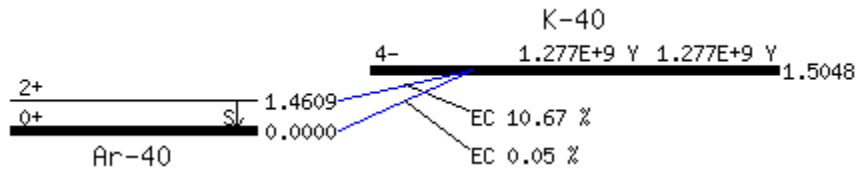
$$\begin{aligned}
 {}_{19}\text{K}^{39} & 93.260 \text{ a/o} \\
 {}_{19}\text{K}^{40} & 0.012 \text{ a/o} \\
 {}_{19}\text{K}^{41} & 6.730 \text{ a/o}
 \end{aligned}$$

Only K ⁴⁰ is radioactive with a long half-life of 1.28x10⁹ years. With a branching ratio of 89 percent it emits a negative electron to decay into the stable Calcium ⁴⁰ isotope:



where: ν^* is an antineutrino associated with the negative beta decay process.

With a branching ratio of 11 percent, it undergoes an electron capture process with the emission of a gamma photon turning it into the Argon ⁴⁰ isotope:



Presently its power generation is:

$$P(t) = 1.21 \times 10^{20} \left[\frac{\text{Joules}}{\text{year}} \right]$$

As the half-life of K ⁴⁰ is 1.28x10⁹ years, we can use the law of radioactive decay:

$$P(t) = P_0 e^{-\lambda t} \quad (3)$$

where:

$$\lambda = \frac{\ln 2}{T_{1/2}} \text{ is the decay constant}$$

$$T_{1/2} \text{ is the half-life}$$

to estimate its power generation in the past P₀, say 2.56 billion years ago, from radioactive decay in the Earth's crust as:

$$\begin{aligned} P_0 &= P(t) e^{+\lambda t} \\ &= 1.21 \times 10^{20} e^{\frac{\ln 2}{1.28 \times 10^9} \cdot 2.56 \times 10^9} \\ &= 1.21 \times 10^{20} e^{2 \ln 2} \\ &= 1.21 \times 10^{20} e^{\ln 2^2} \\ &= 1.21 \times 10^{20} \times 2^2 \\ &= 4.82 \times 10^{20} \left[\frac{\text{Joules}}{\text{year}} \right] \end{aligned} \quad (4)$$

Where we have used the relationship:

$$e^{\ln x} = x$$

which was 4 times the current power generation of 1.21×10^{20} [Joules/year].

4.5 EXPERIMENTAL STUDIES

As reported by Deng, Campbell and Burris [30], the postulated abiogenic conversion of inorganic carbon to hydrocarbons can be a reproducible process. By tossing scraps of cast iron into a glass container and adding some diluted acid, the gases that form will be mostly H_2 , but will also contain some hydrocarbons, from methane (CH_4) right up to the gasoline range compounds. The source of carbon here is the carbide that is normally present in cast iron.

The reaction between calcium carbide and water forms the acetylene gas and was used for powering the headlamps on early automobiles, and for the lamps on old miners helmets. Both reactions occur at room temperature and pressure, with no special catalysts or promoters needed.

Theoretical thermo-chemical simulation studies predict that methane bubbles could form when iron oxide, calcite and water are heated to 500-1,500 degrees C and at a pressure of 5.7-7 giga pascals and then decompressed at room temperature to 0.5 giga pascal.

In a laboratory experiment at the Lawrence Livermore National Laboratory (LLNL), a microgram sample of iron oxide, was placed under pressure in a diamond anvil [1]. Methane was formed from FeO , $CaCO_3$ or calcite, and water at pressures between 5 and 11 gigapascals (GPa) and temperatures ranging from 500-1,500 °C. The results were shown to be consistent with multiphase thermodynamic calculations based on the statistical mechanics of soft particle mixtures. The experiment showed the presence of calcium oxide and magnetite, which is a reduced form of iron oxide. Raman spectra of the sample showed a carbon-hydrogen stretching vibration at $2,932 \text{ cm}^{-1}$, corresponding to the methane signature. The bond vibration between carbon and hydrogen became apparent when the sample reaches 500°C , and became stronger around 600°C .

4.6 HELIUM CONTENT OF PETROLEUM

Petroleum contains a large concentration of the helium gas, which is chemically unconnected to biology. There is no biological material that could have attracted it or produced it. Its origin could either have been primordial, as a result of the alpha radioactive decay of the heavy radioactive elements such as Th and U, or as a result of low intensity nuclear reactions. The puzzle is that this non-biological material is highly concentrated by a factor around a thousand in petroleum, and so are the biological molecules.

A question is why the helium which is an unrelated substance to anything biological was found in petroleum. It is possible that He could have become concentrated by mechanical pumping, because, being a noble or inert gas, it is not chemically reactive. To concentrate it, is to mechanically pump it from where it occurs diffusely distributed in the rock. It is highly concentrated by a large factor just in petroleum. So how would petroleum, if it is derived from biological matter, have concentrated its He?

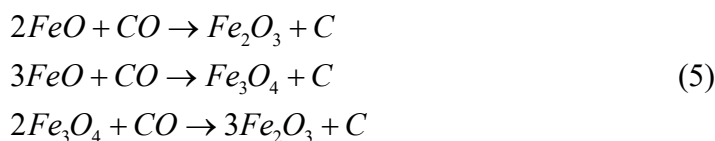
A possible explanation for the way in which He could have become concentrated in petroleum when it was diffusely distributed in all the porous spaces in the rock is that another substance in large quantity came diffusing through those porous spaces and held

the spaces open under high pressure. Petroleum pumped up whatever residual gas was trapped in those porous spaces. Then, when it came to shallower levels, which is where it is eventually found, the petroleum contained whatever it has pumped up from deeper levels below.

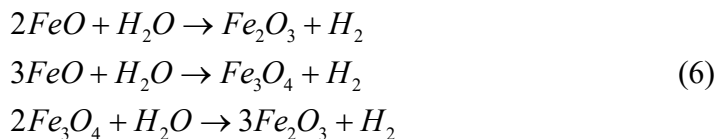
4.7 POSSIBLE MANTLE HYDROCARBON PRODUCING REACTIONS

It has been suggested that the process of hydrocarbon formation took place in the crust following a deep infiltration of meteoritic water along fractures and rifts. The depth reached by the seepage would have been warm enough to decompose water into elemental hydrogen and oxygen. The heat generation in the Earth's mantle from the radioactive decay of Th^{232} , K^{40} and other radioactive elements can be thought to drive processes involving reduction reactions on water, carbon dioxide and carbon monoxide with the help of iron oxides as catalysts.

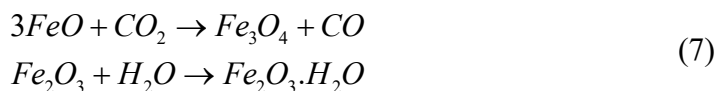
In the presence of iron, some reduction carbon production reactions are:



and some hydrogen production reactions are:



Other related reactions are:



The generated carbon and hydrogen could combine through other reactions to produce hydrocarbons. Rare earths, nickel and possibly cobalt and platinum in addition to iron in carbonatite and ultrabasic rocks could also act as catalysts in moving the reactions and forming the hydrocarbons.

The differential hydrogenation of carbon in the temperature range 230-500 °C at a depth of 7-16 kilometers would have led to the formation of parafinic and aromatic compounds. The hydrocarbon formation would have possibly occurred in the upper mantle or along rifts, deep faults and fractures.

4.8 THE FISCHER-TROPSCH PROCESS

INTRODUCTION

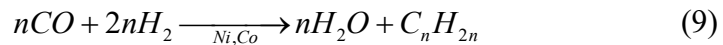
This process has been suggested as a possible mode of formation of abiogenic hydrocarbons in the Earth's mantle and crust. It was developed in the 1920s by German scientists Franz Fischer and Hans Tropsch, hence the name of the process. It uses gasified coal or natural gas to produce paraffin wax that can then be refined into diesel fuel, naphtha, and liquid petroleum gases such as butane and propane. Using catalysts such as Ni, Co, Fe, ThO₂, MgO, Al₂O₃, MnO, and clays, a series of chemical reactions occur that convert carbon monoxide and hydrogen into various hydrocarbons.

In the Fischer-Tropsch industrial process, carbon monoxide is reacted with hydrogen to synthesize hydrocarbons. The synthesis conditions are at 150 bar and 700 K in the presence of a catalyst.

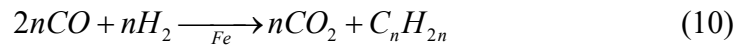
In the case of natural gas methane to liquids applications the suggested basic chemical reaction would be:



With Ni and Co used as catalysts, the following reaction would occur:



If, instead, a Fe catalyst is used the reaction proceeds as follows:

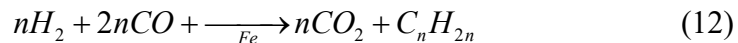


During World War II, Germany being unable to secure sufficient petroleum supplies, used the process to produce about 600,000 metric tonnes of synthetic gasoline in the year 1943.

When the initial products are generated by the gasification of coal or biomass (CH), the chemical reaction is:



An iron catalyst is then used to catalyze the reaction:



The intermediate mixture of carbon monoxide and hydrogen gases is commonly referred to as synthetic gas, or syngas in short. This metastable process yields 200 grams of hydrocarbons from a 1 m³ mixture of CO and H₂. The reaction occurs around a pressure of 150 bar and 700 K.

The reaction being metastable requires that the produced hydrocarbons would be

destroyed unless they are promptly cooled and their pressure reduced.

HISTORY OF THE FISCHER TROPSCH PROCESS

During World War II, petroleum-poor but coal-rich Germany used the Fischer-Tropsch (FT) process to produce diesel and aviation fuel for its army after the Allies curtailed its petroleum imports. In 1944, Germany produced over 90 million tons of synthetic FT petroleum. When General George Patton's USA Third Army entered Germany, it was fueled by FT diesel; he had to drain fuel from the captured German vehicles and use it on his own after over-extending his fuel supply lines.

Synthetic fuels were previously researched in the USA as early as 1925. In the 1940s, a Synthetic Liquid Fuels Act passed by the USA Congress, appropriated over \$80 million for research and production. By the 1950s, the USA was producing thousands of gallons of synthetic gasoline per day at a test plant in Missouri. The discovery of cheap petroleum, combined with a claimed lobbying effort by the petroleum industry, resulted in the government abandoning its synfuel research program. During the petroleum crisis in the late 1970s, the federal government briefly pursued synfuel production, but abandoned the idea when the price of petroleum receded.

The FT process was also used to produce most of South Africa's diesel fuel during its isolation and the international sanctions imposed on it during the Apartheid regime. Since 1955, the South African company Sasol had produced about 1.5 billion barrels of synthetic fuel from around 800 million tons of coal. Sasol production accounts for approximately 29 percent of that nation's fuel.

