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Abiogenic Deep Origin of Hydrocarbons and Oil and Gas Deposits Formation

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Additional information is available at the end of the chapter

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1. Introduction

The theory of the abiogenic deep origin of hydrocarbons recognizes that the petroleum is a primordial material of deep origin [Kutcherov, Krayushkin 2010]. This theory explains that hydrocarbon compounds generate in the asthenosphere of the Earth and migrate through the deep faults into the crust of the Earth. There they form oil and gas deposits in any kind of rock in any kind of the structural position (Fig. 1). Thus the accumulation of oil and gas is

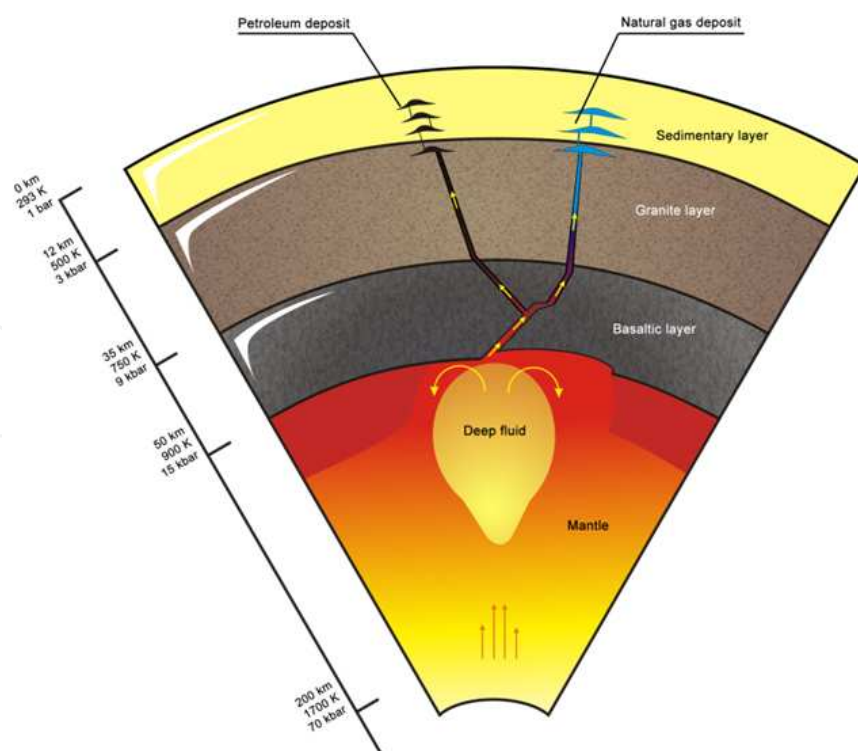


Figure 1. A scheme of genesis of hydrocarbons and petroleum deposits formation.

considered as a part of the natural process of the Earth's outgassing, which was in turn responsible for creation of its hydrosphere, atmosphere and biosphere. Until recently the obstacles to accept the theory of the abyssal abiogenic origin of hydrocarbons was the lack of the reliable and reproducible experimental results confirming the possibility of the synthesis of complex hydrocarbon systems under the conditions of the asthenosphere of the Earth.

2. Milestones of the theory of abiogenic deep origin of hydrocarbons

According to the theory of the abyssal abiogenic origin of hydrocarbons the following conditions are necessary for the synthesis of hydrocarbons:

- adequately high pressure and temperature;
- donors/sources of carbon and hydrogen;
- a thermodynamically favorable reaction environment.

Theoretical calculations based on methods of modern statistical thermodynamics have established that:

- polymerization of hydrocarbons takes place in the temperature range 600-1500 degrees C and at pressures range of 20-70 kbar [Kenney *et al.*, 2002];
- these conditions prevail deep in the Earth at depths of 70-250 km [Carlson *et al.* 2005].

Thermobaric conditions

The asthenosphere is the layer of the Earth between 80-200 km below the surface. In the asthenosphere the temperature is still relatively high but the pressure is greatly reduced comparably with the low mantle. This creates a situation where the mantle is partially melted. The asthenosphere is a plastic solid in that it flows over time. If hydrocarbon fluids could be generated in the mantle they could be generated in the asthenosphere zone only. In the paper [Green *et al.* 2010] published in *Nature* the modern considerations about thermobaric conditions on the depth down to 200 km are shown (Fig. 2).

Composition

Donors of carbon

Mao *et al.*, 2011 demonstrate that the addition of minor amounts of iron can stabilize dolomite carbonate in a series of polymorphs that are stable in the pressure and temperature conditions of subducting slabs, thereby providing a mechanism to carry carbonate into the deep mantle. In [Hazen *et al.*, 2012] authors suggest that deep interior may contain more than 90% of Earth's carbon. Possible sources of the carbon in the crust are shown on the Fig. 3.

Donors of hydrogen

Experimental data published in *Nature* recently [Green *et al.* 2010] shows that water-storage capacity in the uppermost mantle "is dominated by pargasite and has a maximum of about 0.6 wt% H₂O (30% pargasite) at about 1.5 GPa, decreasing to about 0.2 wt% H₂O (10% pargasite) at 2.5 GPa". Another possible source of hydrogen is hydroxyl group in some minerals (biotite, muscovite).

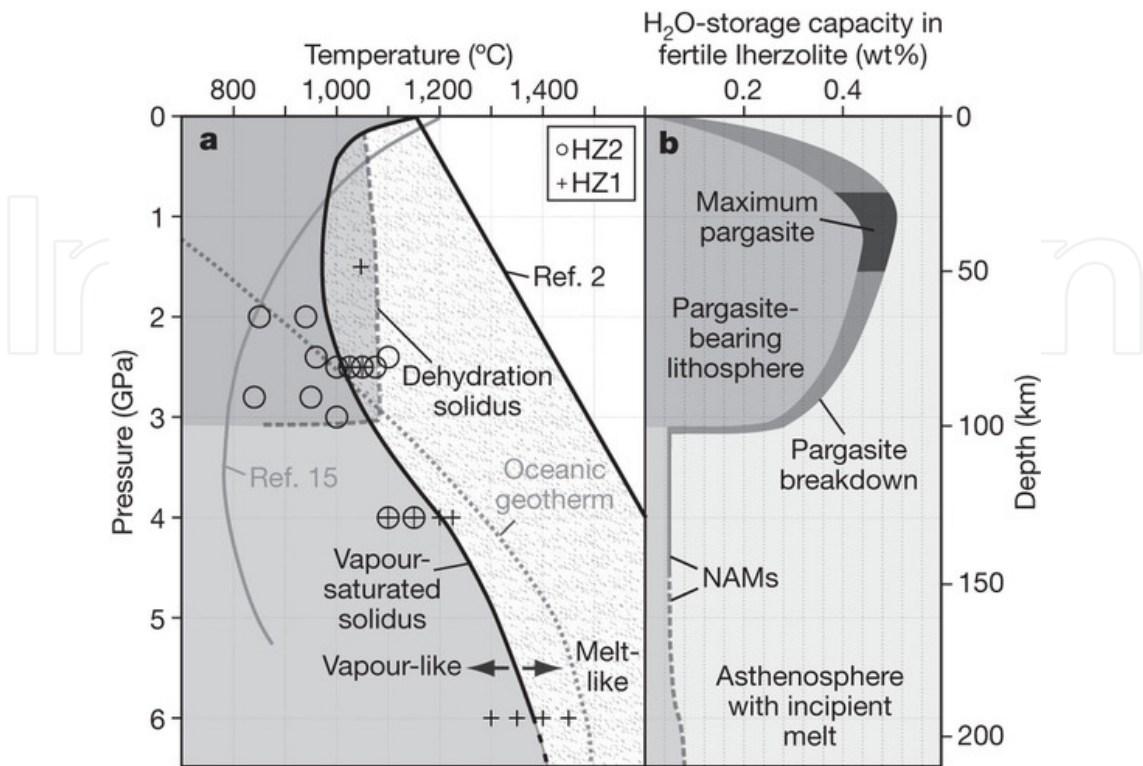


Figure 2. Thermobaric conditions in the depth [Green et al. 2010].

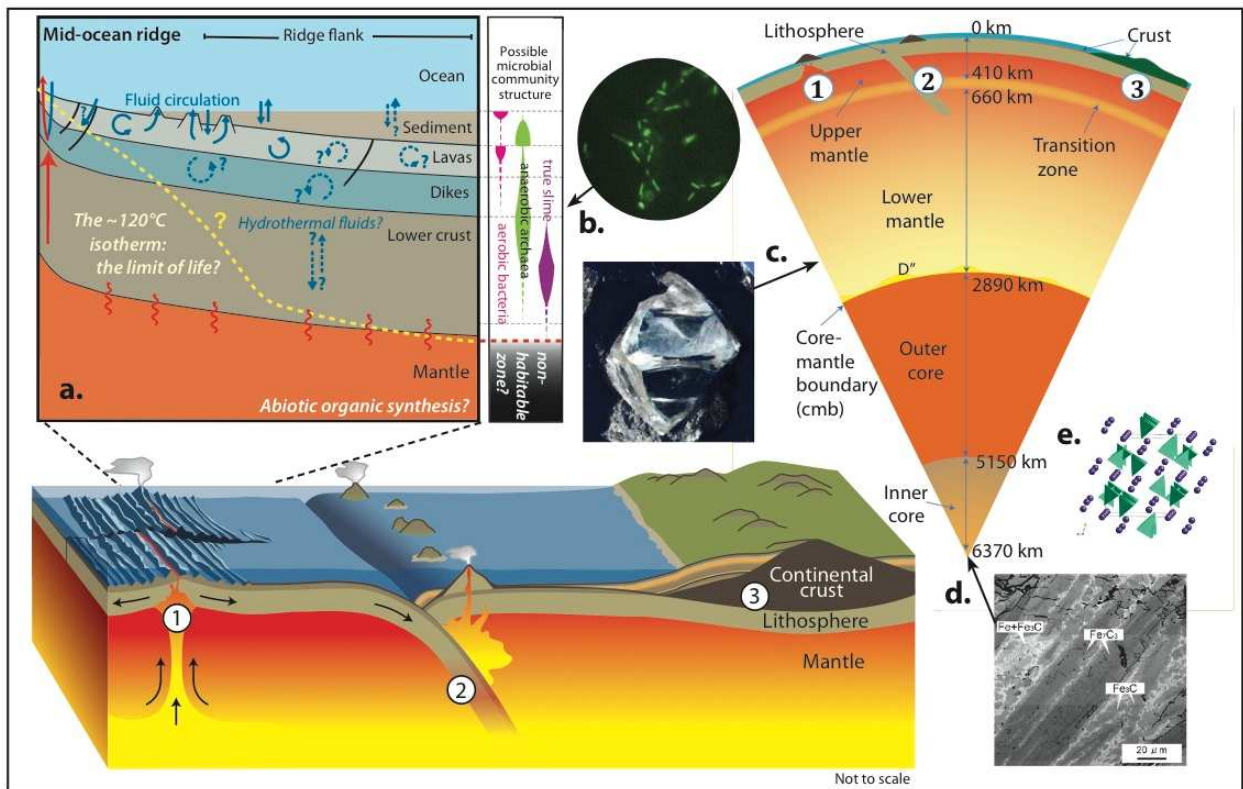


Figure 3. Sources of the carbon in the crust (adapted from images by R. Coggon and K. Nakamura).

The conclusion from the presented data is the following.

