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On the Biogenic Pathway of Formation of Accumulations of Oil and Associated Gases from the Point of View of Isotopic Biogeochemistry

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Abstract

Review Article

The only possible biogenic pathway for the formation of oil and associated gases is considered. In this case, the carbon source for transformations is the carbon from the biomass of "living organisms". The path consists of three segments: 1) Prebiogenic, which is controlled by gravity and synchronizes the movement of lithospheric plates and the synthesis of "living matter" on the next segment. 2) The biogenic segment, where the synthesis of "living matter" occurs by photo- and heterotrophic pathways. At the same time photosynthesis provides heterotrophic synthesis by substrates. 3) The post-precipitation segment involves the conversion of biogenic material into an insoluble three-dimensional organic polymer, called kerogen, and into labile organic compounds, mainly of a hydrocarbon nature, called bitumoids. Part of the latter, migrating and getting in a trap, forms an oil deposit. Associated gas is formed as a result of cracking of the terminal fragments of kerogen and bitumoid. The processes occurring in each segment are confirmed by experimental data on carbon isotopes, as well as reconstructions of the environmental and climatic phenomena based on geological and paleontological data.

Keywords: Gravitational Influence, Lithosphere Plates, Photo- and Heterotrophic Syntheses, Carbon Isotope Fractionation, Photoassimilation and Photorespiration.

In recently published papers [1,2], we put forward a hypothesis of two possible ways of formation of hydrocarbon accumulations in nature. Petroleum was considered in conjunction with associated gas, since in both cases the source of carbon in their formation is a biogenic matter synthesized on the Earth's surface during photosynthesis and by heterotrophic means. We called this pathway a biogenic one.

Huge, gas deposits mainly of methane and its closest homologues, were considered to be abiogenic, since they are formed in mantle as a result of interaction of a hydrogen stream, flowing from the core of the planet, with mantle carbon, trapped there at the time of the planet's origin when agglomeration of meteorites took place.

In this article, we tried to confirm the biogenic pathway of petroleum and associated gas formation using the available isotopic data. When considering the question, the principle of actualism was used, according to which processes in the past obey the same physico-chemical laws, as modern ones, at the same environmental parameters.

According to the model [3,4], the ability to fractionate carbon isotopes is an inherent property of photosynthetic organisms. This ability originated and evolved along with photosynthesis. The carbon isotopic effects that occur in the key processes of photosynthesis (assimilation and photorespiration), based on their magnitude and sign, not only allow us to judge changes in photosynthesis during evolution, but also provide independent information about the carbon cycle associated with it.

Conventionally, the biogenic pathway of oil and associated gas formation can be divided into three segments. 1. The biogenic segment of the global biosphere carbon cycle, which is not related to photosynthesis or isotope fractionation, but nevertheless is necessary for understanding the interrelationship of the processes occurring on the Earth within the framework of a unified point of view. 2. The biogenic segment is associated with the formation of "living matter" - the precursor of sedimentary organic matter (OM), from which oil and associated gas are formed. The segment includes the results of analysis of the fractionation of carbon isotopes in metabolic processes. 3. The segment of the conversion of sedimentary hydrocarbons into oil and associated gas includes not only chemical transformations at this stage, but also fractionation of carbon isotopes accompanying the transformation and destruction of hydrocarbons in sedimentary rocks.

The Prebiogenic Segment of the Global Biosphere Carbon Cycle

The presence of a prebiogenic segment of the biogenic pathway for the formation of petroleum and associated gas is justified by the fact that it transmits the influence of gravity on the Life processes occurring on the Earth's surface. Evenmore, the loss of CO_2 consumed for photosynthesis and other processes of the segment is replenished.

Consideration of the processes of the first segment begins with the statement that the observed constant motion of the lithospheric plates that make up the solid shell of the Earth is a consequence of the gravitational influence of the bodies of the solar system on the Earth orbiting the Sun [3]. A reflection of this impact is the uneven movement of the lithospheric plates, consisting of a short period called "orogenic", when the plates move with acceleration, and a long period called "geosynclinal", when plate movement occurs with deceleration. This dynamic is consistent with the observed pulsation nature of many geological processes, which have a stormy short part preceding a quiet long one [5,6]. Orogenic periods coincide with a tectonically active state of the Earth's crust (volcanism, magmatism, mountain formation), geosynclinal periods coincide with a tectonically quiet state (erosion, weathering, and flattening). Orogenic and geosynclinal periods form orogenic cycles that repeat over time.