Plants built in response to fuel embargoes in South Africa are estimated to produce around 200,000 barrels of petroleum per day. Aircraft departing from Johannesburg International Airport have done so using a semi-synthetic blend of 50 percent jet fuel produced from coal by Sasol and 50 percent derived from traditional crude petroleum refining. Sasol attempted at some point to win final regulatory approval for use of 100 percent synthetic fuel, also derived from coal.

DISCUSSION

A main characteristic of this reaction is that it is metastable under its pressure and temperature conditions. The produced hydrocarbons would be destroyed unless they are promptly cooled and their pressure reduced.

This highly controlled and regulated industrial process probably does not occur in nature and cannot be considered as the sole source for the generation of any natural hydrocarbons.

4.9 ABYSSAL ABIOTIC THEORY

Astronomers have observed that hydrocarbons occur on many planetary bodies such as meteorites, comets and in particular on Titan, a moon of the planet Saturn. They are a common substance in the known universe. They are found in the kind of gas clouds or nebulae that were the origin of stellar systems like our solar system. Is it reasonable to speculate that the Earth contains petroleum and gas for reasons that are all its own and that

these other bodies have it because it was built into them when they were formed.

In *Astrobiology Magazine* the case was made that on the planet Mars, there is an intriguing connection between methane and water vapor found in three broad geographic regions; a result that may suggest looking further for past or dormant microbial life.

An early champion of the abyssal abiotic theory was the famous Russian chemist Dmitri Mendeleev, of the periodic table of the elements' fame.

The theory that petroleum was all biogenic or biotical, originating from fossils had become firmly established before astronomers had definitive evidence of the existence of hydrocarbons on other celestial bodies. In the whole petroleum and coal history, there exists a fact that all of these substances contain some biological material. However, this could also be interpreted with the theory of a primordial hydrocarbon mixture to which biological products have been added.

Geochemists are used to think that hydrocarbons could not occur in the Earth's mantle which begins in depth between 7 and 70 kilometers below the Earth's surface and extends to 2,850 kilometers in depth, since they would interact with other oxides in the mantle and oxidize into CO₂.

In fact, petroleum and natural gas wells are drilled between 5 and 10 kilometers in depth. Recent research in high pressure thermodynamics suggests that the mantle's heat generated by radioactivity and its pressure could allow hydrocarbons to form and exist to a depth of 100 to 300 kilometers. It is claimed that the Earth's mantle could contain hydrocarbon reserves larger in magnitude than in its crust.

4.10 RUSSIAN PETROLEUM PRODUCTION

In 2007, the Russian Federation became the second largest petroleum producer after Saudi Arabia, with the petroleum sector providing funding for 1/3 of its national budget. Natural gas was the second revenue source. Both led to the accumulation of \$592 billion in gold and foreign exchange reserves by 2008. Russia has been reported to have increased its daily petroleum production by 40 percent from an average of 5.9 million barrels per day (bpd) in 1998 to 8.6 million bpd in 2003 and then to 9.7 million bpd in 2008. On February 2002 it surpassed Saudi Arabia in daily petroleum production.

These recent increases have been due primarily to the reactivation of old idle fields, drilling technology improvements, the use of more advanced equipment, the exploitation of some new fields, and, to a lesser extent, due to the adoption of deep well drilling technology.

At the current rate of production, Russia will run out of petroleum relatively earlier than Saudi Arabia, which is estimated to be able to continue for 70 years at the present rate of production. Only two out of Russia's 14 largest petroleum producing field were started after 1991 after the formation of the new Russian Federation. Half of the 14 fields were more than 60 percent depleted in 2006. In 1990, 17.3 million feet of new wells were drilled exploring for new reserves in the former Soviet Union, but only about 3.9 million feet were drilled in the New Russian Federation. To circumvent the foreseen decrease in production, tax breaks were introduced, as well as licenses for exploration in offshore locations, in the eastern provinces and even in the arctic ocean.

However there is not yet sufficient evidence to support further production gains. At its peak, Soviet production was around 12 million bpd. This was at the time, the whole

USSR production, not just Russian production. With the separation of some of the Union of Socialist Soviet Republics (USSR) republics, Russia has lost the supply from the rich Caspian Basin offshore, and onshore petroleum fields in the Central Asian states and Azerbaijan. While the reserves of Kazakhstan and other Caspian Basin states may increase in coming years, outside Sakhalin Island, the Northern Seas, including the Barents and Beaufort Seas, and some fields in the smaller Russian sector of the Caspian Sea, there are no expectations of new reserve finds in Russia. The existing fields in Western Siberia are not yielding significant incremental production.



Figure 1. The Kola SG-3, 40,230 feet deep petroleum well at Zapolyarny, Russia. At the bottom of a layer of metamorphic rock, the rock was found to be fractured and saturated with water originating from minerals deep on the crust. The mud flowing out of the hole came out with an unexpected quantity of boiling hydrogen gas. All of the deep hole projects ended in frustration. There were false start and blockages. There were the high temperatures the drilling machinery encountered deep underground, as well as the cost and the politics.



Figure 2. The White Tiger 17,000 feet deep petroleum field, Vietnam.

4.11 RUSSIAN CONTINENTAL SCIENTIFIC DRILLING PROGRAM: KOLA SUPERDEEP BOREHOLE

Hoping to increase its petroleum production, starting in 1970 Russia initiated a program of deep wells drilling. As an example is the Kola SG-3 deep petroleum well (Fig. 1). The Kola Peninsula is situated about 750 miles north east of Moscow. The Kola site is located north of the Arctic Circle in a closed region of Russia inaccessible to foreign visitors because of its proximity to the Barents Sea and to its borders. It can be accessed by chartered air flight with Aeroflot to Murmansk and by bus to the mining community of Zapolyarny located 40 kilometers east of the Norwegian border. It was an exploratory well which eventually reached a depth of 40,230 feet or 12.2 kms. Since then, Russia drilled more than 310 reportedly successful deep petroleum wells, and placed them into production.

It took the Soviets almost 20 years to drill this far, but the drill bit was still only about one-third of the way through the crust to the Earth's mantle when the project came grinding to a halt in the chaos of post-Soviet Russia. Drilling was stopped in 1992, when the temperature reached 180 °C or 356 °F. This was twice what was expected at that depth and drilling deeper was no longer possible. Following the collapse of the Soviet Union there was no money to fund such projects – and three years later the whole facility was closed down. Now the desolate site is a destination for curious tourists.

Extraction of 11,140 meters of drill pipe at Kola from the hole, changing the drill bit, and lowering the string to the bottom of the hole required a total of 16 hours for the round trip.

Four depths have been achieved from the Kola drill collar, the deepest was 12,261 meters reached in 1985. Serious deviations from the vertical occurred at that depth. The drill string was backed up to above 12 kilometers and the hole was re-drilled. Deviations occurred at 10,750 m and 12,060 m depths, and the hole was re-drilled back to the vertical. One degree off the vertical is tolerated. The target depth of the project was 15 kilometers. The bottom-hole temperature reached 190 degrees Celsius.

JAPANESE DRILLING PROJECT

When the Russians started to drill they claimed they had found free water. This was not believed by most scientists. There used to be common understanding among Western scientists that the crust was so dense 5 km down that water could not permeate through it.

A Japanese project is to get actual living samples of the mantle as it exists right now is organized by the Japan Agency for Marine-Earth Science. In locations like Oman you can find mantle close to the surface, but that is mantle as it was millions of years ago.

If the Earth is like an onion, then the crust is like the thin skin of the planet. It is only 25 (40km) miles thick. Beyond this, is the 1,800-mile deep mantle and beyond that, right at the center of the Earth, is the core.

AMERICAN DEEP DRILLING, PROJECT MOHOLE

Like the space race, the race to explore this unknown “deep frontier” was a

demonstration of engineering prowess, cutting-edge technology and the “right stuff”. The scientists were going where no human had gone before. The rock samples these super-deep boreholes could supply were potentially as important for science as anything NASA brought back from the moon.

The USA had fired up the first drill in the race to explore the deep frontier. In the late 1950s, American Miscellaneous Society came up with the first serious plan to drill down to the mantle. The society was an informal group made up of the leading lights of the USA scientific community. Their crack at drilling through the Earth’s crust to the mantle was called Project Mohole, named after the Mohorovičić discontinuity, which separates the crust from the mantle.

Rather than drill a very deep hole, the USA expedition – observed by novelist John Steinbeck – decided to take a short cut through the Pacific Ocean floor off Guadalupe, Mexico. The advantage of drilling through the ocean floor is that the Earth’s crust is thinner there; the disadvantage is that the thinnest areas of crust is usually where the ocean is at its deepest. Two years before Neil Armstrong walked on the moon, the USA Congress cancelled the funding for Project Mohole when costs began to spiral out of control. The few meters of basalt that were brought up cost \$40 million or £31million.

GERMAN DEEP DRILLING

The Soviets started to drill in the Arctic Circle in 1970. In 1990, a German Continental Deep Drilling Program (KTB) began in Bavaria – and eventually drilled down to 5.6 miles (9km). The technologies needed for the success of these expeditions had to be invented from scratch.

When in 1961 Project Mohole began to drill into the seabed, deep-sea drilling for oil and gas was still far off. No one had yet invented now essential technologies such as dynamic positioning, which allows a drill ship to stay in its position over the well. Instead, the engineers had to improvise. They installed a system of propellers along the sides of their drill ship to keep it steady over the hole.

One of the biggest challenges the German engineers faced was the need to drill a hole that is as vertical as possible. The solution they came up with is now a standard technology in the oil and gas fields of the world. The experience of the Russians was that you have to drill as vertical as possible because otherwise you increase torque on the drills and kinks in the hole. A solution was to develop vertical drilling systems. These are now an industry standard, but they were originally developed for KTB – and they worked until 7.5 kms or 4.7 miles. For the last 1.5–2 kms, 0.9 to 1.25 miles, the hole was off the vertical by almost 200 m.

The German borehole drill rig is still there is a tourist attraction today and the crane lowers instruments for measurement. The site has become in effect an observatory of the planet and an art gallery. The plan was to drill deeper than the Soviets but the allowed phase of 10km or 6.25 miles was not reached because the German unification was costing a lot of money.

At Hole 1256 drilled by the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP)] intact ocean crust was reached.

M2M-MOHOLE TO MANTLE

The “M2M-MoHole to Mantle” is one of the most important projects of the International Ocean Discovery Program (IODP). As with the original Project Mohole, the scientists are planning to drill through the seabed where the crust is only about 6 kms or 3.75 miles deep. The goal of the \$1bn (£775m) ultra-deep drilling project is to recover the in-situ mantle rocks for the first time.

Despite the importance of the project, the huge drilling ship the Chikyū was built almost 20 years ago with this project in mind. The Chikyū uses a GPS system and six adjustable computer-controlled jets that can alter the position of the huge ship by as little as 50cm or 20 in.

