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## REVIEW OF SCIENTIFIC LITERATURE ON THE ROLE OF RADIATION AND CLAY IN PETROLEUM GENERATION

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**Abstract:** The paper deals with analysis of summary materials on petroleum generation and presented conclusions. The role of radiation and clay in oil formation is shown. It was studied that clay minerals help concentrate organic matter by adsorption and subsequently act as catalyst to generate petroleum.

**Keywords:** photosynthetic process, energy, hydrocarbon, clay, petroleum.

Production, accumulation and preservation of undegraded organic matter are prerequisites for the existence of petroleum source rocks. The term "organic matter" or "organic material", as used in this article, refers solely to material comprised of organic molecules in monomeric or polymeric form derived directly or indirectly from the organic part of organisms. Mineral skeletal parts, such as shells, bones, and teeth are not included. First, organic matter has to be synthesized by living organisms and there after it must be deposited and preserved in sediments. Depending on further geological events, part of the sedimentary organic matter may be transformed into petroleum-like compounds. It is important to realize that during the history of the earth the conditions for synthesis, deposition and preservation of organic matter has changed considerably.

Photosynthesis - the basis for mass production of organic matter. The emergence of photosynthesis as a worldwide phenomenon is a noteworthy historical event with respect to the formation of potential source rocks. The photosynthetic process converts light energy into chemical energy. Photosynthesis is basically a transfer of hydrogen from water to carbon dioxide to produce organic matter in the form of glucose and oxygen. The oxygen is freed from the water molecule and not from carbon dioxide. From glucose, autotrophic organisms can synthesize polysaccharides, such as cellulose and starch, and all other necessary constituents.

Photosynthesis is the basic process that accomplishes the mass production of organic matter on earth [1]. Primitive autotrophic organisms, such as photosynthetic bacteria and blue-green algae, were the first organisms responsible for this mass production. A basic prerequisite for photosynthesis is the light-absorbing green pigment chlorophyll. In primitive autotrophs it occurs in a relatively free state in the cell of the organism. In more highly evolved plants it is concentrated in chloroplasts in green leaves. These chloroplasts are complete photosynthetic factories. The oldest recorded forms of organic life are about 3.1 to 3.3 billion years old and are bacteria and algae-like bodies from the Swaziland Group in South Africa (Schopf et al., 1965). However, it is possible that life on earth is at least as old as the oldest known rocks - 3.7 billion years. It is assumed that approximately 2 billion years ago, photosynthetic production of organic matter was fairly well established worldwide, and this time serves as a zero reference point. Before it was reached, another billion years probably was required for the isolated occurrences of most primitive organisms to spread sufficiently for photosynthesis and, hence, for mass production of organic matter to be universally prevalent. Without water there is no life. Therefore, abundant life, even on a most primitive level, was not possible on earth prior to about

4 billion years ago, when water became a common substance on the earth's surface. During that primordial time, the atmosphere was reducing, i. e., there was practically no free oxygen.

It is generally agreed that the early earth's atmosphere was devoid of free oxygen, and that it contained  $H_2$ ,  $CH_4$ ,  $NH_3$ ,  $N_2$  and  $H_2O$ . However, this view is not unopposed, the methane-ammonia hypothesis being especially questioned. In connection with this hypothesis, Calvin (1969) refers to an abiological or chemical evolution that started more than 1 billion years ago. When primitive organisms first appeared about 3 billion years ago, they probably utilized the abiologically produced organic molecules as a source of energy to maintain metabolism. Therefore, the first organisms are assumed to have been heterotrophic. However, the growing population of heterotrophs probably could not be supported forever in this way. It is argued that, by the time these organisms had almost depleted the reservoir of abiologically produced organic matter, photosynthesis developed as a second source of energy. In this way, heterotrophic organisms that were able to use sunlight as an extra source of energy could become independent, and with further evolution could escape the food shortage. Certain purple-colored bacteria living today show these properties. They can act like heterotrophs and utilize organic compounds, and they also contain the green pigment chlorophyll to carry on photosynthesis. The oldest form of photosynthesis, as performed by bacteria, did not produce oxygen. Photosynthetic bacteria are anaerobic. Instead of using  $H_2O$  as a hydrogen donor, they can use  $H_2S$  and excrete sulfur rather than oxygen.

