

Global Redox Carbon Cycle and Photosynthesis Development

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Abstract

The principle of actualism and recent findings on carbon isotope fractionation in photosynthesis, combining with data on isotopic ratio of carbon in sedimentary rocks in form of carbonates and coeval organic matter allowed developing a new model of the redox carbon cycle. According to the model, carbon transfer between biosphere and geospheres is a conversion of the element from the oxidized state to the reduced one, and back. The transfer proceeds under the control of photosynthesis, which is an essential element of the carbon cycle. The lithospheric plates' movement exerts impact on photosynthesis development via periodic injections of CO₂ into "atmosphere – hydrosphere" system during plates' collisions. Due to irregular lithospheric plates' movement the orogenic cycle consists of a short-term orogenic period of active volcanism, magmatism and mountain building and a long-term geosynclinal period of low volcanic activity and quiet development of Earth crust processes. In short-term orogenic periods, when plates move fast and collide frequently, a great amount of CO₂ evolves from the subduction zones of the Earth's crust (where plates collide) and fills the "atmosphere – hydrosphere" system. It causes expansion of photosynthesis. At the same time oxygen concentration drops due to oxidation of reducing magmatic rocks. In long-term geosynclinal period, due to photosynthesis, the CO₂ concentration gradually drops whereas O₂ concentration increases and achieves the maximum by the end of the cycle. In the following relatively extended geosynclinal periods, the collisions of plates are seldom, and the rate of CO₂ emission from subduction zones becomes weaker than the rate of CO₂ assimilation. The pulsating movement of plates exerts an impact on dynamics and development of photosynthesis. It, in turn, determines periodicity of numerous processes, including climatic cycles, changes in the rate of biodiversity, irregular accumulation of organic matter in sediments, uneven stratigraphic oil distribution, sea level changes, etc. The redox carbon cycle is a self-organizing system due to negative feedback between CO₂ assimilation and photorespiration in response to oxygen growth. It made carbon cycle to shift to ecological compensation point. In this point the system become sensitive to separate plates' collisions what results in short-term climatic oscillations.

Keywords: Carbon isotope; Fractionation; Photosynthesis; Sedimentary rocks; Redox carbon cycle

Introduction

The examination of natural carbon cycle is very important for better understanding of evolution of Life and Climate Changes on the Earth as well as for the analysis of the trends in development of the planet itself. These problems are tightly bound. Carbon cycle combining various processes in lithosphere, atmosphere, hydrosphere and biosphere enables to obtain the entire picture of the whole interactions on the Earth. As early as in 1926 famous Russian geochemist V.I. Vernadsky put forward an idea on interconditionality of the biosphere and Earth crust processes. The present work develops his thought. In this context it sounds as follows. Development of photosynthesis, which is a basis for the Life on the Earth, occurred under impact of the movement of lithospheric plates that cover the entire Earth surface and are in permanent motion. The effect of lithospheric plates is realized by means of periodic CO₂ injections, arising during plates' collisions. The plates' movement is a firmly established experimental fact [1-3] though the reason for that is still arbitrary. According to a wide spread point of view this motion is caused by convection of magma in the asthenosphere. Some researchers assert that magma convection is under the impact of celestial bodies in the course of the Earth's motion around the Sun [4].

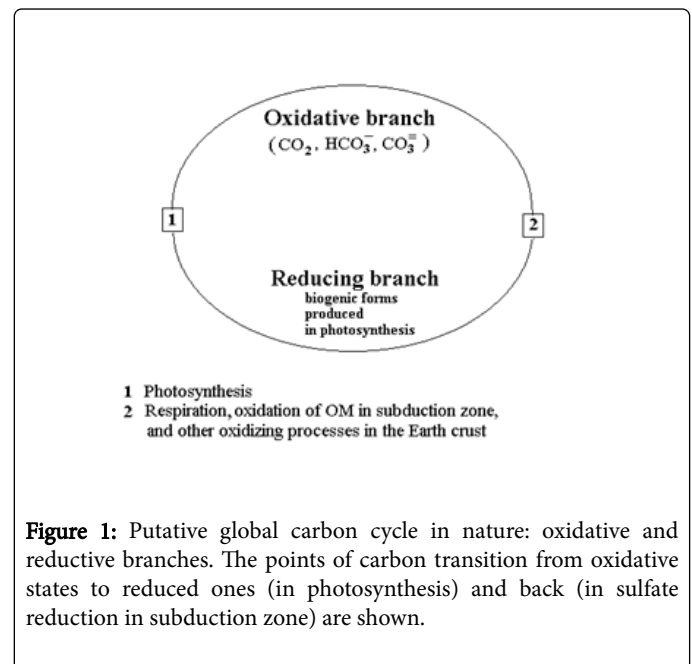


Figure 1: Putative global carbon cycle in nature: oxidative and reductive branches. The points of carbon transition from oxidative states to reduced ones (in photosynthesis) and back (in sulfate reduction in subduction zone) are shown.