There are three main candidate sites. One of those is off Costa Rica, one off Baha, and one off of Hawaii. Each of the sites involves a compromise between the depth of the ocean, distance from the drilling site and the need for a base on the shore that can support a billion-dollar, 24-hours-a-day operation at sea. A robotized drill pipe handling system has been developed.

The scientific data produced from the hole included:

1. A 12 km section of the Pre-Cambrian continental crust exposed for study through cores and down-hole measurements.
2. The hole provided ground truth for evaluating surface seismic surveys attempting to interpret the composition of the subsurface.
3. Significant hydrothermal mineralization, including copper, nickel and gold values, have been intersected at depths below 5 kms.
4. A variety of liquids and gases have been encountered at unexpected depths.
5. Models involving radioactively generated heat from elements such as U^{238} , U^{235} , Th^{232} and K^{40} , which are believed to cause the molten state of the Earth's core were modified.

At the bottom of a layer of metamorphic rock, the rock was found to be fractured and saturated with water originating from minerals deep in the crust. The drilling mud flowing out of the hole came out with an unexpected quantity of boiling hydrogen gas.

4.12 WHITE TIGER VIETNAM FIELD

The Vietnamese White Tiger deep petroleum field is reported to have produced high quality crude petroleum from basalt rock more than 17,000 feet below the surface of the Earth, at 6,000 barrels per day per well (Fig. 2). The Earth's magma could be causing thermal redistribution of conventional oil from one location to another depending on the local geology. Oil extraction from igneous rock formations off the coast of Vietnam may be an evidence that fractured granite formations can accommodate commercially viable petroleum deposits.

The source rock for the hydrocarbons is an algal-rich lacustrine rock which matured during the Oligocene-Miocene pull-apart basin and subsequent burial phases. Migration of the petroleum occurred from the Miocene to recent times, and filled the available fracture and grain space in the highly fractured basement rocks and overlying sedimentary rocks. The Boch Ho field is estimated to contain 1 billion barrels of petroleum, and is produced mainly from the intrusive granitoid plutons. Another estimate is between 1.2

and 1.5 Giga barrels (Gb). The hydrocarbons are reported by some of the Russian scientists observing it to be biotic, originating from the lacustrine sedimentary rock.

Another deep well was drilled at Siljan in Sweden (Fig. 3).



Figure 3. Siljan deep well drill, Sweden.

4.13 HYDROCARBONS IN SYRIA PLATEAU BASALT

Southern Syria is covered by a 1,100 meters thick alkaline plateau of basalt lavas of upper tertiary age. Solid hydrocarbons uncommonly fill and imbibe small fractures of lower quarternary carbonatite. The carbonatite may have been formed by the combination of CO_2 , originating from the asthenosphere, and calcium oxide resulting from the depletion of peridotite. The gray-brown to reddish vesicular carbonatite is in the form of lavas, dikes and tuffs. It is found in six lower Pleistocene scoriaceous basanitic cinder cones, extruding the alkaline plateau basalt at Jabal Al Arab (Mountain of the Arabs) along the border with Jordan.

Carbonatite is also exposed on the surface of the Khaldieh basaltic cone and Bir Hamam, 18 kilometers north-northwest the Khaldieh cone where it is crossed by the Damascus to Soueida highway. The carbonatite lavas and dikes are loaded with ultrabasic and basanite xenoliths. There is a suggestion that there exists an east to west 70 kilometers deep rift connected to the Dead Sea and the Jordan River valley rift, as inferred by the presence of the thick plateau basalt lavas, basanite cones, ultrabasic xenoliths and carbonatite of lithosphere and upper asthenosphere origin.

Drilling to a depth of 1,100 meters in the alkaline plateau basalt does not reveal sedimentary rocks or petroleum bearing mother rocks. This absence of mother rocks

suggested to some investigators an abiogenic origin in the mantle or along rifts and fractures in the basalt for the detected hydrocarbons.

4.14 BITUMEN OCCURRENCE IN THE DEAD SEA

The Dead Sea exists on the northern part of the Great Rift Valley fault line which extends southward through the Red Sea and into East Africa. Over the centuries it has been called: the Stinking Sea, the Devil's Sea, and the Lake of Asphalt. The Jordan River flows down from the north until it reaches the lowest surface point on Earth at 1,370 feet below sea level. The inland sea there is flanked by the rift walls composed of the Judean Hills to the west and the mountains of Moab to the east.

Discharges of bitumen from the Dead Sea have been historically reported as floating on its surface in the form of lumps. Bitumen was the first petroleum product used by humans. Petroleum-derived bitumen is also referred to as asphalt. In many places asphalt refers to bitumen mixed with a mineral aggregate such as sand or gravel for paving roads.

In 1834 a chunk of bitumen weighing 6,000 pounds was reported to have floated ashore. It is thought that earthquakes caused chunks to break from the Dead Sea bed and float to its surface. Another theory is that the bitumen filters up through diapirs or cracks and reaches the sea bottom together with salt rock structures. When the salt rock melts, blocks of bitumen then float to the surface.

Over the centuries bitumen was used to waterproof boats and ships' bottoms, for construction and as an insect repellent. Around the middle of the 4th century BC, the Ancient Egyptians are reported to have used bitumen for mummification, even though this allegation is challenged in favor of the use of the Natrun nitrate salts (etymological origin of the name of Nitrogen as well as the chemical symbol of sodium as Na) from the Wadi Al Natrun or the Natrun Valley in the Western Desert of Egypt.

Around this period of time, the Nabatean ancient civilization, that is the precursors to the modern day Arabs, settled at their capital of Petra by the Dead Sea and monopolized a trade in the bitumen. They brought it ashore, cut it out and then traded it with Egypt, most probably for ship building use.

4.15 RESERVOIR REPLENISHMENT

Some petroleum reservoir engineers were puzzled when they realized that their estimated existing reserves in old wells were increasing rather than decreasing. It could be that their original estimates were underestimated. However, some suggested that what they could be observing in deep petroleum wells was in fact leaking hydrocarbons from the mantle of the Earth diffusing upwards through fractures into the common sedimentary petroleum fields, located relatively close to the surface. A hypothesis exists that as petroleum is drawn out of these known reservoirs through petroleum wells, the field pressure is slightly reduced, thereby allowing more deep petroleum to diffuse up from the mantle and recharge the reservoir from below. However this diffusive process is suggested to have a characteristic time longer than human lifetimes.

The Spindletop dome in Southeast Texas was discovered in 1901 and is still producing even though at a slower rate at depths reaching 10,000 feet.

Some Ukrainian and Russian studies of their ultra-deep wells and those in the White Tiger field in Vietnam, suggest that migration from the mantle could be about 20-30 percent less than production at shallow petroleum field's wellheads. If this were true, the implication is that if the pressure of existing petroleum wells is allowed to be reduced by about 30 percent, petroleum supply and production could be replenished by deep petroleum from the Earth's mantle.

Interestingly, the current approach of injecting water into aging petroleum wells, accomplishes just the opposite: it is meant to increase the reservoir's pressure rather than to decrease it.

About 80 petroleum and gas fields reportedly occur partly or completely in crystalline basement rock in the west Siberian basin, including the Yelley Igai and Malo Itchskoye fields from which all of the production of petroleum and gas occurs entirely and solely in the basement rock from depths between 800 to 1,500 meters below the roof of the crystalline basement. In 1981 on the basis of the theory of abiotic petroleum origin, a group of Ukrainian geologists proposed the drilling of 10 wells for petroleum and gas in the Precambrian crystalline basement of the Dnieper Donets basin in the Ukraine. In Tatarstan, a well designated as 20009-Novoyelkhovskaya was started in November 1989. Its target depth for petroleum and gas was 7,000 meters in the Precambrian basement rock of the southern Tatarian arch, which is the maximum height of the basement. The roof of the crystalline basement rock was observed at the depth of 1,845 m. Significant petroleum shows in that well were reported in the basement granite at depths of 4,500 m and below.

4.16 EUGENE ISLAND POSSIBLE RECHARGE

Abiogenic petroleum's advocates suggest that in the Eugene Island Block 330 field, a large production area is believed to be recharging with a deep source rock is indicated, and the chemical composition of the recharging petroleum indicating that it is leaking from a deep, intermediate reservoir. USA petroleum companies generate seismic data to 60,000 feet in depth in the Gulf of Mexico, about 20,000 feet deeper than the depths that ultra-deep drill ships can usually reach.

Eugene Island 330 is a petroleum field in the Gulf of Mexico, 80 miles off the coast of Louisiana. It was discovered in 1973 and began producing 15,000 barrels of petroleum per day, which then slowed down to about 4,000 barrels per day in 1989. Unexpectedly, the production spiked back up to 13,000 barrels per day. What the researchers found when they analyzed the petroleum field with time lapse 3-D seismic imaging is that there was an unexplained deep fault in the bottom corner of the computer scan, which showed petroleum gushing in from a previously unknown deep source and migrating up through the rock to replenish the existing supply.

The analysis of the petroleum produced at Eugene Island showed that its age is geologically different from the petroleum produced after the refinery first operated, suggesting that it is emerging from a different source. The estimates of probable reserves shot up from 60 million barrels to 400 million barrels.

Jean Laherrère counters that the Eugene Island formation recharge has an explanation and that Eugene Island is depleting, not refilling. The Eugene Island petroleum field is flanked by the largest and best known fault in the Gulf of Mexico called the Red Fault. It places the reservoir in direct communication with the source rocks. The rapid

depletion of the reservoir dropped its pressure, allowing it to be recharged with petroleum from the source-rocks. The decline has resumed, adding only about 10 percent to the total reserve value.

4.17 ORGANIC BIOTIC PETROLEUM ORIGIN: LOMOSONOV THEORY

The dominant organic petroleum origin theory directly links petroleum origination to the decomposition of organic matter. According to the Russian scientist M. V. Lomonosov as far back as in 1757:

“Rock oil originates as tiny bodies of animals buried in the sediments which, under the influence of increased temperature and pressure acting during an unimaginably long period of time transform into rock oil.”

Organic molecules are molecules of matter that contain carbon. This does not mean that they have anything to do with organisms or life. As Carl Sagan pointed out in his book “Comet,” astronomers tend to be nervous about the word organic because of concern that it might be misunderstood as a token of life. So they use the term “carbonaceous” to describe meteorites that are rich in carbon compounds. Kerogen is a tar-like organic compound found in some meteorites, and is routinely generated if meat or hamburgers are overcooked while tailgating or backyard barbecue grilling on Earth.

For two centuries Lomonosov's simple and intuitive theory on the organic origin of petroleum went unchallenged. It implied that the world would run out of this fuel once the rare sedimentary rocks that contained the bodies of animals were drained of their petroleum. It also meant that the basement rocks would not bear petroleum. Basement rocks are rocks that have never been near the surface of the Earth. They lie under the top layer of rocks, most of which are sedimentary and have been recycled many times over by wind and water erosion.

