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NEW ABIOGENICALLY BIOGENIC POSSIBLE GENESIS OF NATURAL GAS

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Abstract

The occurrence of gas containing mainly methane, evolving from carbonate rocks in the locality Koněprusy (Barrandian, Czech Republic) can not be explained by existing theories of natural gas origination. Therefore we developed a new biogenically-abiogenic theory involving participation of archeobacterias.

Key words: natural gas; biogenically-abiogenic theory.

By the evaluation of newly obtained data about metabolism of some bacteria and archaeobacteria, we can arrive at a novel theoretical possibility of the genesis of natural gas.

Natural gas is a mixture mainly of gaseous alkanic hydrocarbons that contain in their molecules from one (C_1) to six carbon atoms (C_6), in some cases even up to twenty carbon atoms (C_{20}). Its chief constituent, in many cases exceeding 80 % vol., is methane. As to other predominant alkanes, we can mention ethane, propane and butane.

Natural gases can contain non-hydrocarbon components, too. However, these generally affect its application in an adverse way. In this role, we usually meet with water vapour, carbon dioxide, nitrogen, helium, sulphane, and thiols.

In accordance with its relevant origin, and notably according to the possible origin of methane, we can rank natural gases, upon lines of the present knowledge, into three basic categories: cosmogenic, planetary, and geogenic. Methane is one of cosmogenic substances that originate in the reaction plasma of stars. Some deposits of natural gas contain the ^{3}He isotope that cannot originate on earth by any nuclear reaction; therefore, he must have been carried to earth from space at the very birth of our planet. In this case, the same holds true of methane as well, which is present in the same particular deposit as helium.

Likewise, we can make a hypothesis that methane was one of the substances of the proto-planetary cloud, by whose contraction our planet came into being.

Geogenic gases are gases that originated in the past and continue to originate on earth even at present. Into this class, natural gases of the majority of classical extracted deposits within the depths from 0,5 to 4-5 km are ranged.

The origin of natural gas is actually being explained either in purely biogenic or abiogenic way. These processes represent essentially the organic or inorganic theory of their origin.

The abiogenic theory of the origin of natural gas includes methanogenic processes that can run in the supermagmatic earth strata between inorganic components. From the historical point of view, we can quote the complete set of them [1]. In the year 1860, Berthelot made a hypothesis that hydrocarbons can originate by the action of carbonic acid on alkali metals in presence of water at high temperature and pressure in areas near the earth magma. In 1871 Baysson made a similar hypothesis. On the basis of their own experiments, Cloez (1878) and Mendeleev (1897) had parallel ideas. Mendeleev also assumed reactions of carbides with water, or rather with water vapour. These could lead directly to methane or to unsaturated hydrocarbons that could consecutively produce saturated hydrocarbons.

$$Al_4C_3 + 12\,H_2O \rightarrow 3\,CH_4 + 4\,Al(OH)_3$$
$$FeC_2 + 2\,H_2O \rightarrow C_2H_2 + Fe(OH)_2$$

Another inorganic theory of the origin of natural gas is the theory of Wismann (1971). According to him, a great deal of resources of natural gas originated as a consequence of insinuation of magma into coal sediments. By the thermal decomposition of coal, the produced carbon dioxide and hydrogen could further react and give rise to methane. As an evidence of this, he put forward the isotope analysis of carbon.

If we admit that even water can enter into abyssal parts of the earth, then we can consider reactions of carbon with water vapour and reactions of carbon with carbon dioxide giving carbon monoxide (the reaction of Boudouarde):

$$C + 2\,H_2 \rightarrow CH_4$$
$$C + 2\,H_2O \rightarrow CO + H_2$$
$$2\,C + 2\,H_2O \rightarrow CO_2 + CH_4$$
$$C + CO_2 \rightarrow 2\,CO$$

The mixture of carbon oxides and hydrogen (so-called synthesis gas) that was formed by the above-mentioned reactions can, catalysed by rocks containing e.g. nickel, iron, cobalt, etc., lead under thermodynamic conditions that reign in the abyssal strata, conformably with the industrial Fischer-Tropsch synthesis, to methane or various other hydrocarbons. From a lot of reactions of this synthesis, which was on a large scale realized in Germany in 1935, we can cite at random the following reactions:

Generation of alkanes

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4\,H_2 \rightarrow CH_4 + H_2O$$
$$n\,CO + (2n + 1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$$
$$2n\,CO + (2n + 1)\,H_2 \rightarrow C_nH_{2n+2} + n\,CO_2$$

Generation of alkenes

$$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O$$
$$n\,CO + n\,H_2 \rightarrow C_nH_{2n} + n\,CO$$
$$3n\,CO + n\,H_2O \rightarrow C_nH_{2n} + n\,CO_2$$

And of alkynes

$$n\,CO + (2n - 1)\,H_2 \rightarrow C_nH_{2n-2} + n\,H_2O$$
$$2n\,CO + (n - 1)\,H_2 \rightarrow C_nH_{2n-2} + n\,CO_2$$

The methane, as well as hydrocarbons that have been formed by the polymerization of alkenes or alkynes can, by this hypothesis, concentrate only very hardly at high pressure in igneous rocks. Hence, they migrate up, into superior stratums, where they can mix in sedimentary zones with e.g. biogenic gas.

