# On the relationship of oil and gas formation and degassing processes with groundwater decomposition

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**Abstract**. The article is referred to important consequence of the biosphere oil and gas formation concept, according to which the process of hydrocarbons generation in the subsoil and degassing of the Earth are a single natural phenomenon. The main role in this phenomenon is played by geochemical circulation of carbon and water through the Earth's surface accompanied by polycondensation synthesis of hydrocarbons by $CO_2+H_2O$ reaction. This reaction is accompanied by a colossal decomposition of groundwater into hydrogen and oxygen within the sedimentary cover of the Earth's crust. Unreacted $CO_2$, as well as $H_2$ and most of the methane produced during the reaction are degassed into the atmosphere, while resulting $C_{5+}$ hydrocarbons remain under the surface filling geological traps in the form of oil and gas. The article presents the results of model experiments, which make it possible to estimate the rate of groundwater decomposition and on this basis explain the current rate of Earth's degassing, as well as the observed $CO_2$, $CH_4$ and $H_2$ ratio in degassing products.

**Keywords**: Earth degassing, carbon and water cycle, biosphere concept of oil and gas formation

## Introduction

As is well known, not a single chemical process in the Earth's crust takes place without water (Vernadsky, 1960). Chemical reactions occur mainly in liquid or vapor-aqueous solutions. At the same time, water, as a chemical compound, is very stable and practically incapable of spontaneous decomposition. The $H_2O$ dissociation constant at ordinary temperature equals to $10^{-14}$, while the water decomposition constant with release of hydrogen and oxygen equals to $10^{-83.1}$ (Garrels, Crayst, 1968). Therefore, decomposition of water into hydrogen and oxygen is extremely unlikely without significant energy from the outside. However, the processes of lithogenesis and metamorphism occur with the participation of water in the Earth's crust (Strahov, 1960; Shvarcev, 1975; Uolter, Vud, 1989), in which groundwater decompose with formation of hydrogen due to the release of energy in chemical reactions (Molchanov, 1981).

Groundwater decomposition during the formation of oil and gas has never attracted the attention of either hydrogeologists or oil industry professionals considered the circulation of groundwater and the formation of hydrocarbons (HC) as natural phenomena independent of each other. Hydrogeologists proceeded from the fact that

the decomposition of water into hydrogen and oxygen is so small that it was not taken into account in the balance calculations of groundwater (L'vovich, 1986; Zekcer, Dzhamalov, 1989; Shvarcev, 1996; Zverev, 2007). Petroleum geologists, in turn, believed (Levorsen, 1970; Gavrilov, 1986; Karcev et al., 1992; Batalin, Vafina, 2008) that groundwater in case of its participation in oil and gas formation, only acts as a means of transporting hydrocarbons during oil and gas reservoir formation and destruction, or as a factor affecting rock's composition and reservoir properties. Many geologists hold these views today.

Formation of oil and gas, as well as subsoil degassing, is not without reason attributed to the most problematic issues of geology. Over the past century, these problems have been tried to be solved, however they have not yet been resolved in disputes between supporters of organic and mineral petroleum origin hypotheses. The adherents of the latter hypothesis associate the origin of oil and gas with the influx of carbon-containing gases and fluids from the deep bowels of the Earth (http://journal.deepoil.ru). However, the hypothesis of deep degassing contradicts the data of geophysics and cosmogony regarding the internal structure of the Earth and the mechanism of its formation (Zharkov, 1988; Braun, Masset, 1984; Vityazev et al., 1990). To this we add that with the current intensity of $CH_4$ and $CO_2$ degassing, the Earth's atmosphere would be completely filled with carbon gases in a time period of ~100 years (Barenbaum, 2004).

## New approach to the problem

The role of groundwater in the processes of oil and gas formation and degassing began to be revised in the mid-1990s. At this period in our country was discovered the replenishment of hydrocarbon reserves within "old" oilfields. In addition, it was turned out (Sokolov, Guseva, 1993) that the formation of oil and gas is a modern process, which depends on production conditions at oilfields. To date, this phenomenon has received a theoretical justification and explanation in the biosphere concept of oil and gas formation (Barenbaum, 2004, 2010, 2013, 2014, 2015, 2017). Drawing on the ideas of V.I. Vernadskiy about the biosphere (Vernadskiy, 2001), this concept revealed the participation in the oil and gas formation of the biosphere carbon cycle inextricably linked with the circulation of meteogenic waters through the Earth's surface. Therefore, this cycle is mainly regional in nature, and its characteristic turnaround time is close to the carbon cycle in the biosphere of ~30-40 years (Kondrat'ev, Krapivin 2004).

According to the biosphere concept, meteogenic water penetrating deep enough into the Earth's crust carries both significant amount of oxidized carbon ($CO_2$, $HCO_3^-$, $CO_3^{2-}$) and water-soluble organic matter, which are involved in the formation of gas-oil hydrocarbons. Moreover, if carbon-containing substances in hydrocarbons act as carbon donors, then water itself, while decomposing, serves as a donor of hydrogen.

Today there are numerous facts confirming validity of the biosphere concept. One of its most important conclusions is that oil and gas hydrocarbons are formed in the polycondensation reaction of $CO_2 + H_2O$ synthesis during geochemical cycle of biosphere carbon and water across the Earth's surface. This reaction is accompanied by the decomposition of a large mass of water in the Earth's crust, which leads to the formation and penetration into the atmosphere of significant amounts of $H_2$, $CH_4$, $CO_2$ and $N_2$ (from air dissolved in water).

This article develops the concept stating that generation of gas and oil hydrocarbons and the degassing of subsurface is a single natural phenomenon caused by decomposition of huge amounts of water in the rocks of the Earth's crust, which is involved with carbon in the geochemical circulation through the Earth's surface.