Cap rocks are rocks that are impervious and they resist the flow of fluids such as water, petroleum and gas and trap these fluids in rocks below.

Reservoir rocks act as a storage medium for petroleum. They have sufficient cracks and fissures to allow the petroleum to flow into the well. Reservoir rocks must be covered by cap rocks to prevent the petroleum seeping up to the surface and escaping.

Source rocks are those in which petroleum is generated. The dominant classical view is that source rocks must have layers containing the bodies of dead plants and animals and that these gradually change into petroleum.

The abiogenic view is that all basement rocks have the potential to be source rocks because petroleum has non biological origins deep within the Earth.

The dominant biogenic theory states that a portion of the lipid fraction of microorganisms deposited in anaerobic sediments is the original source of petroleum. Proteins and carbohydrates make up to 85 to 95 percent of the weight of these microorganisms, and are rapidly degraded by microbial activity. The remaining 5 to 15 percent could be preserved in anaerobic sediments; representing unique deposition conditions that result in organically rich, sedimentary rock intervals in some stratigraphic sequences. Lipid materials preserved in the original sediments polymerize into kerogen,

an insoluble organic material. As these organically rich rock intervals are heated by the Earth's heat generated from radioactive substances' decay, and burial in sedimentary basins, the hydrocarbon polymers within the kerogen thermally crack through a free radical mechanism to yield liquid and gaseous petroleum hydrocarbons.

A study based on helium isotopes abundances suggested that any abiogenic hydrocarbons account for less than 200 parts per million (ppm) of the cumulative current global petroleum production.

4.18 C. WARREN HUNT ANHYDRIDE THEORY

In a December 1998 conference on "Petroleum Potentials in the Crystalline Basement" held in Kazan, Tatarstan, C. Warren Hunt presented a paper that advanced the concept that petroleum was created by biological life as microbes acted on methane (CH₄), which effuses from the Earth's interior.

The paper entitled: "Anhydride Theory: a New Theory of Petroleum and Coal Generation" sets forth the proposition that petroleum is a mixture of anhydrides of methane, and that these are created by the progressive stripping of hydrogen from methane by microorganisms, either with or without associated fossil biomass. Coal would also be a result of the bacterial addition of methane derived carbon to peat.

4.19 THOMAS GOLD PRIMORDIAL HYDROCARBONS THEORY

Born in Vienna in 1920 and passing away in 2004 in Ithaca, New York, Thomas Gold was an astronomer as well as geoscientist (Fig. 4). He had a transient childhood: he moved to Berlin, Germany at age 10 and then left for England with his father, a businessman, as a refugee. He went to secondary school in Switzerland, before going to Cambridge University shortly before World War II. He was held in a British internment camp as a suspected enemy alien for a year. He later participated in the development of radar systems. He moved to Harvard University in the USA, and then joined Cornell University in 1959. He became the chairperson of the astronomy department and director of the Center for Radiophysics and Space Research.



Figure 4. Thomas Gold (1920-2004)

In the late 1970's, Thomas Gold learned about the Ukrainian-Russian theory of deep, abiotic petroleum origins promulgated by many scientists such as Vladilen Alexeivich Krayushkin at the Institute of Geological Sciences in Kiev, Ukraine, A. I. Kravtsov, V. B. Porfir'yev, P. N. Kropotkin, Rh. K. Muslimov, and others. He also became aware of the work by Richard R. Donofrio, a mainstream geophysicist at the University of Oklahoma about the subject of bolide impacts structures and the potential of their locations for harboring petroleum reservoirs. He was exposed to the work of Canadian-American geologist C. Warren Hunt about the origin of petroleum from microbial action.

He seems to have synthesized a hybrid of these ideas, and in his 1998 book: "The Deep Hot Biosphere," he proposed that petroleum and coal are not remnants of ancient surface life that became buried and subjected to very high temperatures and pressures. Instead he argued that these deposits are produced from primordial hydrocarbons dating back to when the Earth was originally formed. He suggested that volatile gases then migrate towards the surface through cracks in the crust, and either leak into the atmosphere as methane, become trapped in sub surface gas fields, or lose their hydrogen through microbial action to become petroleum, tar or coal. The implication was that there must be reserves of fossil fuels vastly in excess of the sedimentary quantities that the gas and petroleum industry currently exploits.

Photosynthesis where chemical energies are created from the sunlight has been thought to be the only way life could be supported. Findings of gas fumaroles and liquids coming up from volcanic vents at the oceans floors which feed enormously intense forms of life such tube worms, support the possibility of life under conditions other than photosynthesis. The principal forms of life that are living there are microbial, which feed the larger creatures up the food chain.

4.20 IMPACT CRATERS AND PETROLEUM OCCURRENCE

Buried impact crater formations are suggested to create possible underground traps

for petroleum, but these craters rarely seem to be above the types of rocks that are supposed to contain petroleum.



Figure 5. The Chicxulub Crater boundary in the upper left hand side at the Yucatan Peninsula, Mexico, generated by the Shuttle Radar Topography Mission (SRTM).
Source: NASA.

According to the abiogenic petroleum theory, the natural traps formed by impact craters formations will be even more promising as places to look for petroleum because the “source rocks” containing the petroleum are everywhere.

About 65 million years ago, it is postulated that a large asteroid hit the Earth in a shallow sea off the coast of Mexico forming the Chicxulub Crater (Fig. 5). It is thought to have caused a mass species extinction leading to the demise of the dinosaurs and the rise of the mammals, including humans, which now dominate the Earth. The crater is about 150 miles or more across. It was briefly formed by the liquefaction of the sea floor and chunks of rock were scattered into a mile-thick layers for hundreds of miles in all directions. Ocean tsunamis caused by the impact would have churned up more piles of broken rocks on the coastlines thousands of miles away.

Over geological time, layers of sediment covered the impact crater and they lay undisturbed for millions of years. Prospectors started looking for petroleum in the region, unaware that the Chicxulub crater lay buried deep beneath the surface. They were successful, and commercial petroleum production began. But it was not until the year 1990 that the signs of a crater were recognized. The rubble could be the source of most of Mexico's petroleum reserves. Some geologists began to suspect that impact crater formations could make good traps for petroleum.

Petroleum from deep underground gradually works its way upward through cracks and fissures in rocks. Petroleum prospectors are encouraged for significant finds if the reservoir rocks that contain the petroleum are covered by a contorted layer of cap rocks because this can confine the petroleum in natural reservoirs. A petroleum well is usually

drilled until it breaks through the cap rocks and reaches the petroleum-saturated reservoir rocks below.

The rubble from an astral impact often forms a porous rock known as breccia that is full of cracks and fissures; making it excellent for extracting petroleum through a well. Domes, basins, deep cracks, along with crumpled, folded landforms are other typical features of an impact crater that make them promising for petroleum prospectors.

There are hundreds of thousands of petroleum wells in the USA, but only a dozen or so are known to be associated with impact structures. Like Chicxulub, none of the craters were discovered until after commercial production of petroleum began.

Deep under the layers of sedimentary rocks that cover most of the USA one can speculate that there should be at least 20 undiscovered buried impact craters. Canada's geology is different and most craters are on or near the surface. An estimate of the petroleum producing potential of undiscovered impact craters in the USA is 50 billion barrels or double the current proven USA reserves.

An Australian site is the Bedout Structure some 200 miles off the coast of Broome. There are tentative signs that this was originally a crater 160 miles in diameter, perhaps bigger than Chicxulub. If it does turn out to be a large impact crater, there could be substantial reserves of petroleum in the region.

The Bedout Structure is also of interest to paleontologists. Its possible age of 250 million years correlates with an observed species mass extinction at the end of the Permian period.

4.21 DEEP DRILLING AT THE SILJAN RING, SWEDEN

At the beginning of the “Deep Gas Exploration Project,” the Swedish government empaneled a high level committee of senior scientists to scrutinize and evaluate both the 18th-century “biological origin” hypothesis for petroleum as well as the Ukrainian-Russian abiotic theory of petroleum.

In this project, Sweden embarked on a massive drilling project at Siljan, which began in 1986 (Fig. 3) at a meteor-made lake north of Stockholm to search for petroleum and gas that may have flowed upward in the meteor fractured ground. Two deep wells were drilled. From 1986 to 1992, two commercial wells were drilled in the Siljan crater, at a reported cost of over \$60 million. The reason for this site’s choice was that the project wished to drill in pure granitic rock with no sediment and no biological matter in it.

The project was not able to produce commercial quantities of petroleum. The reason was attributed to the bacteriological content which clogged up the wells. However, the argument was advanced that the bacteria that were captured at the various levels were those that would only reproduce at the elevated temperatures occurring at the various levels. About 80 barrels of petroleum were extracted, not trace amounts, but neither a substantial amount anyway.

Critics countered that the petroleum was merely contamination from the drilling. They pointed out that the early drilling used injected petroleum as a lubricant, and that this is the likely origin of the oily sludge. It has also been mentioned that sedimentary rocks 20 kilometers away could have been the source of hydrocarbon seepage. During World War II, the Swedes blasted into the bedrock to produce cavities and caverns to stockpile petroleum supplies. They currently face environmental problems as these petroleum

stockpiles are leaking into the groundwater. These stockpiles may have provided the source of the oil supposedly produced from the Siljan crater.

In 1984, the Swedish state-owned power company had an independent team of geoscientists evaluate the Siljan crater for commercial abiogenic gas production. The research team found only minor hydrocarbon gas shows in the crater. However, they did prove through geochemical analysis of petroleum, petroleum stained rocks and organic rocks, that an Ordovician-aged bituminous shale was the source rock for hydrocarbons found in the Siljan crater. They concluded that the claims that this petroleum was abiogenic were without merit.

Nevertheless, based on the Swedish efforts, the Russians drilled 300 deep holes in granitic rock of this type in Russia and reported finding petroleum in most of them. The White Tiger field off the coast of Vietnam is reported to have produced at a substantial rate from granitic based rock.

4.22 ROLE OF MAGNETITE AND BIOLOGICAL ACTIVITY

Microbes can live on petroleum where it is oozing up from deep below if they can extract some oxygen from it. Hydrocarbons are only useful for energy and microbes need an energy supply which can be used for the combustion process which needs oxygen. Microbes have no free oxygen like that exists in the atmosphere, so they have to find their oxygen from materials that are buried in the rocks. There the substances that are the most prolific suppliers of oxygen are iron oxide and sulfur oxide.

It appears that petroleum bearing areas have magnetite, a less oxidized form of iron, and sulfur and sulfides, which are compounds of sulfur, but unoxidized. So to get that kind of magnetite around the petroleum, one could assume that the microbes consumed some of the oxygen to make the magnetite out of the ferrous iron that is in the rock. The magnetite grains are very small and no such small ones occur naturally without the effect of biology. They could thus be biological products and they were found in large quantities in Sweden. It is possible that the iron mines in Sweden that helped launch the renown Swedish iron and steel industry are the same as what were found at the Siljan deep well drilling.