Certain blue-green algae that evolved from photosynthetic bacteria probably were the first oxygen-producing organisms. Although there are a number of photosynthetic pigments, none can completely replace chlorophyll in photosynthetic organisms. Chlorophyll molecules absorb light energy, which elevates electrons to a higher energy level. This gain in energy is transferred to other molecules. Oxygen is believed to have been toxic to organisms of that time. However, a reducing environment assured that divalent iron was abundant in aqueous solutions. This iron could act as a sink for the oxygen produced as a by-product of photosynthesis. It is very likely that the well-known banded iron stones of the Precambrian are formed by this interplay between photosynthesis and a subsequent oxidation of iron to a trivalent form, with precipitation of the insoluble oxides (Cloud, 1968). Autotrophic, photosynthetic organisms were superior to heterotrophs and consequently soon dominated the biological realm. As stated before, about 2 billion years ago, photosynthesis emerged as a worldwide phenomenon. Herewith the foundation for the food pyramid and the evolution of higher forms of life was laid. It is argued that after this event the atmosphere of the earth slowly became oxidizing, i. e., free molecular oxygen became available. Photosynthesis makes use of the energy coming from sunlight, employing only a narrow band of the sun's total radiation. The portion of the spectrum utilized by most photosynthetic organisms is between 4000 to 8000  $\text{\AA}$ , which nearly equals the portion of light visible to the human eye. Rays with shorter wavelengths and higher energy are even harmful to life. Different parts of the visible light spectrum may be utilized by different photosynthetic organisms. The portion-used is determined by the type of pigment an organism employs. It enables photosynthetic algae and bacteria to live at different depth levels in the same body of water. Life in deeper water is correlative to use of longer wavelengths.

The organic carbon budget during the History of the Earth For a mass balance of carbon used in photosynthesis during the history of the earth, it is necessary to add up all organic carbon present on earth in various repositories, such as ocean waters and sediments. The total estimated amount of organic carbon and graphite, which formerly represented sedimentary organic carbon, is approximately  $6.4 \times 10^{15}t$  (Welte, 1970). A more recent estimate by Hunt (1972) is about twice as high. However, Hunt includes in his balance calculation "organic" carbon in basaltic and other volcanic rocks, as well as in granitic and all metamorphic rocks. The biological origin of much of

this "organic" carbon is questionable. Most of the carbon on earth is concentrated in sedimentary rocks of the earth's crust. Part of it is fixed as organic carbon, and a greater part as carbonate carbon. It is estimated that 18 % of total carbon in sedimentary rocks is organic carbon and that 82% of sedimentary carbon is bound in the form of carbonates (Schidlowski et al., 1974). A relationship of course exists between organic carbon and carbonate carbon. The atmospheric CO<sub>2</sub>-reservoir is in a constant exchange with the hydrospheric CO<sub>2</sub>-reservoir. From aquatic environments, carbonates may be precipitated or deposited by organisms (shells, skeletons etc.) to form carbonate sediments. Conversely, carbonate rocks may be dissolved to contribute to the equilibrium reaction between CO<sub>3</sub>, HCO<sub>3</sub> and CO<sub>2</sub> in waters. Primary organic matter is formed directly from the atmospheric reservoir by terrestrial plants, or by photosynthesis of marine plants from dissolved CO<sub>2</sub>, in the hydrosphere. Terrestrial and marine organic matter, in tum, is largely destroyed by oxidation. Thus CO<sub>2</sub>, is returned for re-circulation in the system. Only an almost negligible portion of the organic carbon in the earth's crust, including the hydrosphere, is found in living organisms and in a dissolved state. The major part of the organic carbon (5.0 x 10<sup>15</sup>t) is fixed in sediments. Another sizeable part of the organic carbon (1.4 x 10<sup>15</sup>t), mainly, in the form of graphite-like material or metaanthracite, is fixed in metamorphic rocks of sedimentary origin. If it is correct that all this organic carbon has been formed either directly or indirectly by photosynthesis during the earth's history, there should have been a corresponding amount of oxygen liberated simultaneously according to the equation of photosynthesis . This amount must be accounted for by free oxygen, together with formerly free oxygen presently used by oxidation processes of substance other than biological organic matter. At present, we find free oxygen in the atmosphere (in air 20.95 vol %) and varying amounts dissolved in ocean waters (general range 2-8 ml O<sub>2</sub> per l). Formerly free oxygen is found in both dead and living organic matter. However, most formerly free oxygen has been utilized by the oxidation of various forms of sulfur and iron. This oxygen is bound today in sulfates and in oxides of trivalent iron, and is distributed throughout the earth's crust, including the hydrosphere. As stated before, it is believed that the primordial atmosphere of the earth was reducing and the elements sulfur and iron occurred only in divalent form. Oxygen produced by photosynthesis, therefore, was used to oxidize sulfides to sulfates and divalent to trivalent iron. The total free and formerly free oxygen found on earth amounts to approximately 16.9 x 10<sup>15</sup> t.

This balance calculation for oxygen and organic carbon on the basis of photosynthesis indicates to us that most of the oxygen not bound in carbonates and silicates has indeed been produced by photosynthesis. Therefore, there should be a relationship between organic carbon in fossil sediments and oxygen levels of paleoatmospheres.