Below are the arguments, facts and experimental results that allow to prove this opinion and show that this conclusion is a direct consequence of the biosphere concept of oil and gas formation.

## Initial stage of research

One of the first to notice the formation of hydrogen in the Earth's crust from water was V.I. Vernadskiy and A.P. Vinogradov (Molchanov, 1981). It was later established (Semenov, 1959) that the course of many chemical processes, in particular polycondensation reactions, is determined by free radicals, i.e. broken chemical bonds. It was found that free radicals could be generated by intracrystalline defects in minerals. Diffusing to the surface of mineral grains, these defects form an energy-saturated layer that reduces the Gibbs energy of chemical reactions. As a result, reactions thermodynamically possible at a temperature of 500ºC and more can occur in the rock mineral matrix under "standard" conditions (T = 25ºC and P = 1 atm.).

Reaction of $H_2O$ decomposition with the release of hydrogen involved in the polycondensation synthesis of hydrocarbons from $CO_2$ and $H_2O$ is also attributed to such reactions, as shown by V.I. Molchanov (Molchanov, 1981; Molchanov et al., 1988; Molchanov, Gontsov, 1992), N.V. Cherskiy and V.P. Tsarev (Chersky, Tsarev, 1984; Cherskiy et al., 1985). These authors have experimentally proved that the energy-saturated layer required for the synthesis of hydrocarbons can be created artificially by mechanical activation of carbon-containing mineral media in presence of water. This layer also appears on the surface of the rock mineral matrix under conditions of their natural occurrence and is affected by the tidal influence of the Moon, as well as tectonic, seismic and other natural processes. A diploma for scientific discovery No.326 (Trofimuk et al., 1982) officially approved this fact.

A necessary condition for the hydrocarbon synthesis is the creation of reducing conditions on the surface of minerals in contact with water, under which water is able to generate «active» atomic hydrogen reacting with carbon oxides. It was identified in the article (Cherskiy, Tsarev, 1984) that sea water contact with samples of carbon-containing rocks mechanically activated by friction generates a wide spectrum of hydrocarbons from saturated, unsaturated, and aromatic, both gaseous, liquid and solid.

The study of crude non-biodegraded oils and natural bitumen showed (Barenbaum, 2007; Barenbaum, Ablya, 2009) that molecular mass distributions of n-alkanes in them are almost identical to those obtained in Fischer-Tropsch synthesis (Glebov, Kliger, 1994), as well as to those which were formed in the experiments of N.V. Cherskiy and V.P. Tsarev at room temperature and atmospheric pressure.

Looking ahead, we emphasize that the following conclusion of the biosphere concept (Barenbaum, 2015; Barenbaum, Klimov, 2015) is fundamentally important: the bulk of "abiogenic" hydrocarbons extracted from the depths in the form of oil and gas come not from some great depths (http://journal.deepoil.ru), but directly formed in the sedimentary cover of the Earth's crust in the reaction of polycondensation synthesis of hydrocarbons from $CO_2$ and $H_2O$.

## Experimental part of the work

In recent years, the reaction of hydrocarbon synthesis from $CO_2$ and $H_2O$ has been studied experimentally and theoretically at OGPI RAS when filtering carbonated water (water with dissolved $CO_2$) through bulk model media containing iron shavings or shale (Barenbaum et al., 2012; Zakirov et al ., 2013; Semenov et al., 2014; Barenbaum, Klimov, 2015). In contrast to the experiments of other authors, when modeling the process of hydrocarbons formation from $CO_2$ and $H_2O$, we used the well-known property of Fe to decompose water, generating active hydrogen under room temperature-pressure conditions.

Most of the experimental studies were carried out on the author's equipment (Zakirov et al., 2013; Barenbaum et al., 2012), and the other part of experiments was carried out on a specialized laboratory equipment (Semenov et al., 2014; Barenbaum et al., 2015) at room temperature and pressure close to atmospheric. The experiments made it possible to establish that the polycondensation synthesis of hydrocarbons from $CO_2$ and $H_2O$ is accompanied by the formation of free molecular hydrogen.

The corresponding chemical reaction in relation to the synthesis of n-alkanes can be represented by the following phenomenological formula (Barenbaum, 2014):

$$nCO_2 + (n + \mu + 1)H_2O + \text{æ}Fe = C_nH_{2n+2} + \mu H_2 +$$
$$+ \text{æ}(FeO) + (3n + \mu + 1 - \text{æ})O, \qquad (1)$$
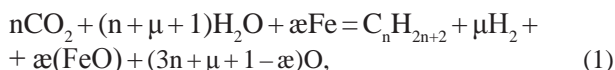
where n is the number of carbon atoms in the molecule, μ and æ are the stoichiometric coefficients.

Thermodynamic calculations show that the synthesis of hydrocarbons by reaction (1) becomes possible under standard conditions (T = 25°C and P = 1 atm) only with sufficiently complete removal of oxygen from the system. In our experiments, iron shavings served as the necessary "absorber" of oxygen, which also played the role of a "catalyst". In the rocks of the Earth's crust, these functions can obviously be performed by many chemical elements and their compounds.

The experiments generally confirmed the results of V.I. Molchanov, N.V. Cherskiy and V.P. Tsarev. They also showed that if hydrocarbons are deposited in the form of bitumens on iron chips, and oxygen oxidizes its surface, then hydrogen in excess enters the gas phase (Table 1).

Data from Table 1 indicate that in the gas phase there are hydrogen, methane and its homologues, as well as carbon monoxide originally not presented in the system. In this case, the gas phase almost entirely consists of

$H_2$. The oxygen arising from the decomposition of $H_2O$ is almost completely consumed on the oxidation of Fe, and its penetration into the gas phase is negligible. The presence of nitrogen, as well as a certain amount of oxygen, is determined by air, which was originally dissolved in water. It is significant that the excess of nitrogen over oxygen is much higher than their ratio in the air.