One can also surmise that a great deal of the microbial activity found in the crust of the Earth is related to mining operations. The formation of many metal deposits is unexplained as to the reason why these metals are clustered together. An answer as to why they got concentrated is because at great depths and at high pressures, it is very much easier to make complex molecules that contain metals. Then they come up and disintegrate and leave the metal atoms behind as copper, zinc and lead deposits.

A related topic has to do with the methane hydrates at the bottom of the oceans. Places on the ocean floor that are cold and at high pressure allow an ice that is a mixture of methane and water to form the methane hydrate. It is possible that methane has come up everywhere and met up with the cold water and there it turned under high pressure into the methane hydrate ice.

It is proposed that the total amount of the element carbon that is sitting on the ocean floors in the form of methane hydrate exceeds all the Earth's coal and petroleum. At some geological times volcanic activity, asteroids or comets impacts may have released this stored methane gas causing bouts of global warming and possibly mass species extinctions.

4.23 CORRELATION WITH SEISMIC AND VOLCANIC ACTIVITY

The correlation between the occurrence of seismic and volcanic activity and hydrocarbon basins in some parts of the world is worth noticing. In South East Asia hydrocarbon deposits in Indonesia and Malaysia positively correlate with crustal activity as shown in Fig. 6. This also occurs in California where its petroleum and natural gas deposits curiously occur along the tectonic plate motions along the San Andreas Fault (Fig. 11).

It must be pointed out as a caveat that in the field of statistics, correlation does not imply causation.

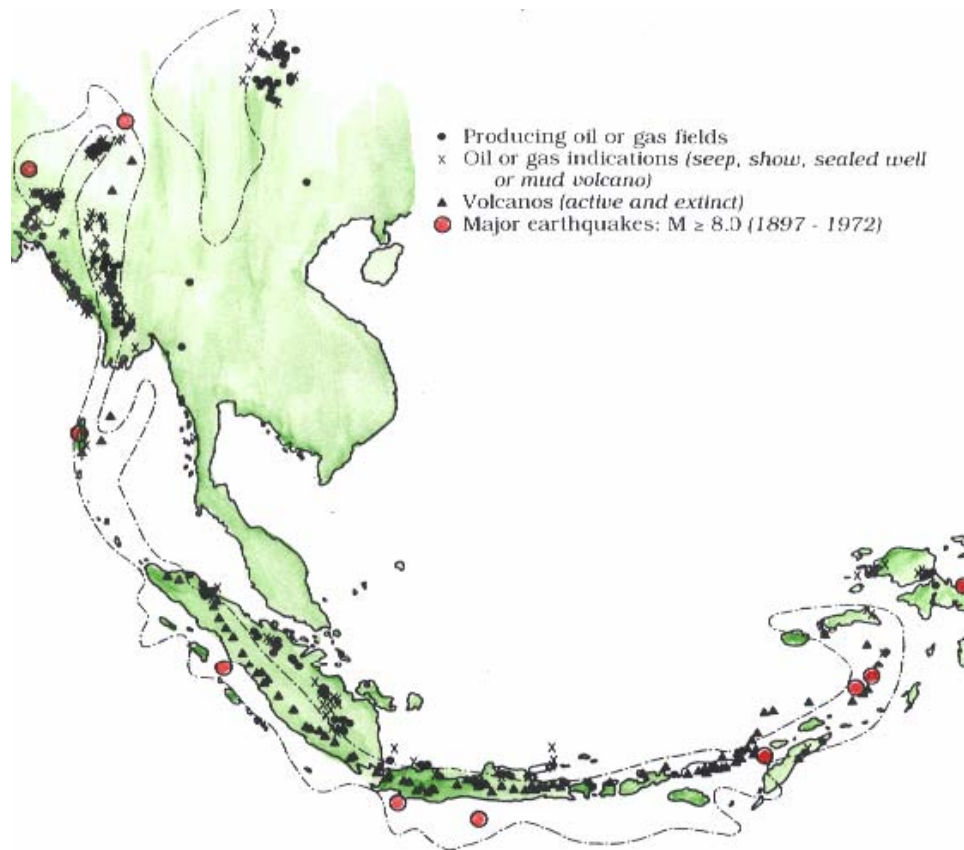


Figure 6. Correlation between seismic and volcanic activity and petroleum occurrence in South East Asia. One can notice the curious circular shape as a possible remnant of an ancient crater resulting from an astral impact.

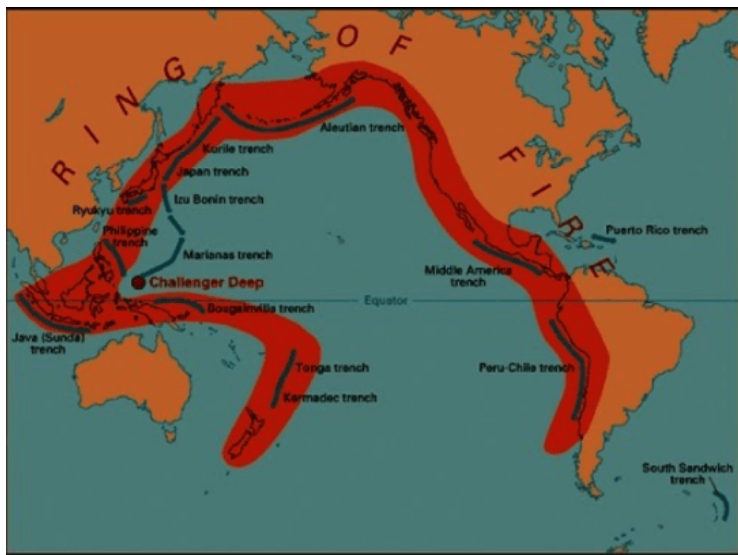


Figure 7. Ring of fire surrounding the Pacific Ocean.

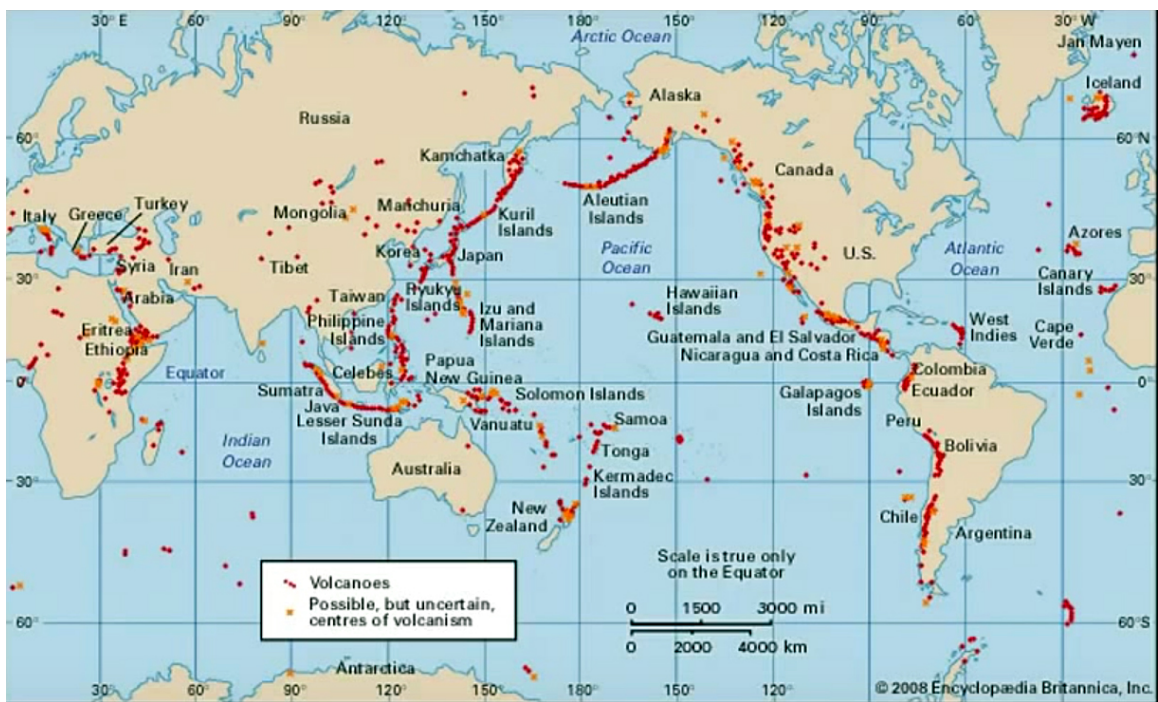


Figure 8. Earth's volcanism. Source: Encyclopedia Britannica.

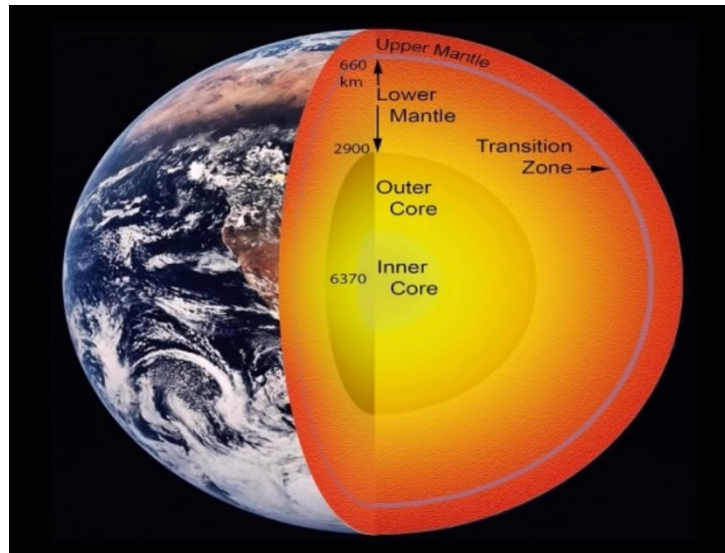
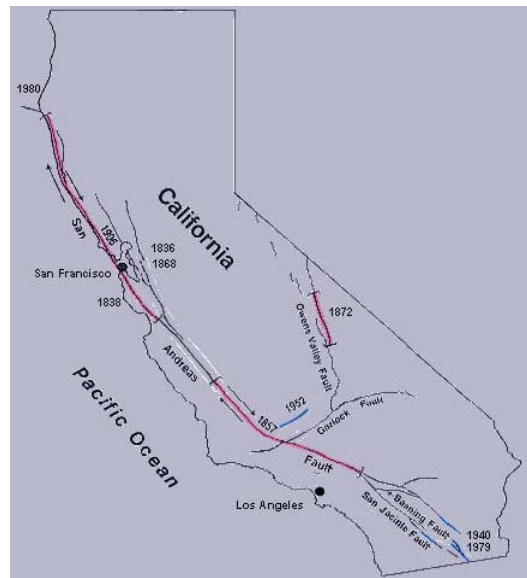
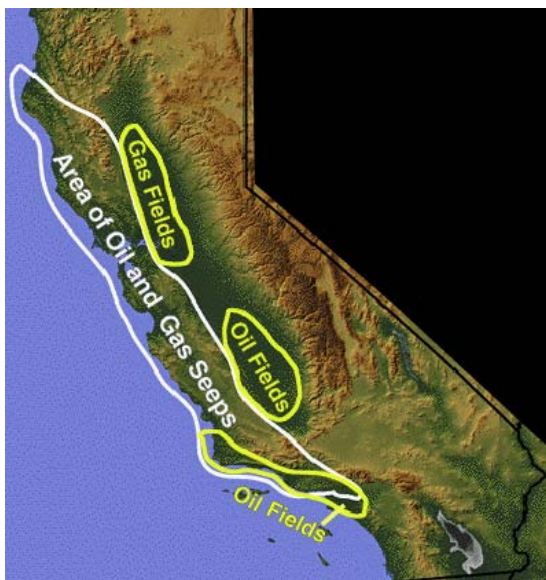


Figure 9. Earth's composition.