The source of carbon as such, in deeper sections of the earth crust, is not problematic. Some 4 milliards of years ago, as the earth became cold; it enriched itself gravitationally with heavier elements in its centre. A round of them could thereafter create carbides. The next source of carbon is carbon dioxide, which, after its concentration in the gaseous envelope of the earth, deposited gradually in the earth crust in the form of carbonate or as organic matter. Metal stratums then went through several homogenisation cycles and slow drifts in depths of 500 to 700 km.

Nowadays, four carbon cycles are generally presented. One of them, so-called geochemical cycle, describes the depth levels of the earth and at the same time stabile compounds of carbon that occur in these levels. The schematic representation of this cycle can be seen on Fig. 1. From the figure, it can be found that the carbon circulation itself is mediated by methane and by carbon dioxide. Thereafter, methane can migrate, depending on simultaneously running diffusion processes, into gas-tight strata of various deposits from which it is extracted at present.

The basic condition of the biogenic origin of natural gas is the creation of a sufficient quantity of organic substrate, which, under the influence of a series of biogenic factors converts into petroleum or natural gas. It can be supposed that a significant growth of organic matter on earth took place only cca 0,7-1.10^9 years ago [2]. At that time, oxygen is postulated to occur in the atmosphere in quantity greater than 1 %. This factor has made possible the development of aerobic processes and the protection of higher organisms from UV radiation. Thus, we can also hear the argument that in sediments older than from the geological period of Cambrian, there is practically no petroleum. On the other hand, in sediments from the Caenozoic era, we find about 50 %, from the period of younger Mesozoic era (the Cretaceous period) approx. 18 %, and from the Permian and Carboniferous period about 15 % of world reserves of petroleum and natural gas. It goes without saying that in addition to primeval vegetal residues accumulated in watercourses, sea gulfs and so on, it was also plankton and dead animal residues that contributed to the creation of organic sediments.

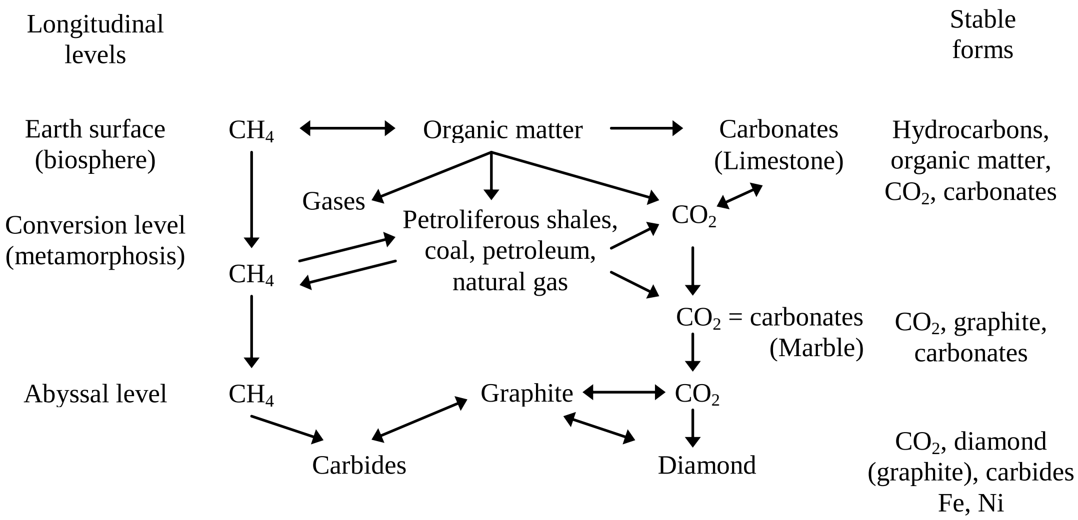

Figure 1. Geochemical carbon chain.

Some other fundamental arguments that are connected with the biogenic theory of the natural gas origin:

Principal deposits of petroleum and natural gas are situated in sedimentary rocks in which hydrocarbons were identified as well.

Deposits of petroleum and natural gas were found only in certain geological conditions.

In petroleum and organic substances of sedimentary rocks, organic substances called biological markers were found. These originated previously in organic living organisms.