In our experiments, the yield of $H^2$, as well as yield of $CH_4$ and its homologues, depended significantly on the $CO_2$ content in carbonated water (Fig. 1). Catalytic activity of the iron shavings was decreasing during the experiments, and the water in the reactor was ceasing to decompose. In all experiments carried out at different reactor volumes and different pressures of $CO_2$ in water, a maximum of $\sim 0.1 \div 1$ g per liter of $H_2O$ have been decomposed in the reactor.

This paper discusses the experimental results (Barenbaum and Klimov, 2015), which allowed for the first time to raise the question on groundwater decomposition rate in the process of oil and gas formation, as well as on the extent of this phenomenon.
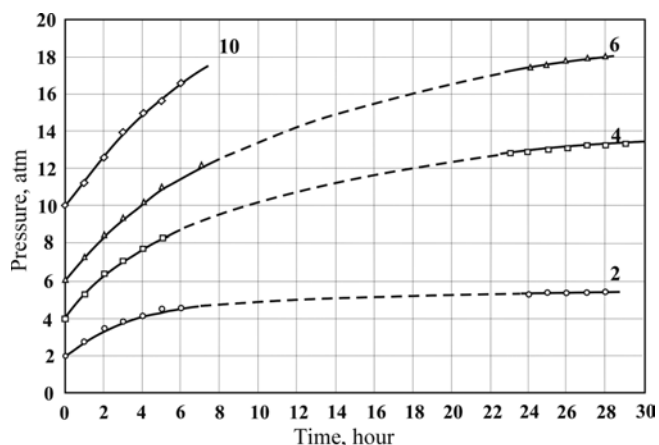


*Fig. 1. Changes of pressure over time in the reactor. Curves indicate the saturation of water with $CO_2$ at its pressure in the mixer of 2, 4, 6 and 10 atm*

## Measuring the rate of water decomposition

Experimental equipment scheme is shown in Fig. 2

The experiment consisted in measuring the volume of gas formed in the reactor (3) some time after it was filled with carbonated water. As a reactor there was used a stainless steel beaker with an internal volume of 45 ml, which was filled with 25 g of fine steel shavings in order to simulate an "activated" rock. Under a small initial pressure, ~35 g of carbonated ("meteogenic") water was poured into the glass, which was emitted by a solution

| Component | Hydrogen | Nitrogen | Oxygen | Methane | Ethane | Propane | Butane | | 2 |
|---|---|---|---|---|---|---|---|---|---|
| Content, % | 95.562 | 3.688 | 0.657 | 0.039 | 0.018 | 0.0125 | 0.0049 | 0.002 | 0.017 |

*Table 1. Chemical composition of the gas phase after treatment with alkali*
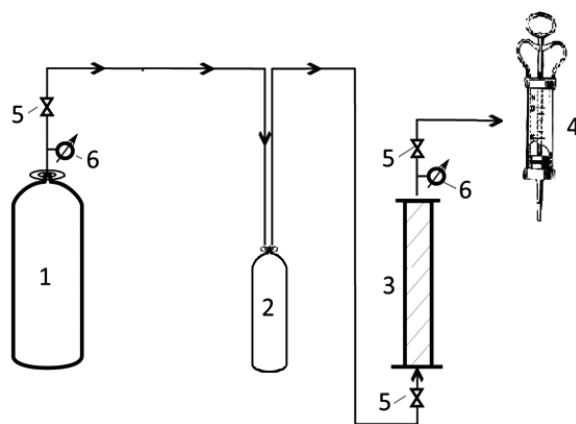
*Fig. 2. Experimental equipment scheme. 1 – CO₂ cylinder; 2 – mixer for saturation of water with CO₂; 3 – reactor with activated medium; 4 – syringe for sampling and measuring gas phase volume; 5 – valves; 6 – manometers*

of $CO_2$ in distilled water. Water saturation by $CO_2$ was made in 5 l tanks (2), where from a cylinder (1) under pressure of 2-5 atm was supplied chemically pure $CO_2$. Water saturation time by $CO_2$ was assumed 18 hours. The separation of gas from liquid and measuring its volume at the outlet of the reactor was carried out using a syringe (4). The error in measuring the volume of gas with a syringe at atmospheric pressure was ~0.5 cm³.

The experiment consisted of filling the reactor (3) with carbonated water from the mixer (2) followed by shut off of the valves at the inlet and outlet of the reactor allowing chemical reactions to take place in it. Along with other possible reactions in the reactor, decomposition of water occurred with the formation of $H_2$, which caused an increase in pressure recorded by a pressure gauge (6). The composition of the newly formed gas shows (Table 1) that the pressure increase in the reactor is mainly created by $H_2$ resulting from $H_2O$. Thus, mass of the destroyed water can be measured by volume of the generated $H_2$.

In the course of the experiment, 5 cycles of gas

volume measurements were performed, including from 4 to 6 consecutive experiments of different duration. Duration of each cycle ranged from 3 to 6 days. The measurements were carried out at room temperature.

When developing the methodology, a number of factors were taken into account, which could introduce errors into the experimental results. The first factor is associated with the possible ingress of air into the measured volume of gas when it is taken by syringe. The second factor is the necessity to maintain a constant saturation of the water with $CO_2$ before the start of each experiment, which was technically difficult to control, but it was necessary to ensure reproducibility of different series of measurements. The third source of errors is caused by the fact that after each series of experiments, the reactor had to be rinsed and sealed again before new measurements with the removal of air that had entered it.