On the depth of 100 km temperature is about 1250 K and pressure is 3 GPa. On the depth of 150 km temperature is about 1500-1700 K and pressure is 5 GPa.

Both donors of carbon (carbon itself, carbonates, CO₂) and hydrogen (water, hydroxyl group of minerals) are present in the asphenosphere in sufficient amounts. Thermodynamically favorable reaction environment (reducing conditions) could be created by a presence of FeO. The presence of several present of FeO in basic and ultra-basic rocks of asthenosphere is documented.

Thus, abiogenic synthesis of hydrocarbons can take place in the basic and ultra-basic rocks of the asthenosphere in the presence of FeO, donors/sources of carbon and hydrogen. The possible reaction of synthesis in this case could be presented as follows:

- reduced mantle substance + mantle gases → oxidized mantle substance + hydrocarbons or
- combination of chemical radicals (methylene (CH₂), methyl (CH₃)). Different combinations of these radicals define all scale of oil-and-gas hydrocarbons, and also cause close properties and genetic similarity of oils from different deposits of the world.

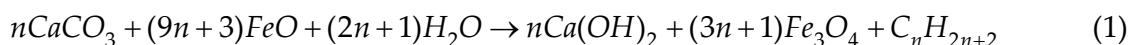
Major element composition of various mantle materials is presented in Table 1 [Carlson *et al.*, 2005].

	<i>Fertile</i>	<i>Oceanic</i>	<i>Massif</i>	<i>Off-Craton</i>	<i>Low-T Craton</i>	<i>High-T Craton</i>
SiO ₂	45.40	44.66	44.98	44.47	44.18	44.51
TiO ₂	0.22	0.01	0.08	0.09	0.02	0.11
Al ₂ O ₃	4.49	0.98	2.72	2.50	1.04	0.84
FeO	8.10	8.28	8.02	8.19	6.72	8.08
MgO	36.77	45.13	41.15	41.63	46.12	44.76
CaO	3.65	0.65	2.53	2.44	0.54	1.08

Table 1. Major element composition of various mantle materials

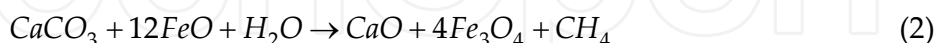
3. Experimental results

One of the first reliable and reproducible experimental results confirming the possibility of hydrocarbons synthesis under upper mantle conditions were published by [Kutcherov *et al.*, 2002]. The authors used a CONAC high-pressure chamber. The stainless-steel and platinum capsules with the volume of 0.6 cm³ were used for the experiments. The filled capsule was placed into the high-pressure chamber, pressurized and then heated to certain pressure and temperature. The treatment in the chamber for the necessary time was followed by quenching to room temperature at a rate of the order of 500 K/s, whereupon the pressure was decreased to normal pressure. The composition of the reaction products was studied by mass spectroscopy, gas chromatography, and X-ray. The initial reactants in the synthesis were chemically pure FeO (wustite), chemically pure CaCO₃ (calcite), and double distilled water. Tentative experiments showed that the synthesis is described by the reaction:



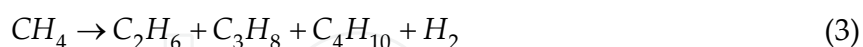
where $n \leq 11$.

[Scott *et al.*, 2004] used the diamond anvil cell method with laser and resistive heating to investigate in-situ the behaviour of the system $\text{CaCO}_3\text{-FeO-H}_2\text{O}$ at a pressure of 5-11 GPa and for a temperature range of 800 – 1500 K. Raman spectrometry and X-ray synchrotron diffraction methods were used for the analysis. In general, the reaction scheme proposed by [Kutcherov *et al.*, 2002] was confirmed by Scott *et al.*'s experimental results:



A comparison of [Kutcherov *et al.*, 2002] and [Scott *et al.*, 2004] experimental results, where the same initial reactants and thermobaric conditions were used, shows us the following. In the case of Raman spectrometry in the diamond anvil cell [Scott *et al.*, 2004] only methane was found. In [Kutcherov *et al.*, 2002] the mixture of hydrocarbons up to hexane was detected. The difference may be explained by different reasons. Quantities of saturated hydrocarbons heavier than methane, on an analogy with [Kutcherov *et al.*, 2002] should decrease dramatically with an increase in molecular weight of hydrocarbons. The sensitivity of the Raman spectrometry method in the DAC is not enough to detect the saturated hydrocarbons in comparison with relatively large volume experiments in the CONAC chamber with gas chromatography. Also fluorescence from iron-containing materials in the cell could be the obstacle to analyze these saturated hydrocarbons dispersed in the diamond anvil cell.

To check the above-mentioned explanation the behaviour of pure methane at pressure range 1-14 GPa at the temperature interval 900-2500 K was studied [Kolesnikov *et al.*, 2009]. The experiments have shown that methane is stable at temperature below 900 K in the above-mentioned pressure range. In the temperature interval 900-1500 K at 2-5 GPa the formation of heavier alkanes (ethane, propane, and butane) from methane was observed:

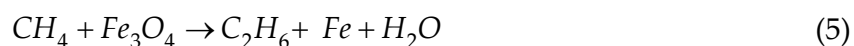


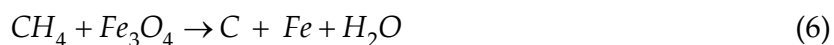
At temperature higher than 1500 K methane dissociates to carbon (graphite) and molecular hydrogen:



In [Kolesnikov *et al.*, 2009] the redox conditions of the mantle were also modeled by introducing into a system of magnetite (Fe_3O_4), which was partially transformed to iron (0) forming a redox buffer.

The introduction of Fe_3O_4 did not affect the thermobaric conditions of methane transformation. Pure iron and water were detected in the reaction products. This gives us the possibility to suggest the following pathway of reactions:



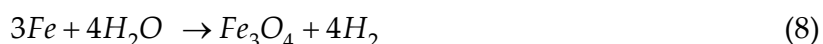


The experimental results confirming the possibility of synthesis of natural gas from inorganic compounds under the upper mantle conditions were published in [Kutcherov *et al.*, 2010]. The experimental results received in CONAC high-pressure chamber and in a split-sphere high-pressure device [6] are shown in Table 2. The gas chromatography and X-ray technique were used to analyze the reaction products.

If the carbon donor was $CaCO_3$ (experiments 1 and 2), the methane concentration in the produced mixture was as that in “fat” (rich in heavy hydrocarbons) natural gas (as at the Vuktilskoe gas field). If the carbon donor was individual carbon (experiments 3 and 4), the hydrocarbon composition corresponded to “dry” (methane-rich) natural gas (as at the Severo - Stavropolskoe gas field). Rapid cooling (quenching) fixes CH_4 and C_2H_6/C_2H_4 in the reaction products. After cooling for 4 h (experiment 4), the amount of CH_4 and C_2H_6/C_2H_4 in the reaction products increases by a factor of tens, and heavier hydrocarbons up to C_4H_{10}/C_4H_8 emerge. Thus, the time of cooling of the fluid forming at high pressure (e.g., in the course of its jet migration to the surface) has a significant effect on the final composition of the fluid. A decrease in the rate of cooling of the initial fluid results in synthesis of heavier saturated hydrocarbons in the mixture. Then, at the first stage, in case of quenching (experiment 3), the reaction is the following:



and in case of slow cooling (experiment 4), the reaction is



At the second stage, in both cases, hydrocarbons can be assumed to form from carbon and hydrogen by the reactions



Cooling shifts the equilibrium of the reaction between $Fe(0)$ and water toward the formation of hydrogen and stronger iron oxidation. The fact that reaction (8) involves more hydrogen than reaction (7) does results in an increase in the amounts of hydrocarbons in reactions (9) and (10). However, although the influence of the quenching time is obvious, the full explanation of this effect requires further investigation.

4. Formation of oil and gas deposits in the light of the abiogenic deep origin of hydrocarbons

The theory of the abiogenic deep origin of hydrocarbons denies the lateral migration of oil and gas in their reservoirs unless a hydrodynamic (hydraulic) fluid movement exists.

Experiment, reagents (mg), cooling rate	Concentration, mol.%									CH ₄ , μmol
	CO ₂	N ₂	CO	CH ₄	C ₂ H ₄ C ₂ H ₆	C ₃ H ₆ C ₃ H ₈	C ₄ H ₈ C ₄ H ₁₀	C ₅ H ₁₀ C ₅ H ₁₂		
Toroidal high-pressure apparatus (CONAC)										
experiment A quenching CaCO ₃ (104.5)+Fe(174.6)+ H ₂ O(45.3)	0.0	tr.	0,0	71.4	25.8	2.5	0.25	0	6.28	
experiment B quenching CaCO ₃ (104.7)+Fe(174.6)+ D ₂ O(42.6)	0.0	tr.	0.0	71.1	25.3	3.2	tr.	tr.	4.83	
Split-sphere high-pressure device (BARS)										
experiment C quenching C(24.5)+Fe(60.2)+H ₂ O(10.1)	0	0	0	96.1	3.84	0	0	0	0.23	
experiment D 4 h. cooling C(21.3)+Fe(98.6)+H ₂ O(15.1)	0	0	0	93.2	6.21	0.42	0.16	0	5.4	
Severo-Stavropolskoe gas field	0.23	-	-	98.9	0.29	0.16	0.05	-		
Vuctyl'skoe gas field	0.1	-	-	73.80	8.70	3.9	1.8	6.40		

Table 2. The experimental results received in CONAC high-pressure chamber and in a split-sphere high-pressure device

Capillary forces which are related to the pore radius and to the surface tension across the oil-water (or gas-water) interface (the process is described by Laplace's Equation) are, generally, 12-16 thousand times stronger than the buoyancy forces of oil and gas (according to Navier–Stokes Equation) in the natural porous, permeable media of subsurface. According to the theory of the abiogenic deep origin of hydrocarbons oil and gas accumulations are born as follows. Rising from sub-crust zones through the deep faults and their feather joints or fissures the deep petroliferous fluid is injected under high pressure into any rock and distributed there. The hydrocarbon composition of oil and gas accumulations formed this way depends on cooling rate of the fluids during their injection into the rocks of the Earth's Crust. When and where the further supply of injected hydrocarbons from the depth stops, the fluids do not move further into any forms of the Earth Crust (anticline, syncline, horizontal and tilted beds) without the re-start of the injection of the abyssal petroliferous fluids. The most convincing evidence of the above-mentioned mechanism of oil and gas deposit formations is the existence of such giant gas

fields as Deep Basin (Figure 3), Milk River and San Juan (the Alberta Province of Canada and the Colorado State, U.S.A.) The formation of these giant gas fields questions the existence of any lateral migration of oil and gas during the oil and gas accumulation process. Those giant gas fields occur in synclines where gas must be generated but not be accumulated, according to the hypothesis of biotic petroleum origin and hydrodynamically controlled migration. The giant gas volumes ($12.5 \cdot 10^{12}$ cu m in Deep Basin, $935 \cdot 10^9$ cu m in San Juan, $255 \cdot 10^9$ cu m in Milk River) are concentrated in the very fine-grained, tight, impermeable argillites, clays, shales and in tight sandstones and siltstones [Masters, 1979]. These rocks are usually accepted as source rocks cap rocks/seals rocks in petroleum geology but by no means of universally recognized reservoir rocks of oil and natural gas. All the gas-saturated tight rocks here are graded updip into coarse-grained, highly-porous and highly-permeable aquifers with no visible tectonic, lithological and stratigraphic barriers to prevent updip gas migration. Therefore, the tremendous gas volumes of above-mentioned gas fields have the tremendous buoyancy but it never overcomes capillary resistance in pores of the water-saturated reservoir rocks. Gas is concentrated in the tight impermeable sand which is transformed progressively and continuously updip into the coarse-grained, high-porous and high-permeable sand saturated by water.