In 1857, one of the largest earthquakes ever recorded in the USA occurred just north of the Carrizo Plain, visible to the right of the San Andreas Fault. With an estimated magnitude of 8.0 on the Richter magnitude scale, the quake ruptured the surface along a 220 miles or 350 kilometers stretch of the fault, rattling the then sleepy pueblo of Los Angeles in the process.

The San Andreas Fault forms the active boundary between the North American and Pacific plates (Fig. 11). It stretches some 800 miles or 1,200 kilometers, making it the longest fault in the state of California.



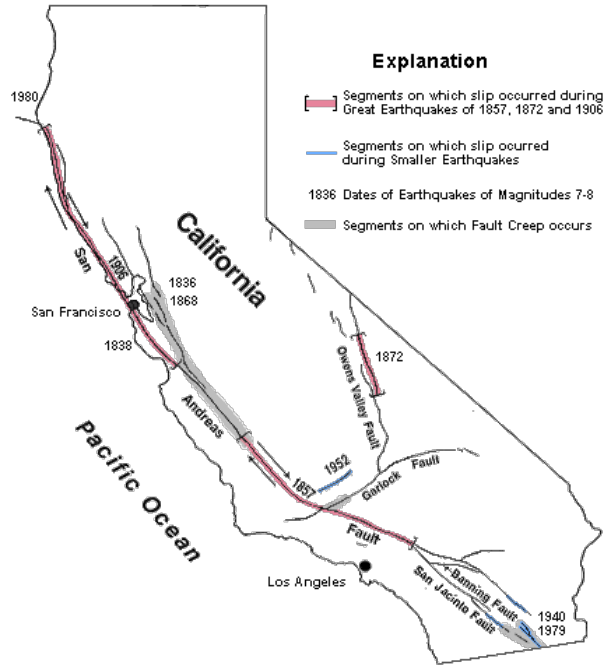


Figure 10. Occurrence of the California hydrocarbon basins along the San Andreas Fault.



Figure 11. San Andreas Fault from the Shuttle Radar Topography Mission (SRTM).
Photo: NASA.



Figure 12. Natural gas leak crater was created in 1971 when the natural gas field top collapsed in Derwese, Turkmenistan.

In geological terms, the Strait of Hormuz at the Arabian/Persian Gulf lies near a location where two continental plates collide. There, the Arabian plate slides under the Eurasian plate. Tectonic shifts pushed up the mountains near Fujairah and may have originated the region's petroleum. Twenty percent of the world's crude petroleum comes from the Gulf region. Over 80 percent, or almost 17 million metric tons / day, makes its way on ships through the Strait of Hormuz to Europe and the Far East..

The economies of Japan and South Korea depend on petroleum from the Arabian/Persian Gulf which covers as much as three quarters of their petroleum needs. For China's economy, it is over one half. A portion of the petroleum is pumped through Saudi Arabia's East-West Pipeline to the Red Sea. A pipeline built by the United Arab Emirates (UAE) carries crude petroleum from Abu Dhabi to Fujairah. The container port of Dubai, a major hub in east-west seaborne trade, is dependent upon the strait of Hormuz as the seaports of Abu Dhabi, Kuwait, Bahrain and Qatar.

The Strait of Hormuz is the aorta of the petroleum trade. Traders and smugglers have flourished there, crossing to and fro between the Arab side and the big ports on the Iranian shore. In the 13th century, Marco Polo described the strait as a hub of long-distance trade. When he discussed the strait of Hormuz in his "Travels," Marco Polo wrote that many ships there "are lost, for in that Sea of India the storms are often terrible."



Figure 13. Strait of Hormuz is 34 miles or 54 kilometers in width. Source: NASA.

Chekaliuk [22, 23], suggests that in the process of the postulated deep seated synthesis of petroleum from methane, the volume of the mantle material decreases. This transformation generates conditions favorable for the sinking of the crust of the Earth and the formation of deep basins whose sizes match the scale and size of zones of petroleum reservoirs formations.

The accumulation and filling of petroleum basins with water, and later with sediments, increases the geostatic loading in the zones of synthesis. This would stimulate the condensation of petroleum and the enlargement of molecules and thereby additional sinking of those areas of the Earth's crust.

The enlargement of a volume of hydrocarbon center could result in the formation of deep faults which progress into a disturbance from the active zone to the Earth's surface. The convective transfer of the hydrocarbon center from one depth to other ones to the surface of the Earth could cause the destruction of this center and its enlargement of volume. The natural gas in the Earth's crust could be causing earthquakes as it is trying to escape from its mantle.

This theory suggests that sea water flooding of petroleum reservoirs to enhance secondary recovery such as at the Ghawar field in Saudi Arabia, may eventually lead to increased seismic activity in its surrounding region.

The counter argument is that Tectonic movements are known to be able to radically reshuffle rock strata, leaving younger sedimentary petroleum or gas bearing rock beneath basement rock, leading in some cases to the appearance that petroleum has its source in Precambrian crystalline basement, when this may not actually be the case.

4.24 THE PETROLEUM AND COAL CONNECTION

In the La Brea tar pits in Los Angeles, California, buried saber-toothed tigers and other fossils were found. Similar tar pits and lakes exist in Trinidad. The coal currently extracted is a hard, brittle material. It is thought that it was once a liquid, because embedded in the middle of a six foot seam of coal, fossils such as wings of birds or leaves of plants were found. They are undestroyed and preserved, with every cell in the fossil filled with exactly the same coal as all the coal on the outside. A hard, brittle coal is not going to get into each cell of a delicate leaf without destroying it. So it can be thought that it was a thin liquid at one time which gradually hardened. This is attributed to petroleum, which gradually became stiffer and harder. This is an explanation for the origin of coal. So the fact that coal contains fossils does not necessarily mean that it is a fossil fuel.

One can use the opposite argument that those fossils found in coal prove that coal is not made from those fossils. A forest could not be fully mulched up so that it is a completely featureless big black substance and then find in it one leaf that is perfectly preserved.

4.25 CARBONACEOUS METEORITES

The idea that complex hydrocarbons, the main components of petroleum, are a natural part of the Earth's crust comes as no surprise to scientists who study comets and asteroids. Some of the meteorites that fall to Earth are rich in tar like hydrocarbons. Comets such as Halley and Hale-Bopp are thought to have a skin of tar-like material covering a dirty snowball, like an ice cream cone dipped in chocolate syrup.

The early Earth was made of the same materials as comets and asteroids, so the presence of hydrocarbons deep within the Earth is to be expected. It used to be thought that the heat from radioactivity deep underground was sufficient to break up any hydrocarbon molecules. However, a group of Ukrainian and Russian scientists argue that the enormous pressures prevent their decomposition.

It is thought that water on Earth originated from a bombardment by water-rich comets and meteorites. Thus the argument was advanced that even if the Earth did not manage to retain its original supply of hydrocarbons it may be likely that the rain of comets, space dust and asteroids over billions of years would have kept the crust of the Earth topped off with the raw ingredients for petroleum.

Petroleum and coal could have been made from materials in which heavy hydrocarbons were common components. Meteorites, the debris left over from the formations of the planets contain carbon in an unoxidized form as hydrocarbons as petroleum and coal-like particles, yet they definitely did not contain biological life. This is found in one large class of meteorites, the carbonaceous meteorites and on many of the other planetary bodies such as planetary moons in the solar system such as the Titan moon of the planet Saturn.

The carbonaceous meteorites, and particularly the carbonaceous chondrites have a chemical composition that includes the presence of carbon with a weight concentration of 0.1-6.0 percent. Their age is typically 3.0-4.5 billion years. Their origin is abiotic, thought to be formed in supernovae star explosions forming the heavy elements. The crystal structures of these objects suggest that they have existed in the cold of space close to the absolute zero temperature and below the freezing point of water since the time of their formation; excluding the possibility that life or biological matter ever existed on them.

Theporphyrins, isoprenoids, terpinenes and chlorins found in petroleum were also found in about 44 meteorites are shown in Table 2.

Table 2. Materials found in petroleum and in meteorites.

Meteorite type	Meteorite name
Amphoterite	Chainpur Ngavi Semarkona
Bronze chondrites	Charis Ghubara Kulp Tieschitz
Carbonaceous chondrites	Alais Bali Bells Cold Bockeveld Eracot Felix Groznaia Haripura Ivuna Kaba Kainsaz Karoonda Lance Mighei Mokoia Murchison Murrey Orgueil Ornans Pseudo Renazzo Santa Cruz St. Capraix Staroye Boriskino Tonk Vigarano Warrenton
Enstatite	Abee Hvittis Indarkh
Hyperthene chondrites	Bishunpur Bruderheim Gallingebirge

	Holbrook Homestead Krymka
Iron	Arus Yardymli Burgavli Canyon Diabolo Odessa Toluca
Aubrite	Norton County
Ureilite	Dialpur Goalpara Novo Urei

The carbon material in these meteorites is found in both liquid and solid forms. However it cannot be considered as a source of abiogenic petroleum since their heating upon impact on the Earth surface or their explosion in its atmosphere could have decomposed their hydrocarbon molecules. Some scientists thus conclude that meteorites and comets can be considered as a source of the Earth's carbon and water, but not its hydrocarbons.

4.26 TITAN'S METHANE

The Cassini-Huygens mission was a cooperative project of the USA's NASA, the European Space Agency and the Italian Space Agency. The Jet Propulsion Laboratory (JPL), a division of the California Institute of Technology in Pasadena, California, managed the mission for NASA's Science Mission Directorate, Washington, D.C. The Cassini orbiter was designed, developed and assembled at JPL. The radar instrument was built by JPL and the Italian Space Agency, working with team members from the USA and several European countries.