The influence of these factors was reduced with the use of the technique explained in Fig. 3, which shows the results of measuring the volume of gas at the outlet of the reactor after one of a series of experiments. The technique consisted in the fact that in the course of the experiment the reactor was repeatedly filled with carbonated water from the mixer, and the volume of gas was measured after different periods of exposure (duration of water presence in the reactor), considered as "background" and "informative" measurements. Measurements with an exposure time of 1 min were considered as background. The gas selected in them almost completely consisted of $CO_2$, and its volume corresponded to that which was separated from water as the pressure decreased from initial to atmospheric, at which the measurements were made. Experiments with an exposure time of 21 hours or more were considered informative. In this case, along with $CO_2$, the gas also contained $H_2$ formed from water. The difference effect between informative and background measurements made it possible to measure the amount of the emerged



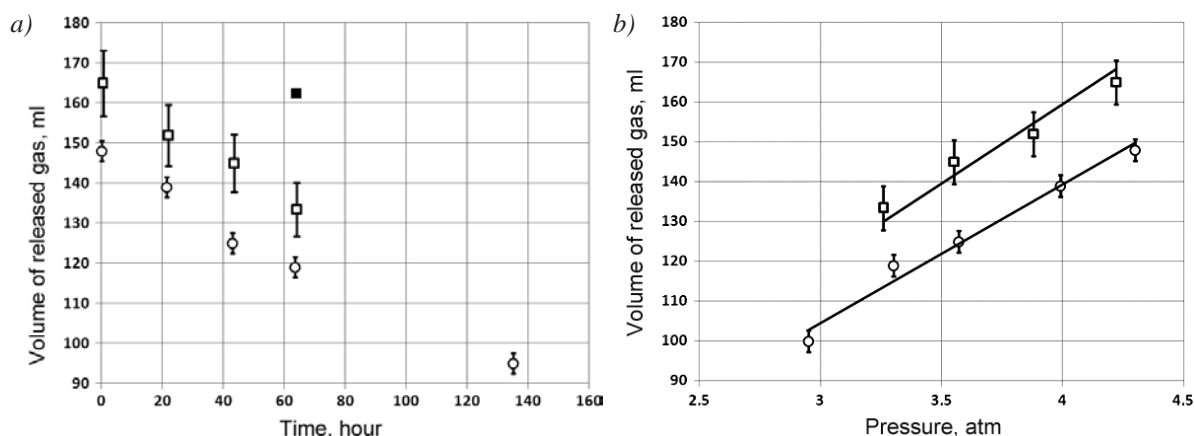*Fig. 3. Volume of released gas, depending on: a) the time elapsed since the beginning of the experiment, b) initial pressure of meteogenic water in the reactor. Circles – background measurements, squares – informative measurements. Measurement with an exposure of 71 hours is shown by a dark square. Straight lines indicate approximating dependencies. Errors: background – 2.4% rel., informative measurements – 6.8% rel.*

$H_2$, and according to this data, find the amount of water disintegrated in the reactor. As the number of measurements increased in the experiment, the amount of water and the pressure of $CO_2$ in the mixer decreased with time. The volumes of gas (V) released in the reactor also decreased (Fig. 3a). In Fig. 3b the same volumes are given depending on the initial pressure of the gas $P_o$ in the reactor.

Since the solubility of gases is linearly related to pressure, the V ($P_o$) dependences were approximated by straight lines passing through the point P = 0. Dependences found by least squares method are as follows: $V = 34.7 P_o$ for the background measurements, and $V = 39.0 P_o$ for informative measurements. In the latter case, the volume of gas in the experiment with an exposure of 71 hours is recalculated to 21 hours, as for all other measurements.

### Analysis of the experimental results

Since the gas sampling technique was standardized, possible systematic errors during the transition to the differential effect were reduced. Experiments have shown that the replacement of iron shavings, the new preparation of carbonized water, as well as the sequence of background and informative measurements did not affect the difference effect. After averaging the results of a series of experiments performed at initial pressures, $P_o = 3.0 \div 4.3$ atm and an exposure time of 21 hours, the difference effect was $\Delta V = 22 \pm 6$ ml. Assuming that the $\Delta V$ effect is created by gaseous hydrogen, which at atmospheric pressure has a density of $\rho_H = 1 \cdot 10^{-4}$ g/cm$^3$, the mass of the hydrogen formed is calculated as $m_H = \Delta V \cdot \rho_H = (2.2 \pm 0.6) \cdot 10^{-3}$ g. Taking into account that the share of $H_2$ in water is 11.1%, the mass of decomposed water was $M = m_H/0.111 = 2.0 \cdot 10^{-2}$ g. Taking into account that the mass of water in the reactor was ~ 35 g, its decomposed part was $M/35 \sim 5.7 \cdot 10^{-4}$. From where the rate of carbonized water decomposition in the reactor turned out to be $\sim 2.7 \cdot 10^{-3}$ g per 1 liter of $H_2O$. Hydrogen included in the HC was not taken into account.

Taking into account the effect of flattening (Fig. 1), there was decomposed $\sim 0.1 \div 1$ g per liter of carbonated water during the experiments. Taking this data as a basis, we inevitably come to the conclusion that in the Earth's crust, and above all in its sedimentary cover, a significant amount of groundwater should be decomposed annually (Barenbaum, 2017a).

The main question is how large this mass of water is and whether it is sufficient to explain the current rate of HC generation, as well as the intensity of $CH_4$, $CO_2$ and $H_2$ degassing from the depths.

Biosphere concept of oil and gas formation gives us the answers to these questions (Barenbaum, 2014, 2015, 2017).

### Biosphere concept of oil and gas formation

The fundamental difference of the biosphere concept from other theories is that it requires a balance between the "descending" and "ascending" flows of carbon and water during circulation through the Earth's surface.