5. Natural gas and oil in the recent sea-floor spreading centers

Petroleum of abyssal abiogenic origin and their emplacement into the crust of the Earth can take place in the recent sea-floor spreading centres in the oceans. Igneous rocks occupy 99 % of the total length (55000 km) of them while the thickness of sedimentary cover over the spreading centres does not exceed 450-500 m [Rona, 1988]. Additionally sub-bottom convectional hydrothermal systems discharge hot (170-430 degrees C) water through the sea bottom's black and white "smokers". Up to now more than 100 hydrothermal systems of this kind have been identified and studied by in scientific expeditions using submarines such as «ALWIN», «Mir», «Nautile», and «Nautilus» in the Atlantic, Pacific and Indian oceans respectively. Their observations pertaining to the deep abiogenic origin of petroleum are as follows:

- the bottom "smokers" of deepwater rift valleys vent hot water, methane, some other gases and petroleum fluids. Active "plumes" with the heights of 800-1000 m venting methane have been discovered in every 20-40 km between 12°N and 37°N along the Mid-Atlantic Ridge (MAR) over a distance of 1200 km. MAR's sites – TAG (26°N), Snake Pit (23°N), Logatchev (14°45'N), Broken Spur (29°N), Rainbow (37°17'N), and Menez Gwen (37°50'N) are the most interesting.
- At the Rainbow site, where the bottom outcrops are represented by ultramafic rocks of mantle origin the presence of the following substances were demonstrated (by chromatography/mass-spectrometry): CH_4 ; C_2H_6 ; C_3H_8 ; CO ; CO_2 ; H_2 ; H_2S , N_2 as well as petroleum consisted of n- C_{16} –n- C_{29} alkanes together with branched alkanes, diaromatics [Charlou *et al.*, 1993, 2002]. Contemporary science does not yet know any microbe which really generates n- C_{11} – n- C_{22} alkanes, phytan, pristan, and aromatic hydrocarbons.

- At the TAG site no bottom sediments, sedimentary rocks [Simoneit, 1988; Thompson *et al.*, 1988], buried organic matter or any source rocks. The hydrothermal fluid is very hot (290/321 degree C) for any microbes. There are the Beggiatoa mats there but they were only found at some distances from “smokers”.
- Active submarine hydrothermal systems produce the sulfide-metal ore deposits along the whole length of the East Pacific Rise (EPR). At 13°N the axis of EPR is free of any sediment but here aliphatic hydrocarbons are present in hot hydrothermal fluids of black “smokers”. In the sulfide-metal ores here the methane and alkanes higher than n-C₂₅ with prevalence of the odd number of carbon atoms have been identified [Simoneit, 1988].
- Oil accumulations have been studied by the «ALVIN» submarine and by the deep marine drilling in the Gulf of California (the Guaymas Basin) and in the Escanaba Trough, Gorda Ridge [Gieskes *et al.*, 1988; Koski *et al.*, 1988; Kvenvolden *et al.*, 1987; Lonsdale, 1985; Peter *et al.*, 1988; Simoneit, 1988; Simoneit *et al.*, 1982; Thompson *et al.*, 1988] of the Pacific Ocean. These sites are covered by sediments. However, petroleum fluids identified there are of hydrothermal origin according to Simoneit, Lonsdale [1982] and no source rocks were yet identified there.
- As for other sites over the Globe, scientific investigations with the submarines have established that the methane “plumes” occur over the sea bottom “smokers” or other hydrothermal systems in Red Sea, near Galapagos Isles, in Mariana and Tonga deepwater trenches, Gulf of California, etc. [Baker *et al.*, 1987; Blanc *et al.*, 1990; Craig *et al.*, 1987; Evans *et al.*, 1988; Horibe *et al.*, 1986; Ramboz *et al.*, 1988]. Non-biogenic methane (10⁵-10⁶ cu m/year) released from a submarine rift off Jamaica [Brooks, 1979] has been also known.

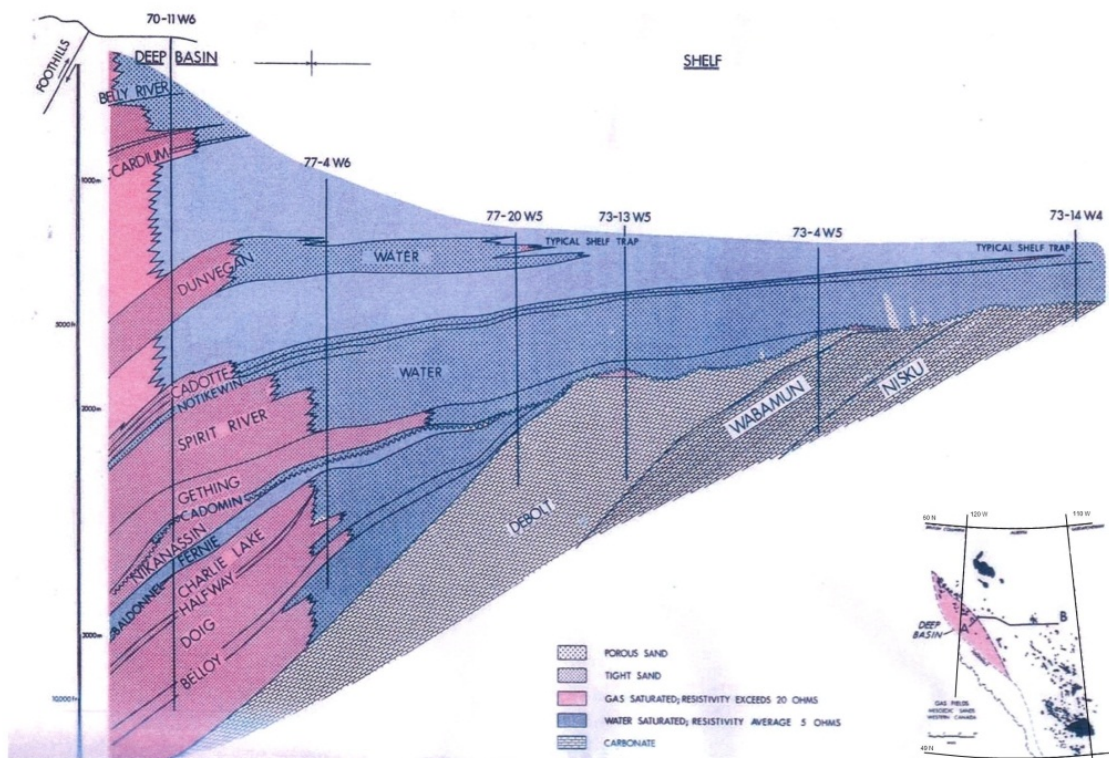


Figure 4. Cross section of Alberta showing gas-saturated sands of Deep Basin [Masters 1979].

A recent investigation along the Mid-Atlantic Ridge 2,300 miles east of Florida confirms that the hydrogen-rich fluids venting at the bottom of the Atlantic Ocean in the Lost City Hydrothermal Field were produced by an abiotic synthesis of hydrocarbons in the Mantle of the Earth (Fig. 3) [Proskurowski *et al.*, 2008]. Quantitatively speaking the sea-floor spreading centres may vent $1.3 \cdot 10^9$ cu m of hydrogen and $16 \cdot 10^7$ cu m methane annually [Welhan *et al.*, 1979].

Data discussed below confirm the following:

1. Source rocks accounting for the volume of the petroleum venting described are not available;
2. The natural gas and petroleum fluids in the recent sea-floor spreading centres can be explained as a result of the vertical migration of the Mantle fluids.

6. Bitumen and hydrocarbons in native diamonds

A presence of bitumen and hydrocarbons in native diamonds, carbonado and kimberlites could be taken into consideration as the evidence confirming the abyssal petroleum origin. Studying the native diamonds, carbonado and kimberlites under the microscope many scientists from several countries have found the numerous primary fluid inclusions which have been opened due to the specific methods. Fluid contents of primary fluid inclusions have been recovered without any contamination and studied by mass-spectrometry/gas-chromatography. Results of such investigations carried-out on the samples from Africa, Asia, Europe, North and South America can be summarized as follows.

The well-known diamond-producing mines such as the Dan Carl, Finsh, Kimberley, and Roberts Victor are located in the kimberlite pipes of the **South Africa**. There the African shield is characterized by the remarkable disjunctive dislocations and non-orogenic magmatism which has produced a great number of the carbonatite and kimberlite intrusions and explosion pipes in the area around Lake Tanganyika, Lake Malawi and Lake Victoria between 70 Ma and 3000 Ma ago [Irvine, 1989]. These lakes are in the Great East-African Rift Valley. The Valley's margins and disjunctive edges consist of the African shield crystalline rocks. 258 samples of diamonds from this area have been investigated under the microscope [Deines *et al.*, 1989]. The investigation has shown the presence of primary fluid inclusions in all samples investigated. These samples have been disintegrated into the small particles in vacuum of about $1.3 \cdot 10^{-6}$ Pa and 200 degrees C. The gas mixture from each sample was received. Mass-spectrometric/gas-chromatographic studies of the mixtures are shown in Table 3.

The same hydrocarbons and gases mixtures were detected in natural diamonds from **Congo, Brazil** [Melton *et al.*, 1974] and **Zaire** [Giardini *et al.*, 1982] (Table 3).

The composition of the primary fluid inclusions composition has been studied by mass-spectrometer in seven native **Arkansas** diamonds. The result of investigation has confirmed

the presence of the different kinds of hydrocarbon in all samples (Table 3) [Melton *et al.*, 1974].

In a **Brazil** carbonado primary fluid inclusions comprise a set of heavy hydrocarbons (Table 3). Pyrope ($\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$) and olivine which were recovered from diamond crystals and kimberlites of the Mir, Ruslovoye, and Udatchnoye Eastern diamond-bearing pipes, **East Siberia, Russia** contain a number of different hydrocarbons (Table 3) [Kulakova *et al.*, 1982; Kaminski *et al.*, 1985]. According to Makeev *et al.* [2004] 9-to-27 forms of metallic films were found and studied upon the crystal faces of diamonds from **Brazil** and from the Middle Timan, Ural and Vishera diamonds in the European part of **Russia**. These films consist of aluminum, cadmium, calcium, chrome, cerium, copper, gold, iron, lanthanum, lead, magnesium, neodymium, nickel, palladium, silver, tin, titanium, ytterbium, yttrium, zinc, zirconium and of precious metals including even Au_2Pd_3 . The thickness of these films is from fractions of micrometer to several micrometers. These films are the evidences for the growth of diamonds from carbon dissolved in the melt of gold and palladium [Makeev, Ivanukh, 2004]. The coarseness of the diamond crystals in kimberlite and lamprophyre pipes depends on the sizes of precious metal droplets in the respective zone – in the Earth's upper, transitional, and lower Mantle.