The existing views on the natural carbon turnover consider it as a trivial transfer of carbon through geospheres to biosphere, and back. We regard it as a transfer of the element, under a control of the redox state of carbon. According to new definition, carbon cycle is considered as a conversion of carbon from the oxidized state, presented by CO₂, bicarbonate and carbonate species in the “atmosphere – hydrosphere” system, into the reduced state, presented by different biogenic forms, produced in photosynthesis and in the following transformations. The reverse transition is realized via respiration of living organisms and via microbial and chemical oxidations, accompanying transformations of “living” matter after burial. Among them is the oxidation of the buried organic carbon, the key contributor of CO₂, by means of thermochemical sulfate reduction in the subduction zone, where lithospheric plates collide. We called this cycle “natural redox cycle of biospheric carbon. Formally the global redox carbon cycle can be presented as a closed loop consisting of the two branches – oxidative and reductive. It has two remarkable points, one of which is photosynthesis, where the oxidized carbon species turn into the reduced state; another point provides the reverse transition (Figure 1).

The suggested mechanism of functioning of the natural carbon cycle

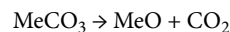
The model is based on the established geological concepts – plate tectonics and orogenic cycles. The plate tectonics concept [1,5,6], or mobilism theory, asserts that lithospheric plates, covering the entire Earth's surface, are in permanent motion. The motion reminds the escalator. In some places of the Earth, in the zone of the mid-Atlantic ridge, where the crust is the most subtle, magma erupts onto the surface and, coming into contact with ocean water, hardens to form a new plate. It pushes other plates, calling their movement. In another place of the Earth (Wadati - Benioff – Zavaritsky zone) plates, moving towards each other, collide. One of them, bending and moving down under the other is absorbed by magma. Area, where collisions occur, is called subduction zone.

The orogenic cycles' concept, developed, in particular, by Rutten [7], who studied the spatial-temporal distribution of sedimentary strata, drew to the conclusion that an intensity of vibrations of the Earth's crust plates over the geologic history was unequal. There were relatively short periods, named as orogenic periods, and the subsequent relatively extended periods of quiet development of the crust, named as geosynclinal periods. The geosynclinal and the orogenic periods both make the orogenic cycle. Rutten [7] has named the alternate orogenic cycles as the Earth's pulse.

Combined both concepts and assuming that plates' movement is uneven; we suggest the following model of redox cycle of biospheric carbon. In orogenic periods of the cycle plates moved rapidly and their collisions occurred more often than in geosynclinal periods, when the plates' rate slowed down and the collisions occurred less frequently [8]. The collisions with the participation of the continental plates bearing the sedimentary rocks with carbon in form of carbonates and organic matter from the point of view of the global carbon cycle are of the greatest interest. During its life span, a continental plate accumulates sedimentary rocks with the burial of organic matter and carbonates.

In orogenic period in subduction zones, where high temperatures and pressures are developed, the destruction of the sedimentary rocks takes place. Under high temperatures and great pressures the rocks are

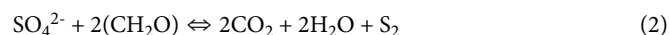
destroyed, but before they are absorbed by magma, the following reactions occur:



“Me” designates Ca₂₊ or Mg₂₊ cations.

These transformations do not change the redox state of carbon, and carbon transfer can be considered as a constant increment of the oxidative pool which does not impact carbon turnover.

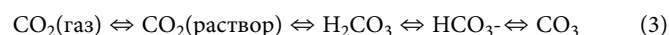
Burial of organic matter and its transformation represent a different case. In thermochemical sulfate reduction, organic matter reacts with evaporated sulfates according to the equation:



The resultant CO₂, together with sulfides, is transferred from the subduction zones onto the Earth surface. This final step of oxidation completes the transfer of the reduced carbon into the oxidative forms.

In geosynclinal periods photosynthesis and weathering become the dominant processes. Hence CO₂ in “atmosphere – hydrosphere” system is depleted.