From the analysis of the dynamics of lithospheric plates' movement of [3,7], the following mechanism of synchronization of this movement with biogenic processes occurring at the next segment of the formation of "living matter" follows. It represents the activation of anaerobic thermochemical sulfate reduction in the subduction zone, which occurs when oceanic lithospheric plates collide with large continental plates. Such "active" collisions occur during a short orogenic period when the plates are moving with acceleration. During a long geosynclinal period, thermochemical sulfate reduction is not activated during slow plate's movement with deceleration. Thus, the synchronization of processes on the first and second segments of the biogenic pathway is ensured by switching on (orogenic period)/off (geosynclinal period) the anaerobic thermochemical sulfate reduction.

Accelerated plates' movement is caused by a magma flow breaking through the lithospheric shell. Contacting with water, magma flow freezes and turns into a new plate.

The latter, pushing apart neighboring plates, causes their accelerated movement. In the subduction zone, oceanic plates collide with a heavy continental plate. In this case, a huge amount of energy is released, which initiates thermochemical sulfate reduction [7]. The sulfate reduction reaction oxidizes the OM, coming from the Earth's surface, where it is formed. The oxidant in the reaction is oxygen from the sulfate ion of gypsum, formed from ocean water, and the reducing agent is carbon from organic matter formed on the Earth's surface. The oxidation product carbon dioxide (CO_2) rises to the surface, initiating photosynthesis. On the surface, CO_2 is distributed in the atmosphere and hydrosphere in accordance with the thermodynamic requirements.

In the geosynclinal period, the released energy is insufficient to activate sulfate reduction because of a decrease in the rate of plates' movement, no oxidation of hydrocarbons occurs, and CO_2 does not the surface. Plate collisions are "inactive" during this period. Thus, thermochemical sulfate reduction, via switching on (orogenic period)/

off (geosynclynal period), transmits signals of gravitational influence on the work of biogenic syntheses occurring on the surface, thus synchronizing biogenic processes with the movement of lithospheric plates.

The presence of thermochemical sulfate reduction is confirmed by sulfur isotopic data that illustrates the fractionation of sulfur isotopes in thermochemical sulfate reduction [7,8] as well as by the change in chemical composition of sedimentary rocks formed during orogenic cycles.

The Actually Biogenic Segment of the Oil and Associated Gas Formation Pathway

The main content of the processes on the second segment of the biogenic pathway is the formation of "living matter", which includes the biomass of photosynthesizing and that of heterotrophic organisms. Since the biomass of photosynthesizing organisms is the only carbon source for the nutrition of heterotrophic organisms, let us see first the features of photosynthesis metabolism coupled with carbon isotope fractionation.

An essential property of photosynthesis is the ability of photosynthesizing organisms to fractionate carbon isotopes during CO2 assimilation. As a result, the biomass formed is enriched in the "light" isotope 12C relative to the assimilated carbon dioxide.

Before explaining what factors influence the photosynthesizing part of the biomass of "living matter" during the orogenic cycle, I will briefly outline the main theoretical provisions of carbon isotope fractionation during photosynthesis [7]

1. Photosynthesis consists of two oppositely directed processes – CO_2 assimilation and photorespiration. The first is responsible for the increase in biomass, the second for the decrease.

2. Both processes replace each other. Increased CO_2 assimilation weakens photorespiration and vice versa.

3. CO_2 assimilation is responsible for the enrichment of biomass in ^{12}C,

photorespiration, respectively, for the enrichment of biomass in ^{13}C

4. An increase in the concentration of CO_2 in the environment enhances the enrichment of biomass ^{12}C, an increase in the concentration of O_2 in the environment enhances the enrichment of biomass ^{13}C.

As mentioned above, the dynamics of photosynthesis processes at the second segment is governed by the movement of lithospheric plates controlled by gravity. It is divided into the processes of the orogenic period, when CO_2 enters the surface from the subduction zone, and the processes of the geosynclinal period, when CO_2 does not enter the surface.