<i>Region</i>	<i>Gas mixture concentration, vol. %</i>
Africa Diamonds	CH_4 , C_2H_4 , C_3H_6 , solid hydrocarbons, $\text{C}_2\text{H}_5\text{OH}$, Ar, CO, CO_2 , H_2 , O_2 , H_2O , and N_2
Congo, Brazil, Zaire Diamonds	5.8 of CH_4 ; 0.4 of C_2H_4 ; 2.0 of C_3H_6 ; traces of C_4H_8 ; C_4H_{10} and solid hydrocarbons
Arkansas, U.S.A. diamonds	0.9-5.8 of CH_4 ; 0.0-5.2 of CH_3OH ; 0.0-3.2 of $\text{C}_2\text{H}_5\text{OH}$; 1.2-9.4 of CO; 5.3-29.6 of CO_2 ; 1.5-38.9 of H_2 ; 2.9-76.9 of H_2O ; 0.0-87.1 of N_2 ; 0.0-0.2 of Ar
Brazil carbonado	the homologues of naphthalene (C_{10}H_8), phenanthrene ($\text{C}_{14}\text{H}_{10}$), and pyrene ($\text{C}_{16}\text{H}_{10}$). Total concentration varies from 20 to 38.75 g/t
East Siberia, Russia diamonds and kumberlites	C_6H_6 ; $\text{C}_{12}\text{H}_{10}$; $\text{C}_{20}\text{H}_{12}$; $\text{C}_{16}\text{H}_{10}$, and other polynuclear aromatic hydrocarbons. Total concentration is about 0.136 g/t

Table 3. Results of Investigation of Gas Mixtures from Native Diamonds, Carbonado and Kumberlites

Investigation primary fluid inclusions in diamonds have shown a presence of bitumen in diamonds. The primary inclusions preserved in natural diamonds are bitumen inclusions and contain mantle hydrocarbons. This evidences that the source materials for the abyssal, natural synthesis of diamonds were the hydrocarbon fluids which have saturated the outgassing mantle and enabled mantle silicates to be reduced to native metals. The Brazil natural diamonds were sampled from the Juine kimberlite pipe field of the Mato Grosso State, Brazil. The Juine Later Cretaceous kimberlites contain five mineral associations related to the different facies and depths which are reflected in Table 4. One of the Juine diamonds

sampled near Sao Luis Creek was the lower Mantle diamond and comprised the primary fluid inclusions with the lower Mantle bitumens [Makeev *et al.*, 2004].

$\delta^{13}\text{C}$ for 213 diamonds from the different pipes was analyzed. $\delta^{13}\text{C}$ is ranged from -1.88 to -16 ‰ [Deines *et al.*, 1989]. The chemical and isotope peculiarities of natural diamonds reflect the different Mantle media and environments. Diamonds with $\delta^{13}\text{C}$ from -15 to -16 ‰ come from the region at a lower depth than the natural diamonds with $\delta^{13}\text{C}$ from -5 to -6 ‰.

Conclusions:

1. No doubt, that diamonds, carbonado and kimberlites are formed at great depths.
2. Presence of the inhibited primary hydrocarbon inclusions in diamonds, carbonado and kimberlites testifies that hydrocarbon Mantle fluids were a material for synthesis of these minerals in the Mantle.
3. Presence of abiogenic hydrocarbon fluids in the Mantle of the Earth is scientifically proved evidence.

7. Petroleum in meteor impact craters

Petroleum reserves in meteor impact craters possess a great potential. At the present moment there are about 170 meteor impact craters identified in all continents and in the world ocean bottom. Impact fracturing can occur to depths of 35-40 km and penetrate into the Earth's mantle. The impact fractures are the result of impacts of asteroids, bolides, comets on the Earth. When a massive cosmic object impacts the Earth surface with the velocity in the range from 15 to 70 km/s it accompanies the explosion. According to experiments devoted to mechanisms and models of cratering in the Earth media, the hyper fast impact creates temperature of 3000 degrees C and pressure of 600-900 kbar in the rocks of different compositions and generates their disintegration, pulverization, vaporization/exhalation, oxidation and hydrothermal transformation. As the result of the above-mentioned events and processes the meteorite (comet) impact transforms any non-reservoir rock into a porous and permeable reservoir rock [Curran *et al.*, 1977; Masaitis *et al.*, 1980; Donofrio, 1981].

Petroleum reserves were found in onshore and offshore meteor impact craters carbonate, sandstone and granite rocks over the world [Donofrio, 1998; India, 2006] (Table 4). Granites compose the crystalline basement of meteor impact craters whereas the carbonates and sandstones compose the sedimentary infill of the crater. Their producing depth is determined from 61 to 5185 m; the total production is from 4.8 to 333,879 m³/d of oil and from 7363 m³/d to 39.6·10⁶ m³/d of gas; the total proven reserves are from 15,899 m³ to 4770·10⁶ m³ of oil, 48·10⁶ m³ of condensate and from 56.6·10⁶ to 424.8·10⁹ m³ of gas [Donofrio, 1998].

The richest petroleum meteor impact crater Cantarell is in Mexico. Its cumulative production exceeds 1.1·10⁹ m³ of oil and 83·10⁹ m³ of gas. The current remnant recoverable reserves are equal to 1.6·10⁹ m³ of oil and 146·10⁹ m³ of gas in three productive zones. They produce currently 206,687 m³/d of oil, and 70 % of it is recovered from carbonate breccia only. Its porosity is 8-12 % and the permeability is 3000-5000 millidarcies. Occurring at the

<i>Impact crater</i>	<i>Country</i>	<i>Age, Ma</i>	<i>Diameter, km</i>
Akreman (onshore)	Australia	600	100
Ames (onshore) oil&gas deposits in carbonates and granites	U.S.A.	470±30	15
Avak (onshore) gas deposits in sandstones	U.S.A.	3-95	12
Can-Am (onshore)	Canada and U.S.A.	500	100
Calvin (onshore) oil deposits in carbonates	U.S.A.	450±10	8.5
Chicxulub (offshore) oil&gas deposits in carbonates	Mexico	65	240
Kara (onshore)	Russia	60	65
Marquez (onshore) oil&gas deposits in carbonates and sandstones	U.S.A.	58±2	12.7
Newporte (onshore) oil&gas deposits in carbonates and sandstones	U.S.A.	<500	3.2
Popigai (onshore)	Russia	39	100
Red Wing Creek (onshore) oil&gas deposits in carbonates	U.S.A.	200±25	9
Sierra Madera (onshore) gas deposits in carbonates	U.S.A.	<100	13
Shiva (offshore)	India	15	500
South Caribbean crater (offshore)	Colombia	65	300
South Cuban crater (offshore)	Cuba	65	225
Steen River (onshore) oil deposits in carbonates and granites	Canada	91±7	25
Viewfield (onshore) oil&gas deposits in carbonates	Canada	190±20	2.5
Wredefort (onshore)	South Africa	1970	140

Table 4. Parameters of the biggest and petroleum productive impact craters

Tertiary Cretaceous boundary this breccia is genetically related to Chicxulub impact crater the diameter of which is now measured to be 240 km [Grajales-Nishimura *et al.*, 2000].

Calculating with an average porosity, permeability and water saturation of the over crater breccia and fracturing of the undercrater crystalline Earth Crust together with the rocks which surround the crater the petroleum potential of the single meteor impact crater having the diameter of 20 km can exceed the total proven oil-and-gas reserves of the Middle East [Donofrio, 1981]. Donofrio [1981] also estimates that during the last 3000 Ma the meteorite-comet bombardment of the Earth must have created 3060 onshore meteor impact craters of similar diameters. Krayushkin [2000] calculates with 7140 submarine meteor impact craters can be equal to about $12 \cdot 10^{14}$ m³ of oil and $7.4 \cdot 10^{14}$ m³ of gas.

The oil and gas in the meteor impact craters cannot be biogenic according since:

1. Any intercrater source rocks are destroyed, disintegrated, melted and pulverized together with all the other rocks at the site of the meteorite impact [Masaitis *et al.*, 1980];
2. After the impact any lateral petroleum migration from the non-crater zones into the crater through the concentric ring uplifts of 100-300 m high and concentric ring trenches of 100-300 m deep which surround the central uplift of the crater is not enabled.

8. Oil and gas deposits in the Precambrian crystalline basement

Crystalline crust of the Earth is the basement of 60 sedimentary basins with commercial oil and gas deposits in 29 countries of the world. Additionally, there are 496 oil and gas fields in which commercial reserves occur partly or entirely in the crystalline rocks of that basement. 55 of them are classified as giant fields (>500 Mbbls) with 16 non-associated gas, 9 gas-oil and 30 undersaturated oil fields among them (Table 5).

<i>Deposit</i>	<i>Country</i>	<i>Proven reserves</i>
Achak (gas field)	Turkmenistan	155·10 ⁹ cu m
Gugurtli (gas field)	Turkmenistan	86·10 ⁹ cu m
Brown-Bassett (gas field)	UK	73·10 ⁹ cu m
Bunsville (gas field)	U.S.A.	85·10 ⁹ cu m
Gomez (gas field)	U.S.A.	283·10 ⁹ cu m
Lockridge (gas field)	U.S.A.	103·10 ⁹ cu m
Chayandinskoye (gas field)	Russia	1,240·10 ⁹ cu m
Luginetskoye (gas field)	Russia	86·10 ⁹ cu m
Myldzhinskoye (gas field)	Russia	99·10 ⁹ cu m
Durian Mabok (gas field)	Indonesia	68.5·10 ⁹ cu m
Suban (gas field)	Indonesia	71·10 ⁹ cu m
Gidgealpa (gas field)	Australia	153·10 ⁹ cu m
Moomba (gas field)	Australia	153·10 ⁹ cu m
Hateiba (gas field)	Libya	411·10 ⁹ cu m
Bach Ho (oil and gas field)	Vietnam	600·10 ⁶ t of oil and 37·10 ⁹ cu m of gas
Bombay High (oil and gas field)	India	1640·10 ⁶ t of oil and 177·10 ⁹ cu m of gas
Bovanenkovskoye (oil and gas)	Russia	55·10 ⁶ t of oil and 2400·10 ⁹ cu m of gas
Tokhomskoye (oil and gas field)	Russia	1200·10 ⁶ t of oil and 100·10 ⁹ cu m of gas
Coyanosa (oil and gas field)	U.S.A.	6·10 ⁶ t of oil and 37·10 ⁹ cu m of gas

<i>Deposit</i>	<i>Country</i>	<i>Proven reserves</i>
Hugoton-Panhandle (oil and gas)	U.S.A.	223·10 ⁶ t of oil and 2000·10 ⁹ cu m of gas
Peace River (oil and gas field)	U.S.A.	19000·10 ⁶ t of oil and 147·10 ⁹ cu m of gas
Puckett (oil and gas field)	U.S.A.	87.5·10 ⁶ t of oil and 93·10 ⁹ cu m of gas
La Vela (oil and gas field)	Venezuela	54·10 ⁶ t of oil and 42·10 ⁹ ·10 ⁹ cu m of gas
Amal (oil field)	Libya	583·10 ⁶ t
Augila-Nafoora (oil field)	Libya	178·10 ⁶
Bu Attifel (oil field)	Libya	90·10 ⁶
Dahra (oil field)	Libya	97·10 ⁶
Defa (oil field)	Libya	85·10 ⁶
Gialo (oil field)	Libya	569·10 ⁶
Intisar "A" (oil field)	Libya	227·10 ⁶
Intisar "D" (oil field)	Libya	182·10 ⁶
Nasser (oil field)	Libya	575·10 ⁶
Raguba (oil field)	Libya	144·10 ⁶
Sarir (oil field)	Libya	1150·10 ⁶
Waha (oil field)	Libya	128·10 ⁶
Claire (oil field)	UK	635·10 ⁶
Dai Hung (oil field)	Vietnam	60-80·10 ⁶
Su Tu Den (oil field)	Vietnam	65·10 ⁶
Elk Basin (oil field)	U.S.A.	70·10 ⁶
Kern River (oil field)	U.S.A.	200.6·10 ⁶
Long Beach (oil field)	U.S.A.	121·10 ⁶
Wilmington (oil field)	U.S.A.	326·10 ⁶
Karmopolis (oil field)	Brazil	159·10 ⁶
La Brea-Pariñas-Talara (oil field)	Peru	137·10 ⁶
La Paz (oil field)	Venezuela	224·10 ⁶
Mara (oil field)	Venezuela	104.5·10 ⁶
Mangala (oil field)	India	137·10 ⁶
Renqu-Huabei (oil field)	China	160·10 ⁶
Shengli (oil field)	China	3230·10 ⁶
Severo-Varieganskoye (oil field)	Russia	70·10 ⁶
Sovietsko-Sosninsko-Medvedovskoye (oil field)	Russia	228·10 ⁶

Table 5. Giant and Supergiant Petroleum Deposits in the Precambrian Crystalline Basement

They contain $9432 \cdot 10^9 \text{ m}^3$ of natural gas and $32,837 \cdot 10^6$ tons of crude oil, i.e., 18 % of the total world proven reserves of oil and about 5.4 % of the total world proven reserves of natural gas.