It was analytically confirmed that the ratio of carbon isotopes ^{13}C and ^{12}C in petroleum and natural gas, compared to that in organic substances that were at their origin – in so-called necromass – is similar. The ratio of these isotopes in the atmospheric carbon dioxide and in carbonates that have arisen in sediments is, however, diametrically different.

The transformation stages of organic substance during the generation of natural gas, including syngenesis, diagenesis, katagenesis, metamorphism, and a round of other stages that abide by the local thermodynamical and catalytic, geochemical or enzymatic conditions, are described e.g. in [2, 3].

A simplificatory general scheme of organic substances transformation into natural gas (methane) is shown in Figure 2.

The most important metabolic group of the methanation process are methanogenic bacteria that produce the end product of anaerobic decomposition of organic matrix – methane. These bacteria are phytogenically related to primordial organisms originated on the earth, where the „living" environment was strongly reductive. This is why these organisms require for their prosperous metabolism a low reduction potential of - 300 mV.

Metabolism of methanogenic bodies depends on many factors connected with the anaerobic character of medium, temperature, humidity, source and structure of organic carbo-substances, source of energy (see Table 1), symbiosis with other, especially acidogenic bacteria, pH of medium, presence or absence of toxic elements etc. (5-9). Bryant [10] classifies the family of methanogenic bacteria in 3 genera – Methanobacterium, Methanosarcina and Methanococcum.

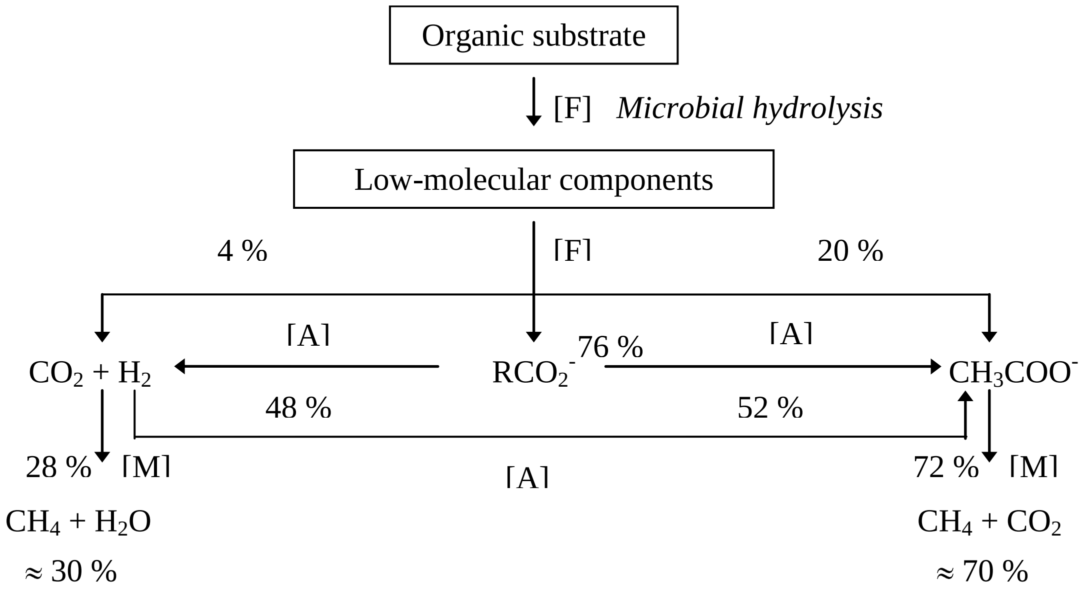

Figure 2 Skeleton drawing of the microbial creation of biogas.
F – fermentation, A – acetogenesis, M – methanogenesis; percentage from [4]

In addition to classical theories about purely biogenic or abiogenic origin of natural gas, we can enunciate, on the basis of the present knowledge, a theory of the abiogenic-biogenic origin of natural gas as well. The following reasoning can permit us to arrive at this theoretical possibility.

Bacterial cellular metabolism includes energy acquisition processes that are chained and fade into one another with processes that take advantage of this energy for syntheses of organic substances.

The basic structural member of organic molecules is carbon. Therefore, the source of carbon is determinative for synthetic processes. For the same reasons, the source of methane, basic component of natural gas, is crucial, too.

According to the source of carbon used in metabolism, we classify organisms into two groups: (1) lithotrophic, (from the ancient Greek *trophe*, nourishment, and *lithos*, stone), i.e. organisms that get their carbon from carbon dioxide (inorganic component), and (2) organotrophic, i.e. those that get carbon from organic compounds disregarding whether carbon is built into the particular organism or, in the form of undesirable substance, given off (exhaled) by it, e.g. in the form of gaseous methane (methanogenic bacteria).