In the orogenic period, owing to the CO_2 influx into the environment, the maximum CO_2 concentration and temperature are achieved. The rate of photosynthesis is also maximal. Due to the shortness of the orogenic period, the rate of photosynthesis during the orogenic period is assumed to be constant. Since CO_2, formed in the orogenic period, inherits “light” carbon isotope composition of OM. The biomass, which is produced in photosynthesis, should be even more enriched in ^{12}C because of photosynthesis effect.

In the geosynclinal period, due to the absence of CO_2 inflow, its concentration in the environment begins to fall providing depletion in the course of photosynthesis. Carbon isotope fractionation in this case is followed by ^{13}C enrichment of biomass thanks to Raleigh effect. The described carbon isotope shifts are confirmed by geological and paleontological data [3].

One more very important process at the second segment should be mentioned. As follows from the model, the change of orogenic cycles is accompanied by a sharp climatic transition from a cold aerobic period, accompanied by glaciations of one orogenic cycle, to a hot anaerobic period of the next orogenic cycle. Not all living organisms can adapt themselves to such drastic changes. There is a mass extinction of a significant number of species. The described sequence of events such as glaciations, traces of mass extinctions, and the associated formation of "black shales" (rocks enriched in OM) [3,7] are in consistence with model predictions. Isotopic data are also correspond to the same sequence. Each orogenic cycle ends with the enrichment in 13C of the remaining environmental CO2, and each subsequent cycle begins with a negative CO2 peak, reflecting oxidation in the subduction zone of isotopically light OM. The discussed sequence is confirmed by geological and paleontological data [3,10, 11] as well.

As noted, the remaining part of the biomass of "living matter" consists of heterotrophic organisms. As known, biomass of photosynthesizing organisms is the basis for heterotroth's nutrition. Numerous studies [12, 13] have shown that heterotrophic diet is not accompanied by noticeable isotopic fractionation, and heterotrophic biomass differs insignificantly by isotopic composition from carbon from diet. In other words, the main fractionation of carbon isotopes occurs during photosynthesis. Therefore, the carbon of "living matter", consisting of photosynthetic and heterotrophic biomass, reflects isotopic shifts occurring at the stage of photosynthesis.

It has long been noticed that photosynthesizing organisms living in different environments (marine, freshwater, terrestrial) differ in the isotopic composition of carbon. Environmental factors, affecting carbon isotope composition of biomass of photosynthesizing organisms can be conditionally divided into two groups: factors, affecting the content and availability of carbon dioxide (temperature, salinity, pH, concentrations of substances dissolved in liquid, mixing) [14,15], and factors controlling photosynthetic conditions (illumination, tilt angle and intensity of incident light light, wavelength, and others) [16,17].The distribution of carbon isotope composition of biomass in nature is random and depends on the predominant environmental factor. Considering that CO2 is a main substrate for photosynthesis having enormous solubility in water, it can be expected that CO2 is one of the factors determining carbon isotope composition of organism in the given environment.

Some later, when it became clear that photosynthesis is an oscillatory process [18,19], we have found that the leading role in the mechanism of photosynthetic oscillations belongs to the most important and oldest photosynthetic enzyme on the Earth, Rubisco (ribulose bisphosphate carboxylase/oxygenase). It has been shown that rubisco has the ability, depending on the content of CO_2 and O_2 in the medium, to regulate the duration of carboxylase and oxygenase functions, i.e. to regulate the ratio of CO_2 assimilation and photorespiration, on which the isotopic composition of biomass carbon depends. Recall that CO_2 assimilation (carboxylase function) is accompanied by enrichment of biomass in ^{12}C, photorespiration (oxygenase function) is accompanied by enrichment of biomass in ^{13}C [9].

Indeed, using the new parameter, it is easy to describe changes in the carbon isotope composition of synthesized biomass in the course of the orogenic cycle. They fully correspond to the processes that follow from the model. During the orogenic period, carbon isotope compostion of synthesized biomass has a maximum value. The CO_2 concentration is maximal as well (CO_2 comes from the subduction zone), whereas the oxygen concentration is minimal. This corresponds to a high rate of CO2 uptake, as well as to an anaerobic environment, and to "greenhouse effect." At the beginning of the geosynclinal period, the CO2 concentration begins to fall, reaching minimum values at the end of the period, while O2 increases. This corresponds to an aerobic environment and a low rate of assimilation. Climate change is coming. Glaciation will occur at the end of the period. In other words, the changes in the environment are well consistent with the description of the processes that follows from the model. At the same time, accounting for changes in oxygen content is equivalent to accounting for the degree of oxidation of the environment.