When solving this problem, it was identified (Barenbaum, 1998, 2010) that hydrosphere waters, biosphere carbon and atmosphere oxygen form a single geochemical circulation system on our planet. The unity and stability of this system ensures participation in the circulation of living matter, which brings the rate of oxygen and carbon circulation in line with the rate of water circulation within the underground hydrosphere.

At present, the geochemical system of the biosphere is in a state close to stable dynamic equilibrium characterized by the rate of the cycle in terms of $CO_2$ equal to $2.7 \times 10^{16}$ g/year. In this state, the main water bodies of the Earth are replenished at a rate of $(2.0 \pm 0.5) \times 10^{19}$ g/year by waters participating in two circulation cycles (Fig. 4). These waters consist of 87-90% "meteoric" waters, and 10-13% "marine"
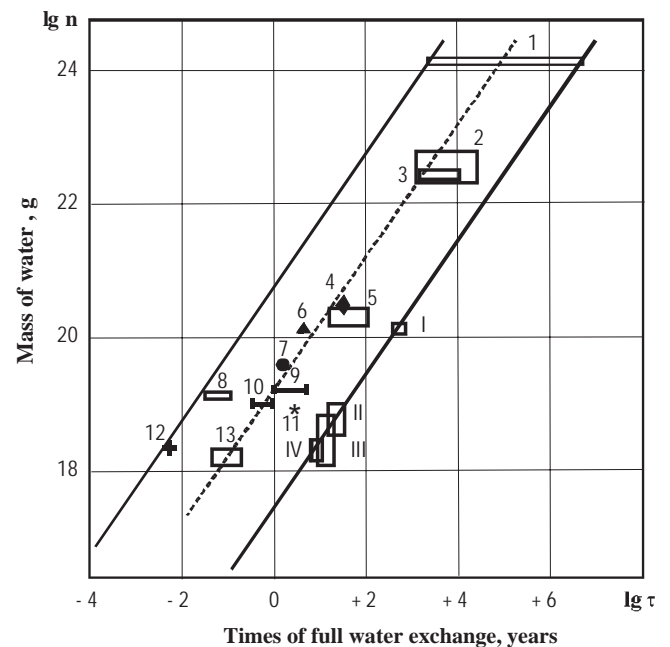


*Fig. 4. Comparison of water quantities and times of water exchange for the main natural reservoirs of the Earth: 1 – World Ocean; 2 – groundwater; 3 – glaciers and ice caps; 4 – lakes, impounding reservoirs and swamps; 5 – lakes; 6 – swamps; 7 – sea ice; 8 – water in the atmosphere; 9 – soil moisture; 10 – snow cover; 11 – icebergs; 12 – atmospheric ice; 13 – rivers; dotted line characterizes the average rate of water exchange. Roman numerals indicate data of the biosphere carbon cycle in terms of $CO_2$: I – World Ocean; II – living matter; III – soil-silt; IV – the atmosphere. The upper oblique straight line corresponds to meteogenic waters circulation at a rate of $C_1 = 5.2 \times 10^{20}$ g/year (L'vovich, 1986), and the lower one corresponds to marine waters circulation through the mid-ocean ridges at a rate of $C_2 = 2.7 \times 10^{17}$ g/year, which coincides with the circulation rate of $CO_2$ in biosphere (Barenbaum, 2010).*

waters. The first one are of local origin, they are formed in the atmosphere and in the form of rain and snow infiltrate through the Earth's surface subsequently entering the area of water bodies feeding. The second is water belonging to the general system of deep circulation of groundwater through the mid-ocean ridges. They received the name "marine" because of proximity of their salt composition to the waters of the World Ocean. In the groundwater of different regions of the globe, meteogenic waters significantly dominate over the marine waters. This conclusion was obtained for waters of rivers, lakes and glaciers, as well as for waters of deep artesian basins, volcanic areas and waters associated with oil and gas accumulations (Ferronskiy, Polyakov, 2009).

The carbon balance in its cycle through the Earth's surface is provided by 4 components. On the ascending branch of the cycle, these components are natural and anthropogenic flows. The first one caused by subsurface degassing phenomenon (Table 2), in which CH4 and CO2 come into the atmosphere from the depths in approximately equal amounts of $(2.5\pm0.2)\times10^{14}$ g/year (Voytov, 1986). According to measurements of recent years (Voytov, 1999; Syvorotkin, 2002), this component may be ten times greater.

The anthropogenic component is represented by carbon, which is extracted from the depths of the Earth as fuel in the form of oil, gas and coal. In particular, in 2017 the world produced 4.3 billion tons of oil, 3.8 trillion m³ of natural gas and 7.8 billion tons of hard coal, which contain ≈14 billion tons of carbon. Thus, it can be assumed that at the present time, about $10^{16}$ g of predominantly reduced carbon comes to the surface from the subsurface.

Carbon downstream is also represented by two components. One is associated with the disposal of carbon (organic and inorganic) in sedimentation processes. According to data (Voytov, 1986), ~$2\times10^{14}$ g of carbon consisting of ~2/3 of carbonates and ~1/3 of dead organic matter are buried into the Earth's crust annually. The second component is carbon, which is transported under the Earth's surface by meteogenic (surface) water. Since most of the carbon fuels extracted from the subsoil is burnt and therefore converted in about three times greater amount of $CO_2$ emitted into the atmosphere, then to balance the ascending and descending carbon flows, it is necessary to supply ~$3\times10^{16}$ g of water-soluble $CO_2$ to the Earth's crust every year. In this case, its content in water should be ~$3\times10^{16}/2\times10^{19}$ ~$10^{-3}$ g/year, which fully satisfies the actual data (Korzh, 1991).