In the crystalline basement the depths of the productive intervals varies of 900-5985 m. The flow rates of the wells is between 1-2 m^3/d to 2,400 m^3/d of oil and 1000-2000 m^3/d to $2.3 \cdot 10^6 \text{ m}^3/\text{d}$ of gas. The pay thickness in a crystalline basement is highly variable. It is 320 m in the Gomez and Puckett fields, the U.S.A.; 680 m in Xinglontai, China; 760 m in the DDB's northern flank. The petroleum saturated intervals are not necessarily right on the top of the crystalline basement. Thus, oil was discovered at distance of 18-20 m below the top of crystalline basement in La Paz and Mara fields (Western Venezuela), 140 m below the basement's top in the Kazakhstan's Oimasha oil field. In the Baltic Shield, Sweden the 1 Gravberg well produced 15 m^3 of oil from the Precambrian igneous rocks of the Siljan Ring impact crater at the depth of 6800 m. In the Kola segment of the Baltic Shield several oil-saturated layers of the Precambrian igneous rocks were penetrated by the Kola ultra-deep well at the depth range of 7004-8004 m.

One of the most success stories of the practical application of the theory of the abyssal abiogenic origin of petroleum in the exploration is the exploration in the Dnieper-Donetsk Basin (DDB), Ukraine [Krayushkin *et al.* 2002]. It is a cratonic rift basin running in a NW-SE direction between 30.6°E - 40.5°E . Its northern and southern borders are traced from 50.0°N - 51.8°N and 47.8°N - 50.0°N , respectively. In the DDB's northern, monoclinial flank the sedimentary sequence does not contain any salt-bearing beds, salt domes, nor stratovolcanoes and no source rocks. Also this flank is characterized by a dense network of the numerous syn-thetic and anti-thetic faults. These faults create the mosaic fault-block structure of crystalline basement and its sedimentary cover, a large number of the fault traps (the faulted anticlines) for oil and natural gas, an alternation uplifts (horsts) and troughs (grabens). The structure of the DDB's northern flank excludes any lateral petroleum migration across it from either the Donets Foldbelt or the DDB's Dnieper Graben.

Consequently, the DDB's northern flank earlier was qualified as not perspective for petroleum production due to the absence of any "source rock of petroleum" and to the presence of an active, highly dynamic artesian aquifer. However, after a while the perspectivity of this area was re-interpreted, re-examined in compliance with the theory of the abyssal abiogenic origin of petroleum starting with the detailed analysis of the tectonic history and geological structure of the crystalline basement in the DDB's northern monoclinial flank. Subsequently respective geophysical and geochemical prospecting programmes were accepted primarily for exploring deep-seated petroleum.

Late 1980's-early 1990's 61 wells were drilled in the DDB's northern flank. 37 of them proved commercially productive (the exploration success rate is as high as 57 %) discovering commercial oil and gas strikes in the Khukhra, Chernetchina, Yuliyevka, and other areas. A total of 12 oil and gas fields discovered worth \$ 4.38 billion in the prices of 1991 and \$ 26.3 billion in the prices of 2008. For the discovery of these new oil and gas accumulations I.I.Chebanenko, V.A.Krayushkin, V.P.Klochko, E.S. Dvoryanin, V.V.Krot,

P.T.Pavlenko, M.I.Ponomarenko, and G.D.Zabello, were awarded the State Prize of Ukraine in the Field of Science and Technology in 1992 [*Chebanenko et al.*, 2002].

Today there are 50 commercial gas and oil fields known in the DDB's northern flank. Data obtained from drilling in many of these areas shows that the crystalline basement of northern flank consists of amphibolites, charnockites, diorites, gneisses, granites, granodiorites, granito-gneisses, migmatites, peridotites, and schists. 32 of commercial fields have oil and/or gas accumulations in sandstones of the Middle and Lower Carboniferous age. 16 other fields contain reservoirs in the same sandstones but separately from them - in amphibolites, granites and granodiorites of crystalline basement as well. Two fields contain oil pools in the crystalline basement only.

An exploration drilling in the DDB's northern flank has discovered five petroleum reservoirs in the Precambrian crystalline basement rock complex at the depths ranging from several meters to 336 meters below the top of crystalline basement. Gas- and oil-shows have been found in the Precambrian crystalline basement rocks as deep as 760 m below the top of crystalline basement. The seal rock for the reservoirs in the Carboniferous period sandstones are shallower shale formations. This is typical for petroleum pools in sedimentary beds. The cap rock for the reservoirs in the Precambrian crystalline basement is the impervious, non-fractured, essentially horizontal, layer-like zones of crystalline rock which alternate with the fractured, un-compacted, bed-like zones of granite, amphibolite and the other crystalline rocks mentioned above [*Krayushkin et al.*, 2001].

The exploration drilling in the DDB's northern flank is still in progress and continues to yield success in the 100x600 km petroliferous strip of the DDB's northern flank. Its proven petroleum reserves are already equal to $289 \cdot 10^6$ tons (\$230 billion at 50 USD/bbl oil prices). The DDB's northern flank is even more attractive with its total perspective "in place" petroleum resources which amounts to about $13,000 \cdot 10^6$ tons (~80,000 bbls) of oil equivalent in an area of 48,000 sq km. The petroleum potential of the DDB's southern flank should not be neglected either with a total "in place" prognostic petroleum resources of about $6000 \cdot 10^6$ tons of oil equivalent in an area of 22,000 sq km. Here several promising leads with oil-shows can be found in the crystalline basement and its sedimentary cover [*Chebanenko et al.*, 1996].

Abyssal abiogenic petroleum has been discovered in China as well: the giant Xinjiang gas field contains about $400 \cdot 10^{12}$ m³ of abiogenic natural gas [*Zhang*, 1990]. Chinese petroleum geologists estimated this quantity in volcanic island arcs, trans-arc zones of mud volcanism, trans-arc rift basins, trans-arc epicontinental basins, deep fault zones and continental rift basins.

Conclusions:

1. According to the traditional biotic petroleum origin hypothesis the DDB's northern flank was qualified as possessing no potential for petroleum production.
2. Based on the theory of the abyssal abiogenic origin of petroleum 50 commercial gas and oil deposits were discovered in this area. This is the best evidence confirming the theory.

9. Deep and ultra-deep petroleum reservoirs

In this part of the chapter we discuss how far the distribution, location and reservoir conditions in the deep and ultra-deep petroleum deposits can be explained by the traditional biotic petroleum origin. The key points are as follows:

- deep and ultra-deep petroleum fields are below “the main zone of petroleum formation” determined by the traditional biotic petroleum origin hypothesis i.e the depth of 2-4 km and in exceptional cases – on the depth down to maximum 8 km.
- reservoir temperature of these fields is much higher than the optimal temperature range of the traditional biotic hypothesis of petroleum formation;
- the biotic hypothesis suggests that with growing depth and temperature hydrocarbons are destructed, reservoir rock porosity drops, thus petroleum reserves should be significantly reduced. A presence of more than 1000 petroleum deposits at the depth 5-10 km all over the world contradicts to these points –a seen below:

There are more than 1000 commercial petroleum fields producing oil and/or natural gas from sedimentary rocks at the depths of 4500-10,685 m. These fields were discovered in 50 sedimentary basins over the world.

Russia. A number of oil-and-gas fields have been discovered in the depth of 4000-4600 m in Russia. The cumulative production of these fields is equal to $421 \cdot 10^6$ t of oil, $45.5 \cdot 10^9$ m³ of the associated oil gas and $641 \cdot 10^6$ m³ of natural gas. Although these fields are not “ultradeep” reservoirs, but they are interesting from our points of view: they are associated with deep faults intersecting the whole sedimentary rock sequence. The “roots” of these deep faults extend underneath the basement part of lithosphere. The roots form vertical columns- (“pipes”) of high permeability/petroleum saturation and chains of oil and gas accumulations are connected to them. It was established that the traces of petroleum migration are entirely absent outside of anticline crests [Istratov, 2004].

Ukraine. 17 giant and supergiant gas fields were discovered in the Lower Carboniferous age sandstones of the Dnieper-Donets Basin at the depth range of 4500-6287 m. At these depths, the total proven reserves of natural gas is $142.6 \cdot 10^9$ cu m. The total recoverable reserves of condensate is $2.3 \cdot 10^6$ t [Gozhik et al., 2006].

U.S.A. In the U.S.A. more than 7000 boreholes with TD deeper than 4575 m were drilled between 1963-1979. In the Mesozoic-Cenozoic rift system of the Gulf of Mexico a regional of the deep-to-ultra-deep (the Upper Cretaceous) sands have been observed. With a width of 32-48 km and a length of 520 km this trend extends along the Gulf of Mexico from New Orleans to the borderline between Louisiana and Texas. Many oil and gas fields were found in this formation over the area indicated at the depths of 4500-6100 m. Most of them have anomalously high reservoir temperature (Freeland field: 232 degrees C) what is much higher than the optimal temperature of petroleum formation from ancient organic materials. The total proven reserves of natural gas in the Tsucaloosa trend are equal to $170 \cdot 10^9$ m³ but there is an opinion that only the central portion of it contains potential resources as much as

$850 \cdot 10^9 \text{ m}^3$ of natural gas and $240 \cdot 10^6 \text{ m}^3$ of condensate. [King, 1979; Matheny, 1979; Pankonien, 1979; Sumpter, 1979].

- In 2009 BP has discovered the Tiber crude oil deposit in the Mexican Gulf. The well, located in Keathley Canyon block 102, approximately 400 kilometres south east of Houston, is in 1,259 metres of water. The Tiber well was drilled to a total depth of 10,685 metres. The Tiber deposit holds between 4 billion and 6 billion barrels of oil equivalent, which includes natural gas (the third biggest find in the US) (<http://www.bp.com/genericarticle.do?categoryId=2012968&contentId=7055818>).