On the Earth surface, due to chemical exchange reactions and in accordance with thermodynamics laws, CO₂ is redistributed in the atmosphere and hydrosphere, composing the common “carbon dioxide – bicarbonate – carbonate” system:



This system is close to equilibrium since the rate of chemical exchange is much greater than the rate of geological processes. The observed differences in carbon isotope composition of the atmospheric CO₂ (δ¹³C (–7%) and of the carbonate species dissolved in sea water (δ¹³C (0%)), evidence for the state close to equilibrium. In fact, the difference is about 5-7% [9,10] corresponding to the thermodynamic (equilibrium) values of isotope separation coefficients α (CO₂ /CO₃²⁻) and α (CO₂ /HCO₃⁻), which are equal to 1.005–1.008 [9,11,12] and typical to Earth surface temperatures (0-30°C).

Under the action of sunlight, photosynthesizing organisms absorb CO₂ and water and convert the oxidized forms of carbon into the reduced ones, producing “living matter”. After the conversion of the buried “living matter” into the sedimentary organic matter, the latter undergoes the oxidation. Then all the processes repeat. They can be shown as Figure 2.

In orogenic periods, depicted by filled triangles on Figure 2, CO₂ concentration in the system should increase abruptly because of frequent collisions of lithospheric plates when sedimentary rock masses fall in subduction zone and are destroyed with CO₂ evolution. The entry of CO₂ into the “atmosphere – hydrosphere” system leads to considerable growth of all oxidized carbon species in the system. At the same time, the atmospheric O₂ concentration decreases. Oxygen, accumulated during the previous geosynclinal period, is utilized in the oxidation of the reduced igneous rocks and reduced sulfur species, lifting from the subduction zones onto the Earth surface.

In the following relatively extended geosynclinal period, the rate of photosynthetic consumption of CO₂ becomes greater than its emission from the subduction zones. CO₂ concentration drops whereas O₂ concentration increases achieving its maximum by the end of period.

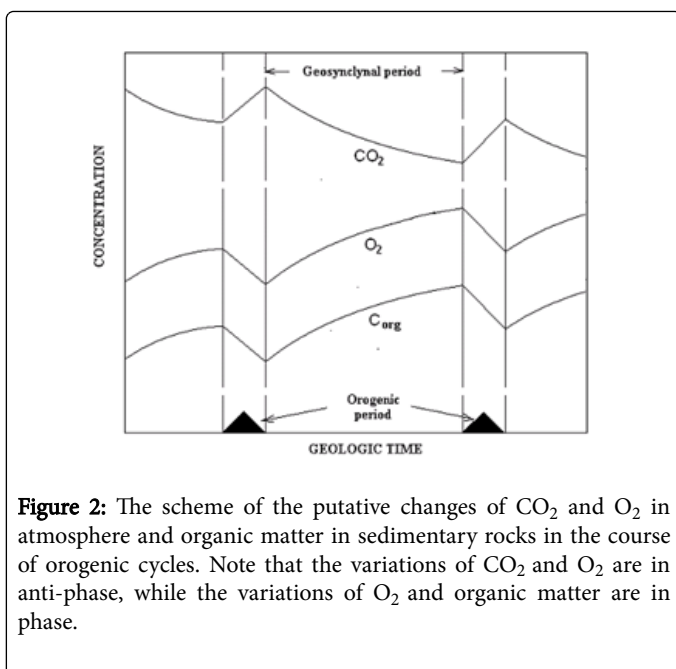


Figure 2: The scheme of the putative changes of CO₂ and O₂ in atmosphere and organic matter in sedimentary rocks in the course of orogenic cycles. Note that the variations of CO₂ and O₂ are in anti-phase, while the variations of O₂ and organic matter are in phase.

Photosynthesis is stimulated by high CO₂ concentrations achievable in the orogenic period. It results in the depletion of the oxidative pool of carbon in the “atmosphere – hydrosphere” system. Taking into account the carbon equilibrium in the “atmosphere – hydrosphere” system, the variations of CO₂ and other oxidized carbon forms in the system can be depicted by the same curve.

To use the model for the analysis of different processes, such as evolution of atmosphere, climatic changes, etc., it is important to know the carbon cycle dynamics which depends on global photosynthesis. Ivlev assume that the photosynthetic reaction may be approximated by first order kinetics. It allows linking the substrates and products of the reaction by the simplest way. This approximation was supported by the results of climatic models [13-15]. According to their estimates, oscillations of the atmospheric CO₂ and O₂ concentrations in Phanerozoic appear in a counter phase, while oscillations of O₂ and buried organic matter rate in sedimentary rocks have the same pattern (in phase). Note that the atmospheric CO₂ appears as a substrate, while oxygen and the assimilated organic matter (CH₂O in this approximation) are the products of the global photosynthesis reaction.