The Huygens probe was launched from the Cassini spacecraft and descended through the smog-like atmosphere of Saturn's moon Titan. It revealed a strangely Earth-like topography of river channels and a frozen sea. Given the extremely cold environment on Titan, as well as Mars, there is little likelihood that Titan's methane is of biological origin.

At minus 179 degrees Celsius or minus 290 degrees Fahrenheit, Titan's liquid hydrocarbons are in the form of methane and ethane are present on the moon's surface, and tholins probably make up its dunes. The term "tholins" was coined by astrophysicist Carl Sagan in 1979 to describe the complex organic molecules at the heart of prebiotic chemistry. Scientists believe that methane might be supplied to the atmosphere by venting from the interior in cryo-volcanic eruptions. As humans are carbon-based life, understanding how far along the chain of complexity towards life that chemistry can go in an environment like Titan will be important in understanding the origins of life throughout the universe,

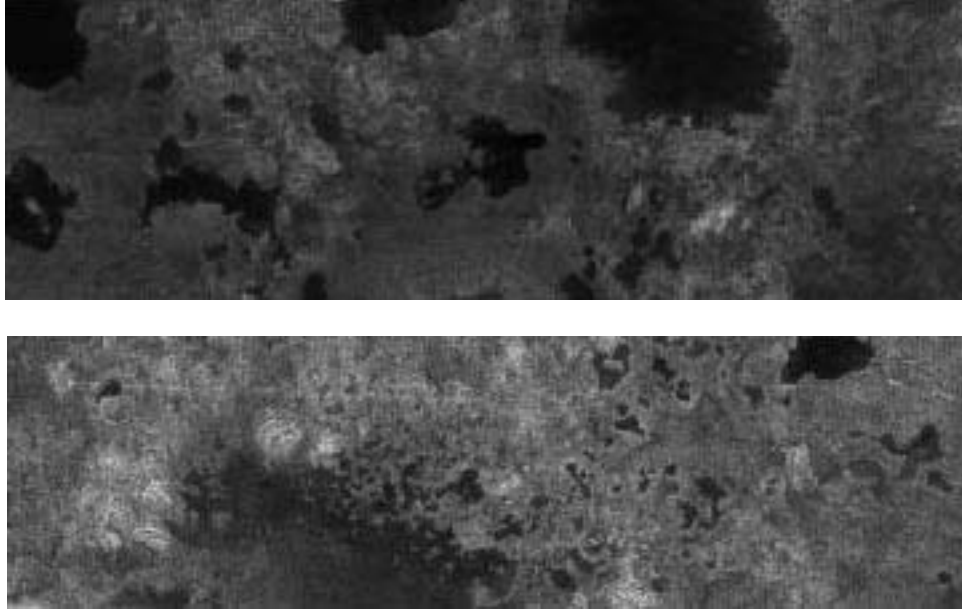


Figure 14. Two images acquired by the Cassini space radar instrument in the synthetic aperture mode on July 21, 2006. The top image is centered near 80 degrees north, 92 degrees west and measures about 420 kilometers by 150 kilometers (260 miles by 93 miles). The lower image is centered near 78 degrees north, 18 degrees west and measures about 475 kilometers by 150 kilometers (295 miles by 93 miles). The smallest details are about 500 meters (1,640 feet) across. Photo: NASA/JPL.

The Cassini spacecraft, using its radar system, discovered evidence for hydrocarbon lakes on Titan. Dark patches, resembling terrestrial lakes, seemed to be sprinkled all over the high latitudes surrounding Titan's north pole.

Liquid methane or ethane may be forming lakes on Titan, particularly near the somewhat colder polar regions. A variety of dark patches were revealed, some with channels leading in or out of them. These channels have a shape that implies they were carved by a liquid. Some dark patches and connecting channels are completely black reflecting back no radar signal suggesting that they are smooth. Rims can be seen around the dark patches, suggesting deposits that might form as liquid evaporates.

Methane in Titan's atmosphere is stable as a liquid under Titan conditions, as is its abundant chemical product, ethane. However, liquid water is not. The dark areas are thought to be lakes of liquid methane or ethane. Titan is the only body in the solar system besides Earth known to possess lakes. These lakes wax and wane over time, and winds may alter the roughness of their surfaces.

A mystery is that methane is destroyed in the Titan's atmosphere by ultraviolet light from the sun, so Titan's methane should have disappeared eons ago, but some little understood process continues to replenish it. One suggested theory is that it is created by the interaction of rock and water deep inside Titan where the temperature could be as high as 750 °F or 400 °C. The process is designated as serpentinization and has been experimentally demonstrated in laboratories on Earth.

The methane on Titan is considered as abiogenic, formed by any one or several of hundreds of possible chemical reactions. Abiogenic formation of petroleum from natural

carbonates such as limestones, on the other hand requires conditions that occur only very deep in the Earth's crust. Thus abiogenic petroleum and gas deposits, if they do exist on Earth, would be too deep to discover or produce economically. They could only be thought to perhaps be replenishing the near-surface reservoirs.

The source of Titan's and possibly Mars' methane being non biological (Figs. 14, 15), strengthens the argument being made by proponents of the theory of abiogenic petroleum.

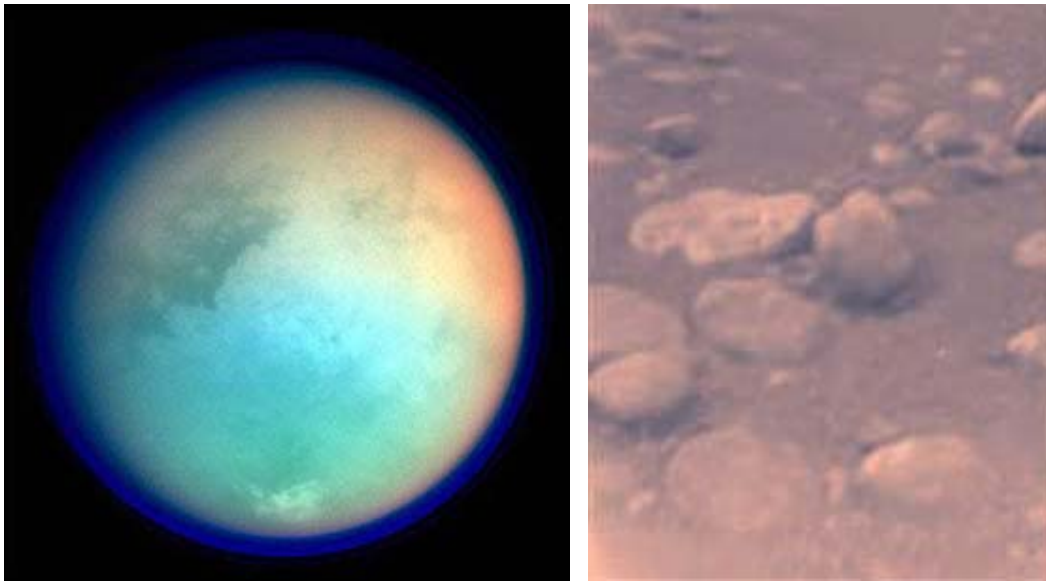


Figure 15. Titan moon of Saturn and its surface. Saturn has 82 moons. Fifty-three moons are confirmed and named and another 29 moons are awaiting confirmation of discovery and official naming. Saturn's moons range in size from larger than the planet Mercury — the giant moon Titan — to as small as a sports arena. Some Saturn moons are: Titan, Rhea, Lapetus, Dione, Tethys, Enceladus, Mimas, Hyperion, Phoebe, Janus, Epymethius, Prometheus and Pandora. Photos: NASA/JPL.

4.27 MARS METHANE

Researchers studying the Martian atmosphere discovered and measured methane using telescopes with infrared spectrometers. These instruments identify chemical compounds by analyzing their unique light absorption properties. NASA's Infrared Telescope Facility and the W. M. Keck telescope identified three spectral lines that indicate the presence of methane.

Methane is the main component of natural gas. Most of the Earth's methane comes from living organisms as they digest nutrients. However, other events, like iron oxidation, can also cause the release of methane.

The discovery of substantial plumes of methane in the northern hemisphere of Mars in 2003 indicates that some ongoing process is releasing the gas. Mars releases methane at a rate comparable to that of the massive hydrocarbon seep at Coal Oil Point in Santa Barbara, California during its northern midsummer.

Mars methane is being released as concentrated plumes at specific latitudes. Such

plumes could come from various kinds of geological events. Underground bacterial communities could also be producing the methane. Or now-extinct living systems could have produced the methane long ago, with it only now being released through pores or fissures created by seasonal temperature variations.

On Earth, 90 percent of the methane in the atmosphere comes from the biochemical activity of life. The rest is produced by geochemical processes. The Mars methane's specific isotopic makeup could reveal whether its origins are biochemical or geological.

If microscopic organisms produce methane, they are likely to exist far below the surface, where it is warm enough for water to remain in a liquid state. Water, carbon, and energy sources are necessary for all known forms of terrestrial life.

On Earth, microorganisms survive about 1.2-1.9 miles beneath the Witwatersrand basin of South Africa, where natural radioactivity splits water molecules into molecular hydrogen and oxygen. The organisms use the hydrogen for energy. It might be possible for similar organisms to survive for billions of years below the permafrost layer on Mars, where water is liquid, with radiation supplying energy, and carbon dioxide providing carbon.

4.28 KIDD CREEK MINE ISOTOPIC SIGNATURES

Abiogenic petroleum advocates argue that like magma, crustal methane gradually works its way up towards the Earth's surface where it can accumulate under salt domes and other petroleum and gas trapping formations. This does in fact happen to a small extent.

Measurements taken deep in the Kidd Creek Mine in Ontario, Canada have implied evidence of abiogenic gas identified by a unique inorganic chemical signature using carbon and hydrogen isotopes.

Natural carbon is nearly all C^{12} , with 1.11 percent being the isotope C^{13} . Organic materials usually contain less C^{13} , because photosynthesis in plants preferentially selects C^{12} over C^{13} . Petroleum and natural gas typically show a C^{12} to C^{13} ratio similar to that of the biological materials from which they are assumed to have originated. The C^{12} to C^{13} ratio is a generally observed property of petroleum and is predicted by the biotic theory; it is not merely an occasional aberration

Barbara Sherwood Lollar, the director of the Stable Isotope Laboratory at the University of Toronto, Canada, reported about three different types of isotopic signatures in terrestrial methane. One is clearly inorganic, the second is organic and the third is a hybrid mixture of both. The last is believed to be formed when microbes consume the hydrogen found in these Precambrian deposits and create their own methane, which mixes with the inorganic methane.

A problem is that to-date nobody has been able to show the inorganic signature in any of the economic deposits, reinforcing the argument that any of the economic deposits found to date are in fact quite consistent with biological origins. The inorganic signature does not show up in the Gulf of Mexico, Russian or Middle East fields.