10. Supergiant oil and gas accumulations

One of the main problems of the traditional biotic petroleum origin hypothesis is the identification of biotic sources and material balance of the hydrocarbon generation for most of supergiant oil and gas fields.

Middle East. In the Middle East proven recoverable reserves are equal to $101 \cdot 10^9 \text{ t}$ of oil and $75.8 \cdot 10^{12} \text{ m}^3$ of gas respectively as of the end 2010 [BP, 2011]. Saudi Arabia's proven reserves are $36 \cdot 10^9 \text{ t}$ of oil and $8 \cdot 10^{12} \text{ m}^3$ of natural gas [BP, 2011]. Most of these reserves are located in ten supergiant gas and oilfields (Table 6) [International, 1976; Alhajji, 2001, *The List*, 2006]. These giant oil fields give oil production from the Jurassic-Cretaceous granular carbonates. All these crude oils have very similar composition referring to a common source. Such source is the Jurassic-Cretaceous thermally mature, thin-bedded organic rich carbonate sequence (3-5 mass %). Organic material is concentrated in dark, 0.5-3.0 mm thin beds alternating with the lightly colored, similarly thin beds poor in organics. Let's make a calculation of the oil might have been generated inside the basins of Saudi Arabia with an estimated "original-oil-in-place" of $127 \cdot 10^9 \text{ m}^3$ [BP, 2011]. Areas within the sedimentary basins where the kerogen is mature (i.e. H/C ratio is 0.8-1.3), were mapped [Ayres *et al.*, 1982] and multiplied by the thickness of the source zones. This simple calculation gives a volume of petroleum source rocks as high as 5000 cubic km. If we accept that

- the volume of kerogen is equal to 10 % of the petroleum source rocks volume,
- the coefficient of transformation of kerogen into bitumen is equal to 15 %,
- that 10 % of this bitumen can migrate out of the petroleum source rocks,

we come to the conclusion, that only $7.5 \cdot 10^9 \text{ m}^3$ of oil could migrate out of the petroleum source rocks. This is less than 6 % of Saudi Arabia's estimated "in place" oil reserves. Note, that if the kerogen transformation parameters are twice as high as taken here (i.e. 20%, 30% and again 20% respectively), the OOIP is still $60 \cdot 10^9 \text{ m}^3$ i.e. half of the booked value.

Where did 94 % of Saudi Arabia's recoverable oil come from? This question is not a rhetorical one because any other source of beds of petroleum is absent in the subsurface of Saudi Arabia as well as of all countries mentioned above, according to Ayres *et al.* [1982], and Baker *et al.* [1984]. Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, Syria, United Arab Emirates and Yemen occur in the same sedimentary basin – the Arabian-Iranian Basin,

where *Dunnington* [1958; 1967] established the genetic relationship, i.e. the single common source of all crude oils.

Canada. The West Canadian sedimentary basin attracts a great attention also. There is the unique oil/bitumen belt extended as the arc-like strip of 960 km length from Peace River through Athabasca (Alberta Province) to Lloydminster (Saskatchewan Province). This belt includes such supergiant petroleum fields as Athabasca (125 km width, 250 km length), Cold Lake (50 km, 125 km), Peace River (145 km, 180 km) and Wabaska (60 km, 125 km). Here the heavy ($946.5\text{--}1.029\text{ kg/m}^3$) and viscous (several hundred-several million cP) oil saturates the Lower

<i>Deposit</i>	<i>Estimated reserves</i>
Ghawar	$10.2\cdot 10^9\text{--}11.3\cdot 10^9$ t of oil $1.5\cdot 10^{12}$ m ³ of gas
Safaniyah	$4.1\cdot 10^9$ t of oil
Shaybah	$2.0\cdot 10^9$ t of oil
Abqaiq	$1.6\cdot 10^9$ t of oil
Berri	$1.6\cdot 10^9$ t of oil
Manifa	$1.5\cdot 10^9$ t of oil
Marjan	$1.4\cdot 10^9$ t of oil
Qatif	$1.3\cdot 10^9$ t of oil
Abu Safah	$0.9\cdot 10^9$ t of oil
Dammam	$0.7\cdot 10^9$ t of oil

Table 6. Supergiant Oil and Gas Deposits in Saudi Arabia

Cretaceous sands and sandstones. These fields contain the “in place” oil reserves equal to $92\cdot 10^9\text{--}187\cdot 10^9$ m³ in Athabasca, $32\cdot 10^9\text{--}75\cdot 10^9$ m³ in Cold Lake, $15\cdot 10^9\text{--}19\cdot 10^9$ m³ in Peace River, $4.5\cdot 10^9\text{--}50\cdot 10^9$ m³ in Wabaska, and $2\cdot 10^9\text{--}5\cdot 10^9$ m³ of oil/bitumen in Lloydminster, totally $170\cdot 10^9\text{--}388\cdot 10^9$ m³ [*Vigrass*, 1968; *Wennekers*, 1981; *Seifert et al.*, 1985; *Sincruide*, 1992; *Warters et al.*, 1995].

The conventional understanding is, that the oil of Athabasca, Cold Lake, Lloydminster, Peace River and Wabasca generated from dispersed organic matter buried in the argillaceous shales of the Lower Cretaceous Mannville Group only. It is underlain by the Pre-Cretaceous regional unconformity and its thickness varies from 100 to 300 m. Its total volume is about $190\cdot 10^3$ cubic km with a 65 % shale content. Having the data of the total organic carbon concentration (TOC), the hydrocarbon index (HI), constant of transformation (K), and all other values from the accepted geochemical model of the oil generation from the buried organic matter dispersed in clays-argillites, it was concluded that the Mannville Group could only give $71.5\cdot 10^9$ m³ of oil. It is in several times less than the quantity of oil (see above) which was totally estimated before 1985 in Athabasca, Cold Lake, Lloydminster, Peace River and Wabasca oil sand deposits [*Moshier et al.*, 1985].

If we accept other estimations of the volume of oil/bitumen “in place” in Athabasca, Wabasca, Cold Lake and Peace River area (~ 122,800 sq km) conducted by Alberta Energy Utilities Board (AEUB) and the National Energy Board (NEB), Canada the gap between the booked and organically generated quantities is even wider (Table 12). AEUB estimated $270 \cdot 10^9 \text{ m}^3$ of bitumen “in place”, while NEB – $397 \cdot 10^9 \text{ m}^3$ [Canadian, 1996].

In the above-mentioned area there additionally are $200 \cdot 10^9$ - $215 \cdot 10^9 \text{ m}^3$ of heavy (986-1030 kg/cu m) and viscous (10^6 cP under 16 degrees C) oil at the depth range of 75-400 m in the Upper Devonian carbonates (Grosmont Formation). They occur in the area of $70 \cdot 10^3 \text{ km}^2$ beneath the Athabasca/Cold Lake/Lloydminster/Peace River/Wabasca oil sand deposits [Wennekers, 1981; Seifert *et al.*, 1985; Hoffmann *et al.*, 1986].

The total estimated reserves of bitumen “in place” in the above-mentioned area are between $370 \cdot 10^9$ and $603 \cdot 10^9 \text{ m}^3$. If besides the Mannville clays and shales which could give $71.5 \cdot 10^9 \text{ m}^3$ of oil only there is no any other petroleum source rock, where is a biotic source for the rest of 82-88% of oil in this area?

Venezuela. Something similar can be observed in the Bolivar Coastal oil field in Venezuela. According to Bockmeulen *et al.* [1983] the source rock of petroleum here is the La Luna limestone of the Cretaceous age. The estimated oil reserves are equal to $4.8 \cdot 10^9 \text{ m}^3$ [The List, 2006] with an oil density of 820-1000 kg/m³. The same kind of calculations that were done for Saudi Arabia above gives us the following result. One m³ of the oil-generating rock contains $2.5 \cdot 10^{-2} \text{ m}^3$ of kerogen which can generate $2.5 \cdot 10^{-3} \text{ m}^3$ bitumen giving $1.25 \cdot 10^{-4} \text{ m}^3$ of oil within the accepted geochemical model of biotic petroleum origin. Having this oil-generating potential and the $4.8 \cdot 10^9 \text{ m}^3$ of estimated oil reserves of the Bolivar Coastal field as a starting point, the necessary volume of oil source rock would be equal to $3.84 \cdot 10^{13} \text{ m}^3$. This is consistent with the oil-generating basin area of 110 km across *if* the oil source rock is 1,000 m thick. The average thickness of La Luna limestone is measured with only 91 m [Bockmeulen *et al.*, 1983]. The diameter of the oil-generating basin would be therefore equal to 370 km and area of this basin is equal approximately 50% of the territory of Venezuela what is geologically highly un-probable.

11. Gas hydrates: the greatest source of abiogenic hydrocarbons

Gas hydrates are clathrates. Looking as ice they consist of gas and water where the molecules of hydrate-forming gas (e.g., Ar, CH₄, C₂H₆, C₃H₈, *i*-C₄H₁₀, Cl, CO, CO₂, He, H₂S, N₂, etc.) are squeezed under the pressure of 25 MPa and more into the interstices of the water (ice) crystalline cage without any chemical bonding between molecules of water and gas. As a result thawing 1 m³ of gas hydrate at the sea level produces 150-200 m³ of gaseous methane and 0.87 m³ of fresh water. Naturally, the formation of gas hydrates takes place under the great velocity of fluid movement and under the certain combination of pressure and temperature. For example, methane hydrate arises under conditions of -236 degrees C and $2 \cdot 10^{-5} \text{ MPa}$; 57 degrees C and 1,146 MPa (Klimenko, 1989; Makogon, 1997; Lowrie *et al.*, 1999; Makogon *et al.*, 2005). There are also the data that the formation of gas hydrate from the

CH₄/C₃H₈/CO₂/H₂O/H₂S-mixture proceeds under such the high temperature increasing/such the high pressure decreasing that the gas hydrate of composition, above, arises and exists really in sea-bottom sediments where the depth of sea is only 50 m, e.g., in Caspian Sea [Lowrie *et al.*, 1999].

Visually the gas hydrates (“combustible ice”) are the aggregate growths of transparent and semitransparent, white, gray or yellow crystals. They can partially or entirely saturate the natural porous media, adding the mechanical strength and acoustic hardness to sediments and sedimentary rocks. Boreholes and seismic surveys have established that methane hydrates occur in the polar regions of Asia, Europe, North America (fig. 10), where the “combustible ice” always is underlain with natural gas [Trofimuk *et al.*, 1975; Panaev, 1987; Collett, 1993; Dillon *et al.*, 1993; Kvenvolden, 1993; Modirisi *et al.*, 2008].

The gas hydrates represent a huge unconventional resource base: it may amount from $1.5 \cdot 10^{16} \text{ m}^3$ [Makogon *et al.*, 2007] to $3 \cdot 10^{18} \text{ m}^3$ [Trofimuk *et al.*, 1975] of methane. Thus, natural gas reserves which could be obtained from “combustible ice” are enough for energy support for our civilization for the next several thousand years.

Top of the supergiant gas hydrate/free natural gas accumulations occur at a depth of 0.4-2.2 m below the sea bottom in the Recent sediments of the world ocean. The bottom of these accumulations is sub-parallel to the sea-bottom surface and intersects beds with anticlinal, synclinal, and tilted forms. This geometry, the geographical distribution of hydrates in the world ocean, their Recent to Pleistocene age and fresh water nature of “combustible ice” could not be explained by terms (source rocks, diagenesis and katagenesis/metagenesis of any buried, dispersed organic matter, lateral migration of natural gas) used in the traditional biotic petroleum origin hypothesis.