Despite of the changes of the above concentrations within the cycle, the changes of the average concentrations of atmospheric CO₂ and O₂ all over the cycles have distinctive features. O₂ concentrations gradually decrease, accordingly CO₂ concentrations gradually decrease, accordingly O₂ concentrations increase from one orogenic cycle to another. The burial rate of organic matter changed in parallel with the growth of average atmospheric oxygen concentration.

It should be stressed a special role of isotope data of elements and that of carbon, in particular, in cycle evolution studies. It is associated with recent findings in carbon isotope fractionation during photosynthesis [8]. It was shown that two processes, CO₂ assimilation and photorespiration, composing photosynthesis, are followed by carbon isotope fractionation with effects of opposite signs. As a result, carbon isotope composition of biomass is determined by the contribution of both effects and depends on the CO₂/O₂ concentration ratio in the atmosphere. At elevated CO₂ concentration in the

environment the CO₂ assimilation plays a dominant role resulting in enrichment of biomass with a “light” isotope ¹²C. In case of high O₂ concentrations in the environment a role of photorespiration increases and biomass gets enriched in a “heavy” isotope ¹³C.

According to the model, the CO₂/O₂ concentration ratio is the main variable that changes within the orogenic cycle and from cycle to cycle. Following the actualism principle, one can take organic carbon as analog of “living” matter in the past, and carbonates as analog of CO₂ corresponding to that time. Then in the orogenic period when the CO₂/O₂ concentration ratio is high, organic carbon should be enriched in ¹²C. On contrary, by the end of geosynclinal period, when the CO₂/O₂ concentration ratio is low, organic carbon should be enriched in ¹³C. Then the difference between carbon isotope composition of organic carbon and coeval carbonates, taken from the same place and time, one can regard as analog of ¹³C carbon isotope discrimination in modern plants. Thus isotope data may be used as an immensely effective and delicate tool of the cycle examination in geological history. This assertion is supported by the fact that samples of rocks with organic carbon and coeval carbonates are the main and widely used factual material in the past studies.

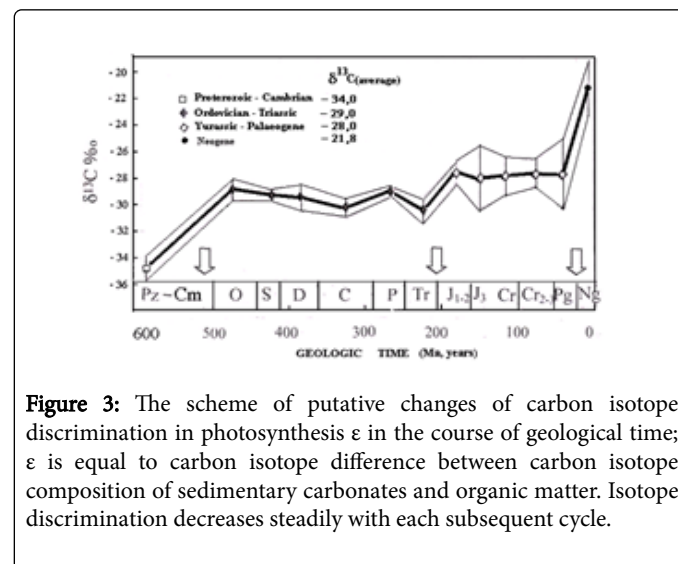


Figure 3: The scheme of putative changes of carbon isotope discrimination in photosynthesis ϵ in the course of geological time; ϵ is equal to carbon isotope difference between carbon isotope composition of sedimentary carbonates and organic matter. Isotope discrimination decreases steadily with each subsequent cycle.

Figure 3 illustrates the variations of carbon isotope discrimination in photosynthesizing organisms with geological time. The aforementioned isotopic difference becomes smaller inside the orogenic cycle, starting from the beginning to its end. The regularity reflects the increase in photorespiration of photosynthesizing organisms in response to the growth of average oxygen concentration from one cycle to another. The assertion is true until the redox carbon cycle is far from the ecological compensation point (see later).

Arguments evidencing in favor of the validity of redox-cycle of biospheric carbon

A decrease of photosynthetic isotope discrimination with geologic time as a result of atmospheric oxygen growth.