Under the Earth's surface, water-soluble $CO_2$ may take part in various chemical reactions, but first of all it participates in the decomposition of $H_2O$ with the formation of HC and $H_2$ according to reaction (1).

| Geostructural zones | Area mln. km² | $CO_2$ | HC | $_2$ | $N_2$ | |
|---|---|---|---|---|---|---|
| *In active volcanism on the surface of the Earth* | | | | | | |
| Explosive stage | | 5.66 | 0.066 | 0.025 | ? | ? |
| Fumarole stage | | 10.38 | 0.170 | 0.012 | ? | ? |
| *In Alpine fold zones* | | | | | | |
| In mud volcanoes | | 3.95 | 10.68 | 0.0014 | 0.16 | 22 10⁻⁵ |
| Areas of Alpine folding | 150 | 400/119 | 50/54 | 10/0.14 | 40/7.5 | 0.35/9.5 10⁻³ |
| *Platforms and ancient folded areas* | | | | | | |
| Shields | 29.4 | 22.5/1.21 | 30/0.063 | 4.2/0.012 | 4/0.147 | 0.2/0.001 |
| Blocks of alkali rock | 5.1 | 1.0/0.01 | 300/1.102 | 100/0.012 | 20/0.127 | 0.35/8·10⁻⁵ |
| Platforms and ancient folded areas, screened by sedimentary cover | 316 | 20/13 | 150/34.1 | 6.3/0.18 | 18./7.11 | 0.27/0.015 |
| *World ocean* | | | | | | |
| Underwater margins | 81.8 | 20/3.24 | 150/8.835 | 4/0.029 | 5/0.51 | 0.3/0.0044 |
| Transitional area | 30.8 | 500/30.49 | 650/14.5 | 12/0.033 | 8/0.31 | 0.6/0.0033 |
| Sea floor | 193.9 | 50/19 | 300/70 | 75/1.3 | 8/1.938 | 0.15/0.005 |
| Mid-ocean ridges | 55.4 | 600/67 | 750/30 | 900/4.48 | 100/6.93 | 0.25/0.0025 |
| Total gas | | 272.89 | 223.51 | 6.084 | 24.732 | 0.0405 |

*Table 2. Flow density for some gases and the value of their unloading in different geostructural zones according to G.I. Voytov (1986). The figure in the numerator is the gas flow density (cm³/m² per year), the figure in the denominator is the gas integral discharge ($10^{12}$ g/year)*

Moreover, in case when formed hydrocarbons fill up geological traps (reservoirs) and can stay there for a long time, then light $H_2$, together with most of the $CH_4$, $N_2$ dissolved in groundwater and unreacted $CO_2$ are degassed into the atmosphere (Table 2).

As is known, oil and gas formation processes are most intensively taking place at the depths of "oil window" (Fig. 5), where the temperature and pressure conditions are determined by hydrocarbons phase composition (Batalin et al., 1992, Batalin, Vafina, 2008).

Fig. 5a (Barenbaum, Batalin, 2001) shows the results of the phase PT-diagram calculation for a hydrocarbons mixture having typical gas-condensate composition: $CH_4$ (70-85%), $C_2H_6$-$C_4H_{10}$ (5-10%), $C_{5+}$(10%). According to calculations, this HC mixture can exist in a homogeneous state only from the outside of the two-phase region. Inside this region, the mixture is divided into two phases: gaseous – "gas" and liquid – "oil". Isopleric lines show the percentage of liquid phase in the mixture. Straight line characterizes the change in PT conditions with depth on the continents. The points of the straight line intersection with the isopleric lines determine the percentage of «oil» in the initial mixture at different depths. Fig. 5b shows the curve of "oil" percentage change with the depth according to the diagram in Fig. 5a. The calculation explains well the position and shape of the oil window in the largest oil and gas basins of the world (Sokolov, Ablya, 1999). In case of changes in the composition of HC mixture and thermobaric conditions, the oil window can be deformed and displace along the depth axis (Lapshin, 2000; Batalin, Vafina, 2008).

Oil and gas formation also causes another effects. The first of these is the failure of groundwater hydraulic connection with the surface in the oil window, which is characteristic of relatively shallow depths (Fig. 6).
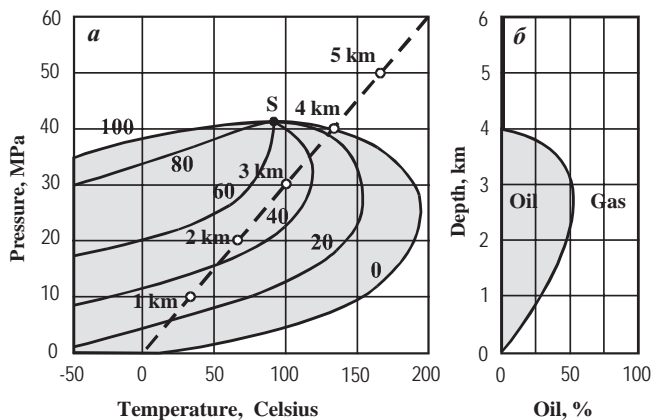
In zone I, the growth of pressure with depth is created by fluids filling pores and fractures, which form channels communicating with each other and with the surface. In zone III, pressure gradient is determined by the weight of the overlying rocks. Rocks of this zone are characterized by low fracturing and porosity, and if they contain water, this water is in a chemically bound state.

As for zone II – the zone of so-called abnormally low and abnormally high reservoir pressures (Dobrynin and Serebryakov, 1989), until recently it did not receive a clear explanation. The prevailing view was that this zone is formed in oil and gas basins due to inhomogeneous lithological transformation and compaction of sedimentary rocks with increasing pressure and temperature with depth.

This explanation is true, but only in part. In the biosphere concept, this zone arises primarily due to the decomposition of water in the fields of hydrocarbons generation. The process is so intense that free water at the depths of the oil window physically ceases to exist. Owing to the transformation of $H_2O$ into $H_2$ and $CH_4$ degassing into the atmosphere, there is a shortage of reservoir pressures (piezo minimum), which serves as a kind of "pump" (Barenbaum, 2015a), sucking water from the upper and lower horizons.