According to the theory of the abyssal abiogenic origin of petroleum all gas hydrate/free natural gas accumulations were formed due to the “one worldwide act” i.e. an upward vertical migration of abyssal abiogenic mantle fluid through all the faults, fractures, and pores of rocks and sea-bottom sediments. In that time, not more than 200 thousand years ago those faults, fractures, and pores were transformed by a supercritical geo-fluid (mixture of supercritical water and methane) into a conducting/accumulating/intercommunicating media. Acting as the natural “hydrofracturing” the abyssal geo-fluid has opened up the cavities of cleavage and interstices of bedding in the rocks and sediments as well. According to Dillon *et al.* [1993] the vertical migration of natural gas still takes place today on the Atlantic continental margin of the United States. Along many faults there the natural gas continues to migrate upwards through the “combustible ice” as through “sieve” that is distinctly seen as the torch-shape vertical strips in the blanking of seismographic records.

On April 10, 2012 Japan Oil, Gas and Metals National Corporation and ConocoPhillips have announced a successful test of technology dealing with safely extract of natural gas from methane hydrates. A mixture of CO₂ and nitrogen was injected into the formation on the North Slope of Alaska. The test demonstrated that this mixture could promote the production of natural gas. This was the first field trial of a methane hydrate production

methodology whereby CO₂ was exchanged in situ with the methane molecules within a methane hydrate structure.

12. Conclusions

1. Geological data presented in this chapter do not respond to the main questions related to the hypothesis of biotic petroleum origin. Only the theory of the abiogenic deep origin of hydrocarbons gives convincing explanation for all above-mentioned data.
2. The experimental results discussed in the chapter confirm that the CaCO₃-FeO-H₂O system spontaneously generates the suite of hydrocarbons in characteristic of natural petroleum. Modern scientific considerations about genesis of hydrocarbons confirmed by the results of experiments and practical results of geological investigations provide the understanding that a part of the hydrocarbon compounds could be generated at the mantle conditions and migrated through the deep faults into the Earth's crust where they are formed oil and gas deposits in any kind of rocks and in any kind of their structural position.
3. The experimental results presented place the theory of the abiogenic deep origin of hydrocarbons in the mainstream of modern physics and chemistry and open a great practical application. The theory of the abiogenic deep origin of hydrocarbons confirms the presence of enormous, *inexhaustible* resources of hydrocarbons in our planet, allows us to develop a new approach to methods for petroleum exploration and to reexamine the structure, size and location of the world's hydrocarbons reserves (www.jogmec.go.jp).

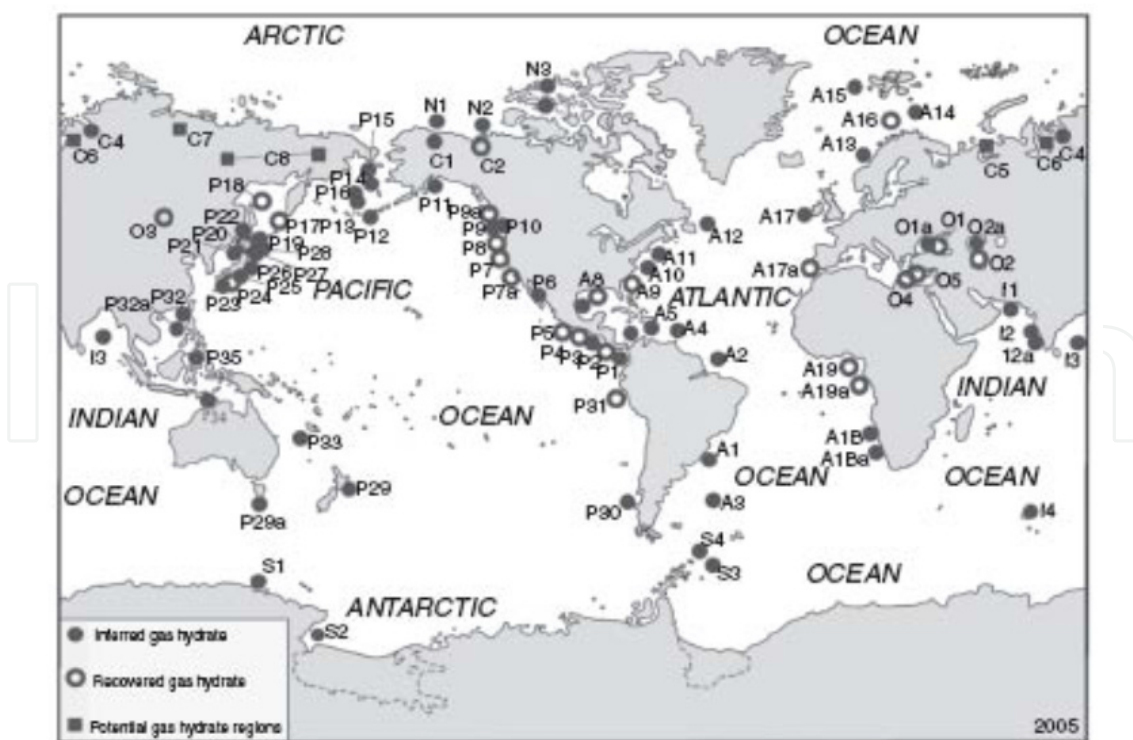


Figure 5. Inferred (63), recovered (23), and potential (5) hydrate locations in the world [Kvenvolden and Rogers, 2005].

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13. References

- Ayres, M. G., M. Bilal, R. W. Jones, L. W. Slentz, M. Tartir, and A. O. Wilson (1982), Hydrocarbon habitat in main producing areas, Saudi Arabia, *Amer. Assoc. Petrol. Geol. Bull.*, 66, 1, 1-9.
- Baker, E. G. (1962), Distribution of hydrocarbons in petroleum, *Amer. Assoc. Petrol. Geol. Bull.*, 46, 1, 76-84.
- Baker, C., and P. A. Dickey (1984), Hydrocarbon habitat in main producing area, Saudi Arabia, Discussion, *Ibid.*, 68, 1, 108-109.
- Blanc, G., J. Boulegue, and J. L. Charlou (1990), Profils d'hydrocarbures légers dans l'eau de mer, les saumures et les eaux intersticielles de la fosse Atlantis II (Mer Rouge), *Oceanol. Acta*, 13, 187-197.
- Bockmeulen, H., C. Barker, and P. A. Dickey (1983), Geology and geochemistry of crude oil, Bolivar Coastal fields, Venezuela, *Amer. Assoc. Petrol. Geol. Bull.*, 67, 242-270.
- BP Statistical Review of World Energy. June 2011,
<http://www.bp.com/sectionbodycopy.do?categoryId=7500&contentId=7068481>.
- Brooks, J. M. (1979), Deep methane maxima in the Northwest Caribbean Sea: possible seepage along Jamaica Ridge, *Science*, 206, 1069-1071.
- Carson, R. W., D. G. Pearson, and D. E. James (2005), Physical, chemical, and chronological characteristics of continental mantle, *Rev. Geophys.*, 43, RG1001.
- Charlou, J. L., and J. P. Donval (1993), Hydrothermal methane venting between 12°N and 26°N along the Mid-Atlantic Ridge, *J. Geophys. Res.*, 98, 9625-9642.
- Charlou, J. L., J. P. Donval, Y. Fouquet, P. Jean-Baptist, and N. Holm (2002), Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR), *Chem. Geol.*, 184, (1-2), 37-48.
- Chebanenko, I. I., V. A. Krayushkin, V. P. Klochko, and V. P. Listkov (1996), Petroleum potential of non-traditional targets in Ukraine, *Geol. J.*, 3-4, 7-11.
- Chebanenko, I. I., P. F. Gozhik, V. A. Krayushkin, V. P. Klochko, B. J. Mayevsky, N. I. Yevdoshchuk, V. V. Gladun, T. E. Dovzhok, P. Ya. Maksimchuk, A. P. Tolkunov, O. G. Tsiokha, and M. G. Yegurnova (2005), *Petroleum in the Basement of Sedimentary Basins*, EKMO Publishing House, Kiev, Ukraine.
- Chepurov A.I. *et al.*, (1999), Experimental study of intake of gases by diamonds during crystallization, *Journal of Crystal Growth*, 198/199, 963-967.
- Collet, T. S. (1993), Natural gas production from Arctic gas hydrates, in *The Future of Energy Gases*, pp. 299-311, US Geol. Survey Profes. Piper 1570, United States Government Printing Office, Washington (D.C.).

- Craig, H., Y. Horibe, and K. A. Farley (1987), Hydrothermal vents in the Mariana Trough: Results of the first *Alvin* dives, *Eos Trans. AGU*, 68, 1531.
- Curran, D. R., D. A. Shockley, L. Seaman, and M. Austin (1977), Mechanisms and models of cratering in earth media, in *Impact and Explosion Cratering*, pp. 1057-1087, Pergamon, Elmsford, NY.
- Deines, P., J. W. Harris, P. M. Spear and J. J. Gurney (1989), Nitrogen and ^{13}C content of Finsh and Premier diamonds and their implication, *Ibid.*, 53, 6, 1367-1378.
- Dillon, W. P., M. W. Lee, and K. Fehllhalen (1993), Gas hydrates on the Atlantic continental margin of the United States – controls on concentration, in *Future of Energy Gases*, U.S. Geological Survey Professional Paper. 1570, pp. 313-330, edited by D.G.Howell, U.S. Govern. Print. Office, Washington (D.C.).
- Donofrio, R. R. (1981), Impact craters: implications for basement hydrocarbons production, *Petrol. Geol. J.*, 3, 3, 279-302.
- Donofrio, R. R. (1998), North American impact structures hold giant field potential, *Oil and Gas J.*, 96, 19, 69-80.
- Dunnington, H. V. (1958), Generation, migration, accumulation, and dissipation of oil in Northern Iraq, in *Habitat of Oil*, pp. 1194-1251, Amer. Assoc. Petrol. Geol., Tulsa, OK.
- Dunnington, H. V. (1967), Stratigraphic distribution of oil fields in the Iraq-Iran-Arabia Basin, *Inst. Petrol. J.*, 53, 520, 129-161.
- Evans, W. D., R. D. Norton, and R. S. Cooper (1964), Primary investigations of the oliferous dolerite of Dypvica, Arendal, S.Norway, in *Advances in Organic Geochemistry*, pp. 202-214, Pergamon, Oxford.
- Giardini, A. A., Ch. E. Melton, and R. S. Mitchel (1982), The nature of the upper 400 km of the Earth and its potential as a source for nonbiogenic petroleum, *J.Petrol. Geol.*, 5, 2, 130-137.
- Gieskes, J. M., B. R. T. Simoneit, T. Brown, T. Shaw, Y. Ch. Wang, and A. Magenheimer (1988), Hydrothermal fluids and petroleum in surface sediments of Guaymas Basin, Gulf of California: a case study, *Canad. Mineralogist*, 26, 3, 589-602.
- Gozhik, P. F., V. A. Krayushkin, and V. P. Klochko (2006), Towards the search for oil at the depth of 8,000-12,500 m in the Dnieper-Donets Basin, *Geol. J.*, 4, 47-54.
- Green, D. H., W. O. Hibberson, I. Kovacs, and A. Rosenthal (2010), Water and its influence on the lithosphere–asthenosphere boundary. *Nature*, 467, 448-451, doi:10.1038/nature09369.
- Grajales-Nishimura, J. M., E. Cedillo-Pardo, C. Rosales-Dominguez, D. J. Moran-Zenteno, W. Alvarez, Ph. Claeys, J. Ruiz-Morales, J. Garcia-Hernandes, P. Padilla-Avila, and A. Sanchez-Rios (2000), Chicxulub impact: The origin of reservoir and seal facies in the southeastern Mexico oil fields, *Geology*, 28, 4, 307-310.
- Hazen R.M., R.J. Hemley and A.J. Mangum (2012), Carbon in Earth's interior: Storage, cycling, and life, *EOS, Transactions American Geophysical union*, 93, 2, 17, 2012, doi:10.1029/2012EO020001
- Hoffmann, C. F., and O. P. Strausz (1986), Bitumen accumulation in Grosmont platform complex, Upper Devonian, Alberta, Canada, *Amer. Assoc. Petrol. Geol. Bull.*, 70, 9, 1113-1128.