A gradual decrease of ¹³C isotope discrimination with geological time in photosynthesizing organisms living in the past was revealed by Popp et al. [16] and Hayes et al. [17]. The authors have considered carbon isotope discrimination like a difference between the carbon

isotope ratio of coeval carbonates and organic matter in sedimentary rocks and called it ϵ parameter.

In the Neoproterozoic era, from 1000 Ma to 541 Ma, carbon isotope discrimination was found to be greater than 32%. In the period from Cambrian to Jurassic ϵ changed to 28% and later in period from Cretaceous to Cenozoic it was less than 28%.

The observed decrease of isotope discrimination with time became understandable if we take into account, what was mentioned before, the new representations on carbon isotope fractionation in photosynthesis, and the increasing role of photorespiration in the course of orogenic cycles [18,19] in parallel with growing average oxygen concentration in the atmosphere.

Within the orogenic cycle the maximum oxygen concentration was achieved by the end of orogenic cycles and most ^{13}C enriched organic matter was also produced at that time. The comprehensive analysis of the observed isotopic shifts leads to the conclusion that there is no other visible reason, but photorespiration, that could explain a decrease of carbon isotope discrimination in the past photosynthesis [8] (Figure 3).

It was proved that high environmental CO_2/O_2 ratio stimulates CO_2 assimilation, whereas low CO_2/O_2 ratio stimulates photorespiration [20]. It means that in the periods when CO_2/O_2 ratio was low (high oxygen concentration), photorespiration should greatly contribute to living matter causing ^{13}C enrichment of biomass. Correspondingly, the buried organic matter which inherits this biogenic material should be enriched in ^{13}C as well.

The mentioned ϵ parameter may be used as the indicator of orogenic and climatic cycles. At the beginning of the orogenic cycle, when CO_2/O_2 ratio is maximal and the contribution of photorespiration is low, ϵ parameter is also at its maximum and corresponds to the warming period. Conversely, at the end of the cycle, when CO_2/O_2 ratio is minimal and photorespiration increases, ϵ parameter reaches minimum and corresponds to the cooling period.

Popp et al. [16] found a coherence of ϵ values for the samples in Cenozoic and climatic cycles. Hayes et al. [17] having examined carbon isotope composition for over than 5000 samples of coeval carbonates and sedimentary organic matter spanning Precambrian and Phanerozoic, found statistically significant difference of ϵ values in interglacial periods and those in periods of glaciations. The results were supported by Huang et al. [21] and Bornemann et al. [22].

The relationship of orogenic cycles and biodiversity. The use of ϵ parameter to examine the relationship. In some works a periodicity in a rate of change of biodiversity (a rate of appearance of the new fauna and flora species per geological unit) in time was revealed [23]. It was supposed that periodicity is caused by the increase of oxygen concentration in the Phanerozoic atmosphere [24]. The assumption was supported by close coherence of the curves illustrating time dependence of a rate of change of biodiversity and other parameters, strongly related with oxygen concentrations. The peaks of all curves fully coincided and corresponded to oxygen maximum (Figure 3) [24].

The physical sense of this link is quite clear. The elevated O_2 concentrations in the atmosphere stimulate (photo) respiration in photosynthesizing organisms, which is followed by superoxide radical's formation. They attack gene molecules causing mutations. Though in a cell there are some enzymes, which destroy radicals reducing them to H_2O and O_2 , at the time of oxygen growth, the enzymes fail to cope with the abundance of radicals and to diminish their amount to the

safe level. As a result, mutations appear and the rate of change of biodiversity increases.

Rothman [25] found a good correlation of ϵ parameter and the rate of change of biodiversity for land plant families as well as for marine animals. His results prove the relation of orogenic cycles and biodiversity rate.

The observed periodicity of mass extinction of plant and animal species on the Earth has a close agreement with the previous correlation. These events are also linked with a change of CO_2/O_2 ratio in the atmosphere over time [26]. According to the model, the abrupt change of CO_2/O_2 ratio in the atmosphere occurring in orogenic cycles' transitions should lead to the extinction events, because they are followed by the change of aerobic conditions to anoxic ones causing mass extinction of aerobic organisms.

Some other facts evidencing in favor of orogenic cycles existence. Uneven stratigraphic distribution of sediments rich in organic matter reflects the periodic change of orogenic cycles. In fact, Bazhenova and Sokolov [27], examining the stratigraphic distribution of Domanic oil source rocks, revealed that these sediments rich in organic matter were present on different continents at the same stratigraphic levels. They are found practically in all systems of the Phanerozoic and of the Precambrian. The stratigraphic levels, where domanicoids were fixed, are Ediacaran – Cambrian, Devonian - Carboniferous, late Jurassic – early Cretaceous.