Menzel and Ryther (1970) also estimated that about 0.1% of the annual production of organic matter is buried in surface sediments. Only this tiny fraction of organic matter is preserved in sediments, whereas the remainder is recycled, mainly in the euphotic zone of the top water layer in the oceans. This is why oceanographers speak of a closed system with respect to living phytoplankton and CO<sub>2</sub> in ocean waters. In a study on the origin and fate of organic matter in the Black Sea, Deuser (1971) found a preservation rate of 4%. However, this value of 4% has to be considered as an upper limit, which is reached only under such favorable conditions as are found in the Black Sea. These conditions are an oxygen-free and fairly calm water body without scavenging benthic life at the bottom except for anaerobic bacteria. The sedimentation of certain petroleum source rocks has very likely taken place under similar conditions. In this connection there is frequently an alternation of environments favorable for production and preservation of organic matter and those in which much less organic matter is preserved in sediments. A good example of this is the series of finely laminated sediments, with alternating layers respectively rich and poor in organic carbon, described by Ross and Degens (1974) in young Black Sea

sediments [2-8].

For our considerations, the larger secondary cycle is of greater importance. Once the organic matter has entered a sediment, its long-term fate is mainly governed by tectonic events. In other words, phases of subsidence and increase in burial, or phases of uplift and erosion, determine whether the organic content of a sediment is preserved and transformed into petroleum, or is eroded and oxidized. If organic matter completes the second cycle during the birth evolution and end of a geosyncline, it undergoes increasing burial, and is subjected to diagenesis, catagenesis, and finally metamorphism [12-14]. The processes of diagenesis and catagenesis are of prime importance in the formation of petroleum [2,3,11,18].

It is critical to establish that hydrocarbon formation and migration occurred after the formation of the trap (anticline, etc.) that is to hold the oil. There is still very little known about the manner in which hydrocarbons formed in argillaceous source rocks migrate and accumulate in porous reservoirs. Some evidence exists, however, that the clay mineral kerogen complex plays a role in modifying hydrocarbon compositions during migration [9,10,15-17].

Kerogen is the most important form of organic carbon on earth. It is 1000 times more abundant than coal plus petroleum in reservoirs and is 50 times more abundant than bitumen and other dispersed petroleum in nonreservoir rocks (Hunt, 1972). In ancient nonreservoir rocks, e.g., shales or fine-grained lime stones kerogen represents usually from 80 % to 99% of the organic matter, the rest being bitumen.

The clay minerals are important compositions in source rocks and reservoir rocks that can generate and store oil and gas respectively. The presence of clay minerals strongly influences the physical and chemical properties of conventional sandstone, carbonate and unconventional shale. For clay minerals in source rocks, they are important for quality evaluation of the hydrocarbon generation, expulsion and migration. Clay minerals help concentrate organic matter by adsorption and subsequently act as catalyst to generate petroleum. The transformation of montmorillonite to illite and increasing ordering of I/S can indicate the hydrocarbon generation and expulsion events [2,15,19-22].

## **Conclusions**

1. Photosynthesis is the basic process that accomplishes the mass production of organic matter on earth.
2. A relationship exists between organic carbon and carbonate carbon.
3. Clay mineral kerogen complex plays a role in modifying hydrocarbon compositions.
4. The clay minerals are important compositions in source rocks and reservoir rocks that can generate and store oil and gas respectively
5. The processes of diagenesis and catagenesis are of prime importance in the formation of petroleum.

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## ОБЗОР НАУЧНОЙ ЛИТЕРАТУРЫ О РОЛИ РАДИАЦИИ И ГЛИНЫ В НЕФТЕОБРАЗОВАНИИ

**М.К. Исмаилова**

**Резюме:** В статье рассмотрены анализы научных материалов по формированию нефти и представлены выводы. Биогенная теория, согласно которой нефть сформировалась из остатков древних живых организмов, является доминирующей мировой теорией происхождения нефти. Показано роль радиации и глины в нефтеобразовании.

**Ключевые слова:** процесс фотосинтеза, энергия, углеводороды, глина, нефть.

## NEFTİN YARANMASINDA RADİASİYA VƏ GİLİN ROLU İLƏ BAĞLI ƏDƏBİYYAT XÜLASƏSİ

**M.K. İsmayılova**

**Xülasə:** Məqalədə neftin əmələ gəlməsinə dair elmi tədqiqat işlərinin xülasəsi və nəticələr təqdim edilmişdir. Üzvi maddələrin gildə adsorbsiya olunaraq yığılması və gilə neftin yaranmasında katalizator kimi iştirakı göstərilmişdir. Materialların təhlilinə əsalanaraq neftin formalaşmasında radiasiya və gilənin rolu aşkar edilmişdir.

**Açar sözlər:** fotosintez prosesi, enerji, karbohidrogen, gil, neft.