Another effect is the fact that the water repeatedly involved in the hydrocarbon synthesis is enriched with deuterium – a heavy isotope of hydrogen. According to data (Zykin, 2012), the associated waters within gas reservoirs and containing acidic components, have abnormally high deuterium contents, which are not found in any other natural objects (Fig. 7).
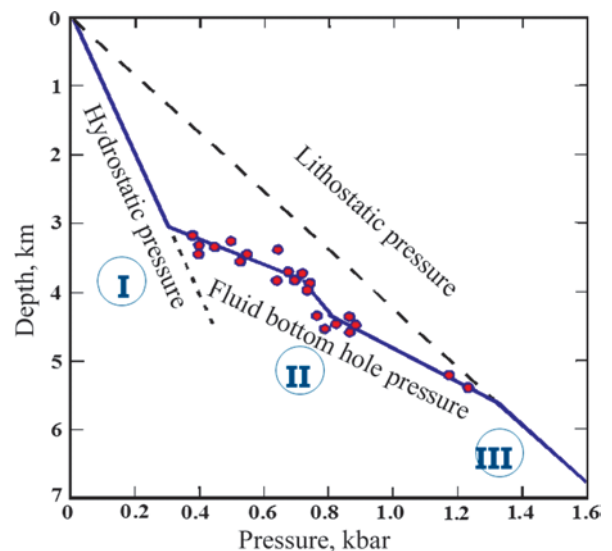


*Fig. 6. Changes in reservoir pressure with depth within sedimentary basins caused by the total hydrodynamic pressure zonality in the subsurface crust hydrosphere (according to Dzh. Uolter and B. Vud (1989) with changes). The numbers indicate zones of hydrostatic (I), transition (II) and lithostatic (III) pressure gradient*
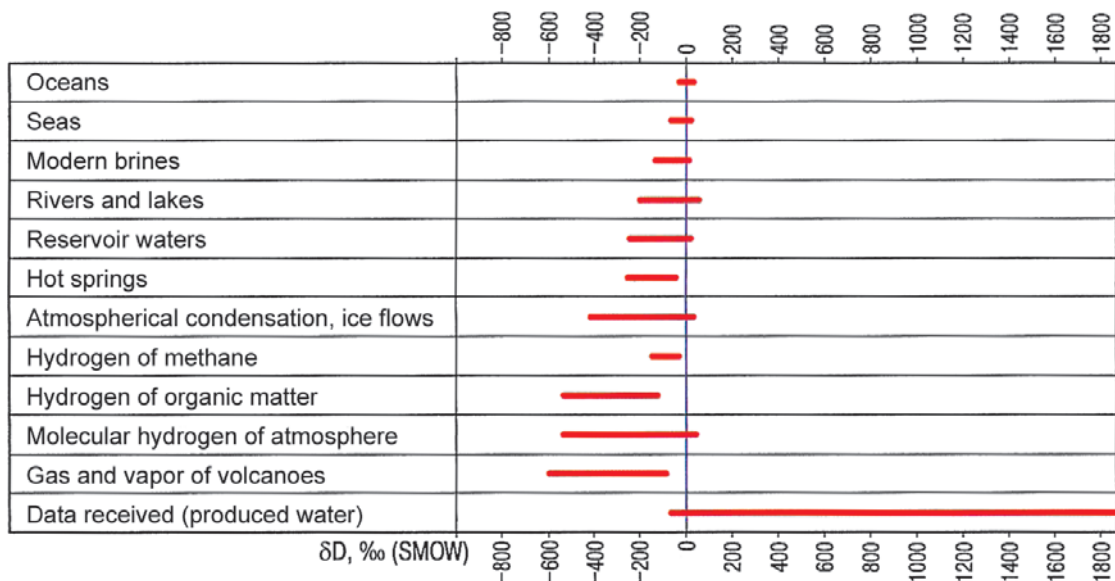


*Fig. 5. Phase diagram of the hydrocarbon mixture with isoplers (a) and the oil saturation curve corresponding to this diagram (b): inclined dashed straight line – depth scale corresponding to the hydrostatic gradient typical of continents; S is the critical point of the mixture*

*Fig. 7. Variations of hydrogen isotopic composition in natural waters and objects (Zykin, 2012)*

## Extent of groundwater decomposition in the Earth's crust

In solving this problem, we proceed from the fact that polycondensation synthesis of hydrocarbons and degassing are processes reflecting different sides of the same phenomenon caused by hydrospheric waters circulation through the Earth's surface and their decomposition in the rocks of the Earth's crust with the formation of hydrocarbons and hydrogen.

Therefore, being connected by formula (1), $CH_4$, $CO_2$ and $H_2$ degassing into the atmosphere not only characterize the intensity of the modern HC formation, but also make it possible to judge the mass of water decomposing within the Earth's crust.
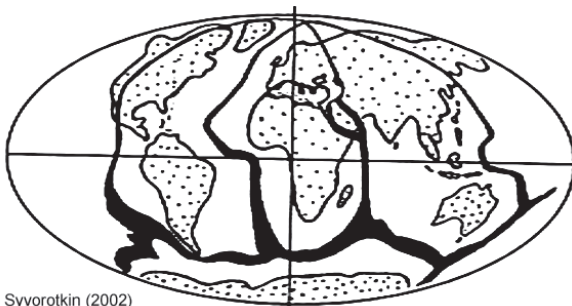


*Fig. 8. Main degassing channels associated with the world rift system according to V.L. Syvorotkin (2002)*

Let us note that the degassing process is exceedingly uneven. According to G.I. Voytov (1986), gas emission in oceans is higher than on the continents. The bulk of the gas enters the atmosphere through the faults of the Earth's crust, primarily through the mid-ocean ridges (Fig. 8).