The non-uniform stratigraphic sediments distribution can be explained in the frames of the natural redox carbon cycle model as follows. Though the kinetics of global photosynthesis and organic matter accumulation is unknown, from the assumed carbon cycle dynamics one can expect that accumulation of organic matter mainly should take place by the end of the cycle, when the most of CO_2 , which entered the "atmosphere – hydrosphere" system in the orogenic period, after some transformation is converted into the organic matter. The formation of sediments rich in organic matter is likely bound to the transitions from one cycle to another when there was a change of aerobic conditions to anoxic causing mass extinction of living organisms. Their biomass is a probable source of organic material. The repeatability of orogenic cycles determines their appearance of domanicoids at different stratigraphic levels in the Precambrian and the Phanerozoic. It should be stressed, that Bazhenova and Sokolov [27] marked that periods of organic matter accumulation were followed by rifting process which in accordance with our model corresponds to the orogenic period, occurring behind the cooling time.

Rich in organic matter shales are considered to be the main sources for oil formation. So one could expect that irregularity in source rocks should bring about to the irregularity oil in distribution. Vyshemirskii and Kontorovich [28] found that the mentioned irregularity in distribution of the discovered oil fields in the world. The same irregularity was discovered in the distribution of oil fields in the former USSR [29]. According to both distributions, the beginning of oil generation falls in time limits 600 to 500 million years ago. This is in an agreement with considerable growth of oxygen concentration in the atmosphere. As it was noted, oxygen concentration is an indicator of organic matter accumulation in sediments. According to some data [30,31] one can accept that in most of Precambrian oxygen concentration was less than 1% and only by the end of Precambrian it started to increase significantly [32]. It is logical to assume, that photosynthesis needs a prolonged time to accumulate organic matter in sediments sufficient to produce hydrocarbons capable to form oil

fields. So the observed irregular oil distribution agrees with the expectations based on the redox-cycle model.

The fourfold ^{13}C enrichment of oils from the Cryogenian period of Neoproterozoic era to the Miocene epoch of Cenozoic era supports the existence of orogenic cycles. Having examined the extensive collection of oils (504 oil samples) differing in age and origin, Andrushevich et al. [33] established that in the course of geological time the oils and their components have been consistently enriched in ^{13}C (Figure 4). The model's logic allows concluding that the most likely reason for this enrichment is the intensified photorespiration of photosynthesizing organisms as a result of the increase of average oxygen concentration in the atmosphere. One should take into account that, despite of variations, in the course of geological time an average atmospheric oxygen concentration steadily grew up. The ^{13}C enrichment of oils reflects that at least four orogenic cycles took place, accompanied by an increase in average oxygen concentration in the atmosphere. Oils inherit the enrichment from organic matter. One more interesting observation indicating the validity of the model stems from the analysis of the above data. Since Jurassic, a scatter in carbon isotopic composition of oils has increased essentially. The variety of land photosynthesis conditions resulted in a wide spectra of $\delta^{13}\text{C}$ values.

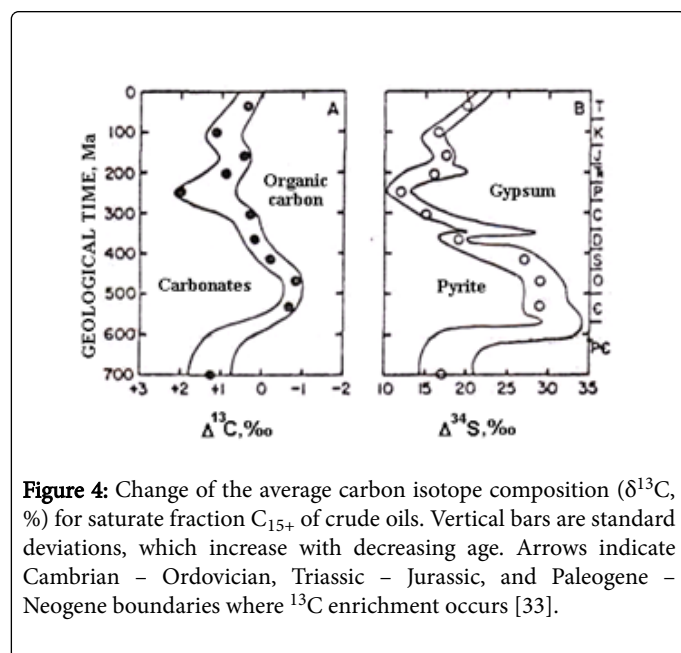


Figure 4: Change of the average carbon isotope composition ($\delta^{13}\text{C}$, %) for saturate fraction C_{15+} of crude oils. Vertical bars are standard deviations, which increase with decreasing age. Arrows indicate Cambrian - Ordovician, Triassic - Jurassic, and Paleogene - Neogene boundaries where ^{13}C enrichment occurs [33].