In the literature a very similar correlation is often used. The term "biomass" in it is replaced by the term "sedimentary matter", and the term "environment" by the term "facies", which covers not only the environment in which life develops, but also the basin in which sedimentation occurs. Moreover, in this basin, the influence of the dominant factor is taken into account, which determines the isotopic composition of biomass carbon (sedimentary OM). Differences in the isotopic composition of OM carbon in such facies are called facial isotopic differences.

Segment of Conversion of Sedimentary OM into Oil and Associated Gas

After the extinction of the "living matter", all metabolic reactions controlled by enzymes, cease.

Complex molecules of the biopolymer break down into individual fragments that react with each other. In many cases, the functional groups located at the ends of the formed fragments are, due to their electronic structure, the most reactive parts of the molecules that determine the direction of transformations.

Almost any biomass includes three main fractions, including protein, carbohydrate, and lipid. Protein fragments are most often amino acids, which have two functional groups: an amino group (-NH2) and a carboxyl group (-COOH). Carbohydrates most often break down into glucose fragments having a carbonyl functional group (H-C=O). Carbonyl and amine functional groups can react with each other, for example, to form imines and enamines [20]. This occurs when aldehydes and ketones interact with primary and secondary amines. The reaction proceeds as a nucleophilic addition to the carbonyl group followed by water cleavage. In cells with the participation of enzymes, the amino group in an amino acid can interact with its constituent carboxyl group, forming an internal salt [20]. Other reactions with simultaneous participation of carbonyl and amino groups with the participation of transaminases provide transamination. It is not known exactly how these functional groups interact under deposition conditions, but in principle such an interaction is possible. Other interactions between protein fragments and carbohydrates are also possible. For example, Maillard reactions and melanoidin type reactions [21] and others. As a result, under the influence of thermobaric factors, the described reactions in the sediment lead to condensation and polymerization processes with the formation of a three-dimensional conglomerate called kerogen.

Unlike proteins and carbohydrates, the lipid fraction does not form polymer chains consisting of repeating units. When they decay, many molecules of different classes are formed. These are mainly nonpolar hydrophobic compounds loosely bound to each other and kerogen by weak hydrogen bonds and equally weak Van der Waals forces [22]. For this reason, the lipid fraction and its degradation products are labile and easily detaches from kerogen under external thermobaric influences, forming bitumoid and oil molecules.

Let us consider the transformations of sedimentary OM at the last segment of the biogenic pathway from the point of view of the available isotopic data. Isotopic differences between kerogen and bitumoids have been observed for a long time [23], and have been determined repeatedly since [24,25]. A steady difference in the isotopic composition of carbon, about 2-4%o, was always recorded between kerogen and bitumoids.

When studying "living matter", it was found that in addition to the carbon isotope fractionation nodes, discussed above during assimilation and photorespiration, cells have another node located at the intersection of central metabolic pathways [9,26]. Glycolysis occurs in this node, ending in a pyruvate dehydrogenase reaction, in which an isotopic effect occurs [27]. This effect is responsible for isotopic differences between biomass fractions, as a result of which lipids are enriched with isotope ^{12}C relative to proteins and carbohydrates. It should be emphasized that differences occur only if fractions are considered for the biomass of the same organism. At the same time, the indicated differences are always reproduced and have approximately the same range. Since they cannot disappear inherited from fractions of "living matter", we conclude that the observed differences between kerogen and bitumen are of the same nature. Usually, the enrichment of bitumoids and oils in ^{12}C relative to kerogen is explained by the kinetic isotopic effect accompanying the destruction of carbon bonds [28, 29]. We conclude that this effect is strogly overestimated.

In this regard, it is interesting to note that in [30] the isotopic differences between kerogen and bitumoid were studied in the course of geological time. It turned out that these differences first appeared about 300 million years ago, when land development began and plants began to need energy-rich lipid resources in order to adapt to the adverse conditions of terrestrial life [31]. Lipids turned out to be such funds This is how isotopic differences appeared between lipids and the carbohydrate-protein fractions, which eventually turned into differences between kerogen and bitumoids.