Maximum degassing occurs in the southern hemisphere of the Earth (Syvorotkin, 2002). The composition of gases and their intensity also vary, showing cyclicity from several minutes to several years (Voytov, 1991). In general, similar amounts of $CH^4$ and

$CO_2$ at a level of ~ $2.5 \times 10^{14}$ g/year are degassed from the depths of the globe (Table 2). In later articles (Voytov, 1999; Syvorotkin, 2002), these estimates were increased by about an order of magnitude, so that they can be taken equal to ~ $10^{15}$ g/year. Hydrogen degassing rates should also be considered much higher than in Table 2 (Larin et al., 2010).

Let's show that the results of our experiments on the water decomposition satisfy quite well the actual data. To this end, let us assume that annually ~$2 \times 10^{19}$ g of water comes under the surface, which transfers ~ $3 \times 10^{16}$ g/year of $CO_2$ to the rocks of the Earth's crust. A part of this amount of $CO_2$ interacts in rocks with $H_2O$, participating in hydrocarbons synthesis according to reaction (1). Another unreacted part of $CO_2$, which is about an order of magnitude smaller, degasses into the atmosphere.

Let's consider the part of $CO_2$ that took part in the formation of hydrocarbons. According to formula (1), it takes 2.75 g of $CO_2$ and at least 2.2 g of $H_2O$ to form 1g of $CH_4$. Let's suppose that all methane formed is degassed from the subsurface. Then, to explain its flux of ~ $10^{15}$ g/year into the atmosphere, then ~ $2.75 \times 10^{15}$ g of $CO_2$ should be consumed annually. Taking into account that $CO_2$, in addition to methane, also participates in the synthesis of heavier hydrocarbons represented by oil and bitumen remained in the depths, for a mass of $CO_2$ annually entering the Earth's crust in an amount of ~ $3 \times 10^{16}$ g, this estimate looks quite acceptable.

We now turn to the water flow rate. According to the formula (1) an unlimited amount of $H_2O$ may be involved in this reaction. Moreover, the synthesis of hydrocarbons consumes a mass of $H_2O$ approximately 20% less than amount of consumed $CO_2$; all the excess $H_2O$ goes to the formation of $H_2$. Therefore, if ~ $10^{16}$ g of groundwater decomposes annually in the processes of oil and gas formation, this amount is enough to explain

the data of Table 2 on methane and hydrogen.

In this regard, we note that in our experiments was decomposed the maximum ~ 0.1÷1 g per liter of carbonated water. If we proceed from this result, then in case of ~ $2\times10^{19}$ g/year water circulation through the Earth's surface , the decomposition rate of $H_2O$ will be ~$2\times10^{19}\times(10^{-4}\div10^{-3})$ ~$10^{15}\div10^{16}$ g/year. That coincides with our estimate of groundwater decomposition rate according to $CH_4$ and $CO_2$ degassing data.

Thus, the rate of water decomposition in our experiments is not so far from the rate of this process, on average across the globe.

### Conclusion

The results of the experiments, as well as arguments and facts allow us to state the following:

1. In the Earth's crust, in reactions of hydrocarbon polycondensation synthesis, annually decompose ~$10^{16}$ g of groundwater containing dissolved $CO_2$. This process involves not only meteogenic (on the continents), but also marine (through the mid-ocean ridges and zones of deep faults on the continents) waters.

2. The hydrogen produced during water decomposition, most of the $CH_4$ and unreacted $CO_2$ are degassed into the atmosphere, while the HC and part of methane remain in the depths forming oil and gas accumulations in case of favorable conditions. Of course, part of the formed hydrogen combines with $O_2$ again turning into $H_2O$.

3. The main mass of $CH_4$, $CO_2$ and $H_2$ is degassed into the atmosphere not from the deep bowels of the Earth, but from the rocks of the Earth's crust and above all from its sedimentary cover. The main role in the processes of oil and gas formation and degassing is played by decomposition of water in the Earth's crust circulating through the surface on the continents. Mass of such water is ~$10^{21}$ g, and its cycle time, like that of the biosphere carbon cycle, is about 40 years (Barenbaum, 2004).

4. It should be assumed that the decomposition of $H_2O$ mainly occurs in the upper 5 km layer of the Earth's crust. With a mass of free water in this layer of ~ $6\times10^{22}$ g (Shvarcev, 1996) and a decomposition rate of ~$10^{16}$ g/year, their life time in the underground hydrosphere will be ~$6\times10^{22}$ g /$10^{16}$ g/year, which is approximately ~6 million years.

5. Amount of free water on Earth is $2.1\times10^{24}$ g. Of these, $1.37\times10^{24}$ g is in the World Ocean and $0.73\times10^{24}$ g is in the underground hydrosphere. Most of the underground hydrosphere waters-4 are represented by deep-seated waters circulating beneath the continents along permeable horizons, ensuring the geological circulation of water through the mid-ocean ridges. According to data (Baskov, Kiryukhin, 1993), every 8 million years a mass of water equal to the volume of the World Ocean pass through the rift zones of the axial parts of the middle oceanic ridges. Therefore, the rate of the geological water cycle of the hydrosphere can be found as $2.1\times10^{24}$ g / $8\times10^{6}$ years = $2.63\times10^{17}$ g/year.

This value coincides with the rate of circulation on Earth of atmospheric oxygen and biospheric carbon, which together with hydrosphere water cycle form a single geochemical system on our planet (Barenbaum, 1998).

These estimates of the rate and extent of groundwater decomposition in the Earth's crust should be taken into account when assessing the petroleum potential of the subsoil.

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