Global coupling of natural carbon and sulfur cycles. Thermochemical sulfate reduction is the coupling point. According to Mackenzie and Pigott [34], the natural sulfur cycle, like the carbon cycle, consists of the oxidative (sulfate) and reductive (sulfide) branches. As it follows from the suggested model, natural carbon and sulfur cycles are coupled via sulfate reduction proceeding in subduction zones. To substantiate this assertion, we should address the data from the work of the mentioned authors Mackenzie and Pigott [34]. Temporal curves demonstrate synchronous isotopic variations of carbon and sulfur of marine carbonates and gypsum (sulfates) in time. Such synchronism prompts itself that both cycles are somehow bound. Each curve has two differently directed humps. Next to them there are inscriptions, made by authors, to indicate minerals of sedimentary rocks that were mostly spread at the corresponding periods. Carbonates and pyrites correspond to the humps in lower parts of the

curves respectively. Organic matter and gypsum correspond to the humps in the upper part of the curves.

If we compare the above substances with the substrates and the products of sulfate reduction, it is easy to see that the substances corresponding to the lower humps on the curves coincide with the reaction products, and the substances, corresponding to the upper humps on the curves coincide with the reaction substrates. Analysis of the isotopic changes of carbon and sulfur proves that the coincidence is not accidental.

By analyzing the dynamics of carbon and sulfur isotopic variations resulting from the curves on, firstly, we should note that thermochemical sulfate reduction is followed by sulfur isotope fractionation [12,35]. Secondly, due to periodic character of the reaction, the substrate is depleted. The depletion is followed by Raleigh effect. The more the reaction proceeds and the more the substrate pool is depleted, the greater the residual substrate (gypsum) is enriched with a "heavy" sulfur isotope ^{34}S . As it follows from the analysis of the lower part of the curves, the enrichment of gypsum with ^{34}S is accompanied with the enrichment of carbonates with a "light" carbon isotope ^{12}C . Both traits evidence in favor of high extent of sulfate conversion. Indeed, in a case of high extent of sulfate conversion another reaction product CO_2 should be also produced in a considerable amount. Thus the CO_2 inherits "light" carbon isotope composition from organic matter. Hence, when "light" CO_2 enters marine "carbon dioxide - carbonate" system with carbon enriched in ^{13}C it makes carbon in the system "lighter" due to chemical isotope exchange.

Quite opposite picture one can deduce from the analysis of upper parts of the curves. The ^{32}S enrichment of gypsum evidences that the extent of sulfate conversion is low. Hence the small amounts of "light" CO_2 are produced and marine carbonates become "heavier" as compared with the previous case. Thus, the coupled isotopic changes of carbon and sulfur of marine carbonates and gypsum, in addition to chemical arguments, give firm proofs that they represent the results of sulfate reduction process occurring in the subduction zones.

Natural carbon cycle evolution. Ecological compensation point

Development of carbon cycle is closely bound to the expansion of photosynthesis. Due to reciprocal interactions between CO_2 assimilation and photorespiration in photosynthesis depending on CO_2/O_2 concentration ratio in the atmosphere carbon cycle spontaneously evolves in the direction to the ecological compensation point. Below this point, the rate of photorespiration (together with respiration) exceeds the rate of photoassimilation, and physiological existence of organisms becomes impossible. As CO_2 and O_2 are mutually related, the compensation point may be determined via consideration of either CO_2 or O_2 concentrations [36]. The authors experimentally proved that at the fixed concentration of one gas, the other can reach the level determined by the corresponding compensation point. Considering these results, Tolbert et al. [36] concluded that the same feedback mechanism acts in the nature, and it is responsible for the achievement of stationary CO_2 and O_2 concentration in the atmosphere.

Taking into account the reciprocal interactions between CO_2 assimilation and photorespiration in photosynthesis, which is the key element of redox carbon cycle, it may be assumed that these processes are the driving forces in achieving the ecological compensation point.

The numerous oxidation processes of the reductive branch, due to O₂ consumption and CO₂ evolution, play a regulatory role via common reaction intermediates, defining the real position (concentrations) of the ecological compensation point. In this position, the full conversion of the reduced carbon into the oxidized forms and back occurs.