If we compare the isotopic composition of carbon in the bitumoid - oil - hydrocarbon gas series, it turns out that the carbon of oil is slightly, but still somewhat enriched in isotope 12C relative to the carbon of bitumoids. The carbon of hydrocarbon gases is quite clearly enriched with the isotope 12C relative to the carbon of bitumoid and oil. There are two reasons for these small differences in carbon isotopic composition. The first is the kinetic isotopic effect, which occurs when C-C bonds in straight-stranded and branched molecules that make up bitumoid and oil are broken. At the same time, low-molecular-weight fragments and homologues of methane are formed, enriched in the isotope 12C [32,33,34]. Moreover, the fewer the number of carbon atoms included in the fragment, the stronger the isotopic effect. This is easily explained, since the isotopic effect is manifested only on atoms located at the ends of a breaking bond. All other atoms included in the molecule retain their isotopic composition and reduce the effect of the effect on the total carbon of the molecule by dilution. Therefore, HC gases and low molecular weight fragments experience the greatest isotopic displacement.

The kinetic isotopic effect has practically no influence on carbon isotope composition of kerogen or bitumoid. Therefore, the main reason for the isotopic differences of the mentioned OM fractions is due to its inheritance from the fractions of "living matter". During the migration of oil into the trap, when the HC mixture is divided by the molecular weight of fractions, but the isotopic differences between them and kerogen remain. These are supplemented by small isotopic differences associated with degradation during migration of molecules into the trap due to the kinetic isotopic effect.

Conclusion

The consideration of the biogenic pathway for the formation of oil and associated gas accumulations within the framework of the global biosphere carbon cycle allows us to conclude that the biogenic pathway is a part of this cycle. The biogenic pathway of oil and associated gas formation can be roughly divided into three segments: 1) the prebiogenic segment of the global cycle; 2) the actually biogenic segment, where “living matter” is produced; 3) the segment for the conversion of sedimentary OM into oil and associated gas.

A detailed analysis of the segments showed that the available data on carbon isotope composition are in good agreement with the idea that the biogenic pathway of oil and associated gas formation consists of the following sequence of events.

The prebiogenic segment provides synchronization of the lithospheric plates’ movement with the processes of biosynthesis of "living matter" on the second segment of the path. It also supplies photosynthesis with CO2. The synchronization mechanism consists in turning on the anaerobic reaction of thermochemical sulfate reduction in the subduction zone during the orogenic period, and in turning it off in the subsequent geosynclinal period. In the reaction the oxidation of OM occurs, which descends into the subduction zone from the surface, where its synthesis takes place. The mechanism is confirmed by data on sulfur and carbon isotope fractionation studies in the course of successive orogenic cycles.

The actually biogenic segment of the pathway begins with the production of photosynthesizing biomass. Photosynthesis, in turn, supplies heterotrophic synthesis with substrates. Combination of photosynthesizing and heterotrophic biomass forms "living matter" biomass. Heterotrophic assimilation is not accompanied by noticeable carbon isotope fractionation. It means, carbon isotope composition of "living matter" (as well as sedimentary OM) is determined by the isotope effects that take place at the stage of photosynthesis.

The regular sequence of events on the biogenic segment is confirmed by studying the carbon isotope composition of marine carbonates over geological time and by studying climatic changes in the course oforogenic cycles reconstructed from geological and paleontological data.

The segment of the pathway associated with the transformation of "living matter" into sedimentary OM after its death is in the following. Under thermobaric conditions of the sediments organic matter matures, which is expressed in the formation of kerogen mainly from the protein-carbohydrate fraction of biomass and in the formation of bitumoid during the destruction of biogenic molecules mainly from the lipid fraction of biomass. It is shown that the isotopic differences between kerogen and bitumoid reflect the ^{13}C enrichment inherited from the protein-carbohydrate fraction of the "living matter" relative to the lipid fraction. The kinetic isotopic effect of the destruction of carbon bonds is superimposed on the carbon isotopic composition of the low molecular weight HC fractions of bitumoid after its separation from kerogen before falling into the trap. This leads to a small additional enrichment of low molecular fractions in ^{12}C relative to high molecular fractions and bitumoids. For reasons of balance, the effect of the kinetic isotopic effect on the isotopic composition is weaker than the inherited isotopic differences.

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