4.29 EARTH'S ATMOSPHERIC GASES

The early Earth's atmosphere is thought to have contained appreciable amounts of carbon dioxide, methane and nitrogen, but not oxygen. The action of volcanic activity producing clouds of dust and water vapor, combined with the Earth's bombardment with cosmic ray particles creating plasma discharge channels, resulted in frequent lightning discharges, which continue to this day in storm events.

As life forms evolved on Earth, photosynthetic organisms used sunlight to synthesize carbohydrates and hydrocarbons from CO_2 and H_2O and released oxygen, which gradually filled up the atmosphere with the 21 percent oxygen in volume that we have today. In the process, carbon was fixated in organic matter and calcium carbonate in sea shells and carbonate rocks.

Theoretically, if all available organic fossil fuels were used up, this would return the fixated carbon in organic matter back to the atmosphere in the form of CO_2 , depleting most of its O_2 content. The existing terrestrial life forms on Earth would have become extinct by then due to oxygen depletion. With the abiogenesis of hydrocarbons as the primary mode of their generation, it is difficult to explain the presence of the large quantity of oxygen in the Earth's atmosphere. A logical conclusion is that the abiogenic path can only be a secondary process.

4.30 BIOMARKERS IN PETROLEUM

Petroleum contains numerous organic compounds such as porphyrins, isoprenoids, pristane, phytane, clorins, terpenes and cholestane. Their presence is construed as an indication that petroleum has a biological origin. However, pristane and phytane are branched alkanes of the isoprenoid class which are not necessarily of biological origin.

Cholestane, $\text{C}_{27}\text{H}_{48}$ is a highly reduced hydrocarbon found in petroleum, but it should not be confused with cholesterol which has a similar chemical structure and carbon skeleton. Cholesterol is of biological origin, and is not found in natural petroleum, while cholestane is.

Isoprenoids, including phytane and pristane are also produced in the Fischer-Tropsch process, which is not a biological phenomenon.

Biological materials such as spores and pollen are found in petroleum, and considered as biomarkers. It is possible, though that they could have been leached into solution in the strong petroleum solvent from organic matter in sedimentary reservoirs. Petroleum in reservoirs on the Permian age in fact also contains spores and pollen of older geological ages such as the Carboniferous and the Precambrian.

4.31 DISCUSSION

When the Earth was formed it should have contained substantial amounts of carbon and hydrocarbons. It is also possible that the heat from radioactive decay may be contributing to the creation of hydrocarbons in the Earth's mantle.

The abiogenic petroleum formation hypothesis holds that as petroleum is drawn out of the known reservoirs through petroleum wells, the field pressure is slightly reduced, thereby allowing more deep petroleum to migrate up from the mantle and recharge the reservoir from below. This suggests that decreasing the existing reservoirs' pressure

should be attempted in view of recharging them, rather than increasing their pressure through water and gas injection.

Care should be exercised in the management of existing reservoirs so as not to allow circumstances favorable to seismic activity to occur.

If substantiated, the study of the abiotic petroleum origin theory could provide practically unlimited hydrocarbon fuels recharge from below the existing sedimentary petroleum basins in the Earth's crust from its mantle.

It is a fact that the great majority of economically exploitable petroleum basins are currently sedimentary and shallow in nature. There possibly exist sources of inorganic hydrocarbons and that some deep natural gas deposits may be associated with primordial methane; diffusion from them may be occurring to the surface; however it is not clear whether abiogenic liquid hydrocarbon fields exist at this time in economically extractable quantities.

REFERENCES

1. Maurina S. Sherman, "Going to Extremes," Science and Technology Review, Lawrence Livermore National Laboratory, July/August, p. 14, 2004.
2. Thomas Gold, "Terrestrial Sources of Carbon and Earthquake Outgassing," J. Petrol. Geol., Vol. 1, No. 3, pp.3-19, 1979.
3. A. I. Kravtsov, "Geochemical Scheme of the Formation of Methane and Liquid Hydrocarbons in Magmatic Processes, and the Basic Criteria of Prospects for Oil and Gas Deposits," in Genesis of Oil and Gas, Nedra Press, Moscow, pp. 314-325, 1967.
4. P. N. Kropotkin, and K. A. Shakhvarstova, "Solid Bitumens, Oil and Fuel Gas in Ultrabasic Intrusions, Trap Brilliants and Volcanic Pipes," in The Problem of Oil Migration and the Formation of Oil and Gas Accumulations, The State Fuel Technical Press, Moscow, pp. 151-164, 1959.
5. N. A. Kudryavstev, "Against the Organic Hypothesis of Petroleum Origins," Petroleum Economy, No. 9, Moscow, p. 17, 1951.
6. N. A. Kudryavstev, "The Modern State of the Problem of Petroleum Origin," in "Colloquium on Problems of the Origin and Migration of Petroleum," Ukrainian Acad. Sci. Press, Kiev, pp. 38-81, 1955.
7. N. A. Kudryavstev, "Geological Evidence of Deep Petroleum Origins," Trans. of the All-Union Research, Geol. Exploration Petroleum Inst., State Technical Press, Leningrad, p. 210, 1959.
8. N. A. Kudryavstev, "Oil, Gas and Solid Bitumens in Igneous and Metamorphic Rocks," State Technical Press, Leningrad, p. 230, 1959.
9. N. A. Kudryavstev, "The State of the Question on Genesis of Oil in the Year 1966," in Genesis of Oil and Gas, Nedra Press, Moscow, pp. 262-291, 1967.
10. N. A. Kudryavstev, "The Genesis of Oil and Gas," Trans. of the All-Union Research, Geol. Exploration Petroleum Inst., Nedra Press Leningrad, pp. 216, 1973.
11. V. B. Porfir'yev, "On the Nature of Petroleum," in Problems of Oil and Gas Origin and Conditions of the Formation of Their Deposits, The State Fuel Technical Press, Moscow, pp. 26-40, 1960.
12. V. B. Porfir'yev, "The Present State of the Problem of Petroleum Formation," in Genesis of Oil and Gas, Nedra Press, Moscow, pp. 292-324, 1967.

13. V. B. Porfir'yev, "On a Criticism of the Theory of the Inorganic Origin of Petroleum," in "Colloquium on the Inorganic Origin of Petroleum," Scientific Thought Press, Kiev, pp. 34-54, 1971.
14. V. B. Porfir'yev, "Experience of Geological Analyses of Questions of Petroleum Content," in "Colloquium on the Inorganic Origin of Petroleum," Scientific Thought Press, Kiev, pp. 3-34, 1971.
15. V. B. Porfir'yev, "Inorganic Origin of Petroleum," Bull. Am. Assoc. Petrol. Geol., Vol. 58, No. 1, pp. 3-33, 1974.
16. V. B. Porfir'yev, "Significance of Theoretical Complex of Petroleum Geology in the Solution of the Problem of Commercial Oil Content," in Regularities of Formation and Distribution of Commercial Oil and Gas Fields, Scientific Thought Press, Kiev, pp. 17-27, 1975.
17. V. B. Porfir'yev, V. A. Krayushkin, V. P. Klochko, V. B. Sollogub, A. V. Chekunov, G. N. Ladyzhenskiy and V. I. Sozanskii, "Geological Criteria of Prospects for New Oil and Gas Reserves in the Territory of Ukraine," Scientific Thought Press, Kiev, p. 150, 1977.
18. V. B. Porfir'yev, V. A. Krayushkin, N. S. Erofeev, G. P. Ovanesov, N. A. Eremenko, I. M. Mikhailov, V. A. Moskvich, I. Ye. Kotelnikov, Z. V. Ulybabov and P. M. Zozula, "Perspectives of Prospects for Oil Deposits in the Crystalline Basement of the Pripyat' Basin," Geological Journal, Vol. 37, No. 5, pp.7-25, 1977.
19. R. H. Dott, Sr. and M. J. Reynolds, "Sourcebook for Petroleum," Tulsa, p. 471, 1969.
20. E. R. Owen, "Trek of the Oil Finders: A History of Exploration for Petroleum," Amer. Assoc. Petrol. Geol., Tulsa, p. 1647, 1975.
21. A. I. Kravtsov and G. I. Voitov, "Evaluation of the Role of Faults in the Gas Exchange between the Lithosphere and the Atmosphere Illustrated in Southern Daghستان," Proc. High. Educ. Institutions. Geology and Exploration, Vol. 19, No. 4, pp. 18-26, 1976.
22. E. B. Chekaliuk, "Petroleum in the Upper Mantle of the Earth," Scientific Thought Press, Kiev, p. 256, 1967.
23. E. B. Chekaliuk, "Energetic Processes in the Interior Part of the Earth and their Role in the Formation of Oil Fields," in Regularities of Formation and Distribution of Commercial Oil and Gas Fields, Scientific Thought Press, Kiev, pp. 66-76, 1975.
24. I. V. Grinberg, "Study of Conditions for the Synthesis of Hydrocarbons and their Genetic Relations to Kerogen-coal Material," in Regularities of Formation and Distribution of Commercial Oil and Gas Fields, Scientific Thought Press, Kiev, pp. 52-66, 1975.
25. I. I. Potapov, "Genesis of Bitumens and Formation of Oil Deposits of the Apsheron in Light of Biochemical, Geochemical, Geophysical, Lithological and Other Regularities," in Proceedings of the Discussion on the Problem of Origin and Migration of Petroleum, Ukrainian Acad. Sci. Press. Kiev. pp. 139-155, 1956.
26. B. Yu. Levin, "Organic Compounds in the Solar System," in Problems of the Origin of Petroleum, Scientific Thought Press, Kiev, pp. 174-222, 1966.
27. V. P. Porfir'yev, V. A. Krayushkin, V. P. Klochko, M. I. Ponomarenko, V. P. Palomar and M. M. Lushpey, "New Directions of Geologic Exploration Work in the Akhtyrka Oil-gas Mining District of the Dnieper-Donets Basin," Geol. J., Vol. 42, No.4, pp. 1-11, 1982.
28. V. A. Krayushkin, "On the Oil and Gas Content of the Precambrian Rock in the Dnieper-Donets Basin," Lectures of the Acad. Sci. of U.S.S.R., Vol. 294, No. 4, pp. 931-933, 1987.
29. T. Gold, "Contributions to the Theory of an Abiogenic Origin of Methane and other

Terrestrial Hydrocarbons," Proc. 27th International Geological Congress, Vol. 13, Oil and Gas Fields, pp. 413-442, 1984.

30. B. Deng, T.J. Campbell, and D.R. Burris, "Hydrocarbon Formation in Metallic Iron/Water Systems", Environmental Science & Technology, vol. 31, no. 4, pp. 1185-1190, 1997.

31. Art Barber, "Soviets Offer Access to World's Deepest Drill Hole," USA Continental Scientific Drilling (CSD) Program, CSD News, Vol. 2, No. 2, p. 7, November 1991.

32. Robert F. Mahfoud, James N. Beck, "Inorganic Origin in Upper Mantle Seen Likely for Solid Hydrocarbon in Syria Plateau Basalt," Oil and Gas Journal, October 28, 1991.