From the origin of photosynthesis until the moment of approaching the ecological compensation point, the total interaction of CO₂ assimilation and photorespiration provide the excess of reductive carbon over oxidative. The excess of carbon was accumulated in deposits in the form of buried organic matter. The corresponding amount of oxygen is accumulated in the atmosphere.

In the frame of redox carbon cycle, the above state is achieved spontaneously owing to the ability of photosynthesizing organisms to regulate their photosynthetic capacity by changing CO₂ photoassimilation/photorespiration ratio which in turn depends on CO₂/O₂ concentration ratio in the environment. The latter is determined by numerous redox processes in both branches of the global carbon cycle. Nearby the ecological compensation point, the redox carbon cycle system becomes very sensitive to the geological and orbital forcing, which exerts impact on plates collisions. This is manifested as the "glacial-interglacial" climatic transitions.

Glacial-interglacial oscillations of CO₂ have emerged as a consequence of proximity of the system to the ecological compensation point [21,37-40]. This possibly happened in the end of Carboniferous when the great expansion of photosynthesis took place and covered the land [41]. Basing on the last burst of oxygen in the atmosphere which corresponds with the time of appearance of last wave of oil generation, most likely the ecological compensation point was achieved in the Neogene (Miocene) [42,43].

Conclusion

The analysis of factual material has confirmed the idea of Vernadsky [44] on interconnection of biospheric and Earth crust processes. It revealed the impact of lithospheric plates' movement on photosynthesis development. Photosynthesis in turn influence on the sedimentation processes resulting in organic matter accumulation in shale. In general all the processes on the planet are directly or indirectly bound.

A new definition of natural carbon cycle, based on the redox state of the element is suggested and corresponding model of global redox-cycle of biospheric carbon is built. It describes well the numerous natural regularities and phenomena.

According to the model, carbon transfer between the geospheres and the biosphere is accompanied by the changes in redox state of carbon. The global redox carbon cycle consists of the oxidized and the reduced branches. The oxidized branch is presented by carbon dioxide, bicarbonate and carbonate species, composing common chemical exchange system in the atmosphere and hydrosphere. The reduced branch is presented by all biogenic forms of photosynthetically assimilated carbon and their derivatives. The transition from the oxidative to the reduced state of carbon occurs during the process of photosynthesis. The reverse transition takes place in numerous processes of oxidation, including respiration of living organisms, the processes of direct and indirect oxidation of buried organic matter. Final powerful oxidation of organic matter occurs in sulfate reduction proceeding in the subduction zones.

The redox carbon cycle has appeared simultaneously with photosynthesis. The cycle has developed in parallel with photosynthesis expansion at the background of long-term orogenic cycles. The orogenic cycle consists of a short-term orogenic period and a long-term geosynclinal period. In short-term orogenic periods, when the plates move fast and their collisions occur frequently, a great amount of CO₂ evolves from the subduction zones of the Earth's crust and fills the "atmosphere – hydrosphere" system. The photosynthesis expansion occurred in parallel with the changes of CO₂ and O₂ concentrations in the "atmosphere – hydrosphere" system. In the orogenic period of the orogenic cycle, the CO₂ concentration increases sharply. In the geosynclinal period of the cycle, the CO₂ concentration gradually drops. Conversely, in the orogenic period O₂ concentration decreases, whereas in the following geosynclinal period, due to photosynthesis, the O₂ concentration grows up, and achieves the maximum by the end of the cycle. In the following relatively extended geosynclinal periods, the collisions of plates are seldom, and the rate of CO₂ emission from subduction zones becomes weaker than the rate of CO₂ assimilation in photosynthesis. As a result, the oxidized carbon pool in the "atmosphere – hydrosphere" system is depleted.

Thus the pulsating movement of plates exerts an impact on dynamics and development of photosynthesis via the injections of CO₂ in the orogenic period. The periodic injections of CO₂ provide irregular expansion of photosynthesis on the globe. Such development of the process of photosynthesis determines numerous processes in biosphere and in the Earth's crust including climatic changes, changes in the rate of biodiversity, irregular accumulation of organic matter in sediments, uneven stratigraphic oil distribution and many other processes.

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Among the set of pieces of evidence supporting the model, a particular role of isotopic characteristics should be especially stressed. Their values and even signs can be used to reconstruct the processes composing the redox global carbon cycle. Very similar isotopic secular curves for carbon and sulfur as well as the signs of the isotopic shifts allow making conclusions about the relationship of the global carbon and sulfur cycles in the nature.

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