According to the way of energy acquisition, we classify organisms into two other groups: (1) phototrophic, i.e. those that convert solar energy into the energy of chemical bonds, and (2) chemotrophic, that get their energy by the oxidation of organic or inorganic substances. Because of the fact that the object of our present deliberation, methane, originates in the medium, where no light radiation occurs, we can consider exclusively chemotrophic bacteria in our abiogenic-biogenic theory of the origin of natural gas. The general classification of organisms is summarized in Table 1.

Table 1. Classification of organisms.

Source of carbon	Source of energy	
	Solar radiation	Oxidation
Carbon dioxide	Photolithotrophic	Chemolithotrophic
Organic compounds	Photoorganotrophic	Chemoorganotrophic*

** Heterotrophic processes – organisms with this kind of metabolism need organic substances produced by other organisms*

Generally, the energy that is being released from a chemical substance during oxidation is gradually transmitted from the molecule of „donor" to the molecule of „acceptor". The higher the energetic difference between these two molecules, the higher the magnitude of released energy. Donors and acceptors of electron can be various organic and inorganic molecules.

Abiogenic-biogenic anaerobic processes taking part in the formation of methane are characterised by the fact that the source of carbon is its inorganic form, carbon dioxide originating by the thermal decomposition of carbonates. The methane- (or natural gas-) forming bacterium gets the energy required for the metabolism from the oxidation-reduction reaction of inorganic substances, i.e. chemolithotrophically. The living organism thus needs, for the production of an organic substance like methane, only convenient inorganic components. The organism gets along with water saturated by CO_2 and an oxidizable inorganic rock. This type of metabolism is proper not only for bacteria, but also for archaeobacteria, the survivals of the oldest evolutionary stages of living organisms. They represent a special evolutionary branch characteristic by pronounced biochemical digressions from other microorganisms and higher living organisms.

A round of chemolithotrophic organisms build carbon into new created organic molecules mostly by the means of the Calvin cycle. In many instances, the autotrophic processes are concerned. Organisms with this type of metabolism do not require for their metabolism any products of other organisms. However, the metabolism of some species is not fully elucidated.

Methanogenic archaeobacteria get their energy from the oxidation of hydrogen (donor) by oxygen from CO_2 (acceptor). Both components can very easily originate in the magmatic earth strata, by the decomposition of inorganic components such as water and carbonates. Chemically, the formation of methane can be, in a simple manner, described by the following reaction:

$$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O + \text{energy}$$

In the respiratory chain, the final acceptor of electrons is by most oxygen. Their donor can be even ammoniac. Products are nitrites and nitrates (Nitrosomonas), nitrates (Nitrobacter), sulphur or reduced sulphur compounds (sulphane), sulphates, sulphites or sulphur (Thiobacillus), iron or manganese compounds, iron(III) or manganese(IV) hydroxide (Thiobacillus ferrooxidans, Siderocapsa), hydrogen, and water (Pseudomonas).

Besides methanogenic bacteria that can live in fissures in the depths of several hundreds of kilometres, there are also, according to the present hypothesis, methanotrophic bacteria that live, on the contrary, on methane, the part of which is oxidized by them to CO_2 and the other part is built directly in organic substances. According to the present knowledge, these organisms require methane at temperature around 100°C and pressure of 50 MPa.
To confirm our abiogenic-biogenic theory, we can take advantage of the following arguments, conformably with [1]:

- Often we find hydrocarbons in volcanic or magmatic rocks;
- Many gas deposits were filled again after being exhausted;
- Methane occurs in rocks of different ages, even if individual strata are temporally separated by tens of millions of years and we cannot unambiguously correlate the occurrence of methane with the biogenic or abiogenic actions mentioned above.
- We identified analytically methane in gases evolving from carbonate rocks in the locality Koněprusy (Barrandien, Czech Republic) [11]. For this methane there are no biogenic and abiogenic possibilities of its genesis.

Conclusion

On the basis of present-day knowledge, we can arrive at the conclusion that one of possible origins of methane, the essential constituent of natural gases, is also the metabolism of chemolithotrophic bacteria, whose source of carbon is CO_2 and who obtain the energy required by the synthesis of organic substances from the oxidative-reductive reactions of inorganic substances. The originating methane diffuses in the respiratory chain of chemolithotrophs from places of their appearance by means of pores in the region of occurrence of biogenic or abiogenic natural gas where it can mix with it. This theory enables us to explain rationally the occurrence of methane in places where it does not yet correspond to generally accepted views.

The proposed theory makes it possible to explain why, in some cases, the previously exhausted deposits of natural gas slowly but surely fill up.

The presented theory explain also the presence of methane in the gases evolving from carbonate rocks in which there were no biogenic or abiogenic possibility of its occurrence.

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