- Horibe, Y. K., K. R. Kim, and H. Craig (1986), Hydrothermal methane plumes in the Mariana back-arc spreading center, *Nature*, 324, 131-133.
- India. Exploration and development (2006), *Oil and Gas J.*, 104, 43, 46.
- Irvine, T. N. (1989), A global convection framework: concepts of symmetry, stratification, and system in the Earth's dynamic structure?, *Econ. Geol.*, 84, 8, 2059-2114.
- Istratov, I. V. (2004), Chechnya sees potential for "nontraditional" deposits, *Oil and Gas J.*, 102, 28, 38-41.
- Kaminski, F. V., I. I. Kulakova, and A. I. Ogloblina (1985), About the polycyclic, aromatic hydrocarbons in carbonado and diamond, *Proceedings of AN of U.S.S.R.*, 283, 985-988.
- Kenney, J. F., V. G. Kutcherov, N. A. Bendeliani, and V. A. Alekseev (2002), The evolution of multicomponent systems at high pressures: VI. The thermodynamic stability of the hydrogen-carbon system: The genesis of hydrocarbons and the origin of petroleum, *Proceedings of the Nat. Acad. Sci.*, 99, 17, 10976-10981.
- King, R. E. (1979), Onshore activity surges in North America, *World Oil*, 188, 6, 43-57.
- Klimenko, A. A., A. V. Botchkarev, and A. F. Nenakhov (1981), To a problem about the gas presence in the Paleozoic beds of the Scythian Plate, in *Questions to Drilling of Wells, Exploration and Exploitation of Gas Fields in Northern Caucasus and Uzbekistan*, pp. 15-18, VNIIOUGP, Moscow.
- Kolesnikov A., V.G. Kutcherov, A.F. Goncharov(2009), Methane-derived hydrocarbons produced under upper-mantle conditions, *Nature Geoscience*, 2, 566 – 570.
- Koski, R. A., W. C. Shanks-III, W. A. Bohrsen, and R. L. Oscarsen (1988), The composition of massive sulphide deposits from the sediment-covered floor of Escanaba Trough, Gorda Ridge: implication for depositional processes, *Canad. Mineralogist*, 26, 3, 655-673.
- Krayushkin, V. A. (2000), The true origin, structure, patterns, and distribution of the world petroleum potential, *Georesources*, 3(4), 14-18.
- Krayushkin, V. A., I. I. Tchabanenko, V. P. Klochko, Ye. S. Dvoryanin, and J. F. Kenney (2001), Drilling and development of the oil and gas fields in the Dnieper-Donets Basin, *Energia (Rivista Trimestrale sui problemi dell'Energia)*, Anno XXII, 3, 44-47.
- Krayushkin, V. A., I. I. Tchabanenko, V. P. Klochko, B. B. Gladun, and O. G. Thiokha (2002), The basement petroleum presence in the Dnieper-Donets Basin, *Geology, Geophysics and Development of Oil and Gas Fields*, 1, 9-16.
- Kulakova, I. I., A. I. Ogloblina, and V. I. Florovskaya (1982), Polycyclic, aromatic hydrocarbons in minerals-satellites of diamonds, and possible mechanism of their formation, *Proceedings of AN, U.S.S.R.*, 267, 6, 1458-1460.
- Kutcherov, V. G., N. A. Bendiliani, V. A. Alekseev, and J.F. Kenney (2002), Synthesis of hydrocarbons from minerals at pressure up to 5 GPa, *Proceedings of Rus. Ac. Sci.*, 387, 6, 789-792.
- Kutcherov V.G., A.Yu. Kolesnikov, T.I. Dyuzheva, L.F. Kulikova, N.N. Nikolaev, O.A. Sazanova, V.V. Braghkin (2010), Synthesis of Complex Hydrocarbon Systems at Temperatures and Pressures Corresponding to the Earth's Upper Mantle Conditions. *Doklady Akademii Nauk*, 433 (3), 361-364.

- Kvenvolden, K. A., and B. R. T. Simoneit (1987), Petroleum from Northeast Pacific Ocean hydrothermal systems in Escanaba Trough and Guaymas Basin, *Amer. Assoc. Petrol. Geol. Bull.*, 71, 5, 580.
- Kvenvolden, K. A. (1993), Gas hydrates – geological perspective and global change, *Review of Geophysics*, 31, 2, 173-187.
- Kvenvolden K.A., and B.W. Rogers (2005), Gaia's breath – global methane exhalations, *Marine and Petroleum Geology*, 22, 579-590.
- Lonsdale, P. A. (1985), A transform continental margin rich in hydrocarbons, Gulf of California, *Amer. Assoc. Petrol. Geol. Bull*, 69, 7, 1160-1180.
- Lowrie, A., and M. D. Max (1999), The extraordinary promise and challenge of gas hydrates, *World Oil*, 220, 9, 49-55.
- Makeev, A. B., and V. Ivanukh (2004), Morphology of crystals, films, and selvages on a surface of the Timanian and Brazil diamonds, in *Problems of Mineralogy, Petrography and Metallogeny*, pp. 193-216, Perm. Univer. Press, Perm, Russia.
- Makogon, Y. F. (1997). *Hydrates of Hydrocarbons*, PennWell, Tulsa.
- Makogon, Y. F., S. A. Holdich, and T. Y. Makogon (2007), Natural gas-hydrates — A potential energy source for the 21st Century, *Journal of Petroleum Science and Engineering*, 56, 14–31.
- Masaitis, V. L., A. N. Danilin, and M. S. Mashchak (1980), *Geology of Astroblemes*, Nedra, Leningrad.
- Masters, J. (1979), Deep Basin gas trap, West Canada, *Amer. Assoc. Petrol. Geol. Bull.*, 63, 2, 152-181.
- Matheny, Sh. L. (1979), Deeper production trend continuing, *Oil and Gas J.*, 77, 15, 105-107.
- Mao, Z., M. Armentrout, E. Rainey, C.E. Manning, P.K. Dera, V.B. Prakapenka, and A. Kavner (2011), Dolomite III: A new candidate lower mantle carbonate, *Geophys. Res. Lett.* 38, L22303, doi: 10.1029/2011GL049519
- Melton, Ch. E., and A. A. Giardini (1974), The composition and significance of gas released from natural diamonds from Africa and Brazil, *Amer. Mineralogist*, 59, 7-8, 775-782.
- Ditto (1975), Experimental results and theoretical interpretation of gaseous inclusions found in Arkansas natural diamonds, *Geochim. Cosmochim. Acta*, 60, 56, 413-417.
- Moshier, S. O., and D. W. Wapples (1985), Quantitative evaluation of Lower Cretaceous Manville group as source rock for Alberta's oil sands, *Amer. Assoc. Petrol. Geol. Bull.*, 69, 2, 161-172.
- Panaev, V. A. (1987), Gas hydrates in World Ocean, *Bull. Moscow Soc. Naturalists, Dep. Geol.*, 62, 3, 66-72.
- Pankonien, L. J. (1979), Operators scramble to tap deep gas in South Louisiana, *World Oil*, 189, 4, 55-62.
- Peter, J. M., and S. D. Scott (1988), Mineralogy, composition, and fluid-inclusion microthermometry of seafloor hydrothermal deposits in the Southern Trough of Guaymas Basin, Gulf of California, *Canad. Mineralogist*, 26, 3, 567-587.
- Proskurowski, G. *et al.* (2008), Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field, *Science*, 319, 5863, 604-607

- Ramboz, C., E. Oudin, and Y. Thisse (1988), Geyser-type discharge in Atlantis-II Deep, Red Sea: evidence of boiling from fluid inclusions in epigenetic anhydrite, *Canad. Mineralogist*, 26, 3, 765-786.
- Rona, P. A. (1988), Hydrothermal mineralization at oceanic ridges, *Canad. Mineralogist*, 26, 3, 431-465.
- Scott, H. P., R. J. Hemley, H. Mao, D. R. Herschbach, L. E. Fried, W. M. Howard, and S. Bastea, (2004), Generation of methane in the Earth's mantle: In situ high pressure-temperature measurement of carbonate reduction, *Proceedings Nat. Ac. Sci.*, 101, 39, 14023-14026.
- Seifert, S. R., and T. R. Lennox (1985), Developments in tar sands in 1984, *Amer. Assoc. Petrol. Geol. Bull.*, 69, 10, 1890-1897.
- Simoneit, B. R. T. (1988) Petroleum generation in submarine hydrothermal systems: an update, *Canad. Mineralogist*, 26, 3, 827-840.
- Simoneit, B. R. T., and P. F. Lonsdale (1982), Hydrothermal petroleum in mineralized mounds at the seabed of Guaymas Basin, *Nature*, 295, 5846, 118-202.
- Sumtper, R. (1979), Strikes sparking action along Tuscaloosa trend, *Oil and Gas J.*, 77, 43, 19-23.
- Thompson, G., S. E. Humphris, and B. Shroeder (1988), Active vents and massive sulphides at 26°N (TAG) and 37°N (Snakepit) on the Mid-Atlantic Ridge, *Canad. Mineralogist*, 26, 3, 697-711.
- The List: Taking Oil Fields Offline (2006), *Foreign Policy*, 155.
- Trofimuk, A. A., N. B. Cherski, and V. P. Tsarev (1975), Resources of biogenic methane of the World Ocean, *Proc. AN Ud.S.S.R.*, 225, 4, 936-943.
- Vigrass, L. W. (1968), Geology of Canadian heavy oil sands, *Amer. Assoc. Petrol. Geol. Bull.*, 52, 10, 1984-1999.
- Warters, W. J., D. J. Cant, P. Tzeng, and P. J. Lee (1995), Western Canada Mannville gas potential seen as high, *Oil and Gas J.*, 93, 45, 53-55.
- Welhan, J. A., and H. Craig (1979), Methane and hydrogen in East Pacific Rise hydrothermal fluids, *Geophys. Res. Lett.*, 6, 11, 829-831.
- Wennekers, J. H. M. (1981), Tar sands, *Amer. Assoc. Petrol. Geol. Bull.*, 66, 10, 2290-2293.
- Zhang Kai (1990), The "in-place" resource evaluation and directions of exploration for the major natural gas accumulations of the non-biogenic origin in Xinjiang, *Petrol. Exploration and Development*, 17, 1, 14-21.