

Carbon Isotopic Data Validate the New Model of Carbon Turnover

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Abstract

A new global redox carbon cycle model is suggested. It claims that lithospheric plates' movement exerts an impact on photosynthesis development. The impact is realized via periodic injections of CO₂ coming from zones of plates' collisions. Carbon dioxide is derived from oxidation of sedimentary organic carbon in thermochemical sulfate reduction proceeding in subduction zones. Carbon turnover is considered as a conversion of the element from the oxidized state (CO₂ + HCO₃⁻ + CO₃²⁻) into the reduced state produced in photosynthesis and in the following transformation. The isotopic data confirm the validity of the model. They explain the observed correlation of carbon isotope composition of sedimentary organic matter with geologic age. It was found that the difference between carbon isotope composition of organic matter and that of coeval carbonates is an analog of the carbon ¹³C isotope discrimination in photosynthesis used for modern plants. The periodicity of isotopic characteristics correlates with periodicity of climatic changes, mass extinctions, with the irregularity of stratigraphic distribution of rocks rich in organic matter and other periodic events in biosphere.

Keywords: Global carbon cycle; Isotope fractionation; CO₂ assimilation and photorespiration; Sedimentary organic carbon; Carbonates; Orogenic and Geosynclinal periods; Ecological compensation point; Lithospheric plates; Climate cycles; Mass extinctions

Introduction

As early as 1926 famous Russian geochemist Vernadsky [1] put forward an idea that Earth crust processes interact with Biosphere processes. The present work develops and elaborates this idea. The new interpretation claims: the moving lithospheric plates exert an impact on photosynthesis development via CO₂ injections into "atmosphere-hydrosphere" system, produced in zone of plates' collisions.

To prove this assertion, a new approach to carbon turnover is needed. That is why; a redox carbon cycle model has been worked out. It is characterized by three main features that distinguish it from other models [2-4].

The Special Features of the Redox Carbon Cycle Model

The first feature is linked with the assertion that CO₂, which fills "atmosphere-hydrosphere" system and determines photosynthesis development, is produced in zone of lithospheric plates' collisions. Carbon dioxide is derived from the oxidation of the sedimentary organic matter in the thermochemical sulfate reduction.

The second feature claims that carbon turnover depends on lithospheric plates' movement, which is irregular. It consists of short-term period of intense movement and quick rates of plates. It provides a number of plates' collisions favorable for thermochemical sulfate reduction and producing considerable amounts of CO₂. In long-term period of quiet plates' movement when the plates' rate is low, weathering and photosynthesis become dominant and CO₂ concentration in the "atmosphere-hydrosphere" system drops.

The third feature, characterizing the model, is the assertion that carbon turnover is not a simple transition of the element between geospheres and biosphere, but is a conversion of carbon from the oxidized state, presented by CO₂, bicarbonate and carbonate ions, into the reduced state, presented by different biogenic forms, produced in photosynthesis, and by the products of their following transformations. The reverse transition is realized via respiration of living organisms, via

microbial and chemical oxidation accompanying transformations of the "living" matter after the burial. Among the oxidative processes the final oxidation of organic matter in the subduction zone is dominant.

Thus, the global redox carbon cycle formally 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 in a number of oxidation processes.

Two Known Geological Concepts are the Basis for the Model

The proposed model is based on two geologic concepts-plate tectonics [5,6] and orogenic cycles [7]. The first proves that plates, covering the entire Earth surface, are in permanent movement. The movement reminds that of escalator. In some places of the Earth, in the zone of the mid-atlantic ridge, where the crust is most subtle, magma erupts onto the surface and, coming into the contact with ocean water, hardens to form a new plate. It pushes other plates, causing them to move. In other places of the Earth, along the continent margins and island arcs, the plates, moving towards each other, collide. One of them, bending and moving down under the other, is absorbed by magma. Area, where the collisions occur, is called the subduction zone.

According to the second concept, the Earth crust fluctuates permanently, but with different intensity. Short-term periods of high intensity, termed orogenic, correspond to periods of great volcanism and strong volcanic and magmatic eruptions. In long-term quiet period, termed geosynclinal, the activity of geologic processes slows down; weathering and photosynthesis become dominant.

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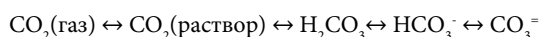
The Essence of the Redox Carbon Cycle Model

I have combined both concepts and supposed that short-term orogenic periods correspond to the time of intense movement of the lithospheric plates, when frequent collisions, provide massive entry of CO₂ into “atmosphere-hydrosphere” system. Long-term geosynclinal periods correspond to the time of dominant role of photosynthesis, what leads to the considerable depletion of CO₂ in the system. The active tectonic activity slows down.

Best of all to understand the carbon cycle functioning is to study the variations of the main components of photosynthesis reaction (1)



within the orogenic cycle. The tentative variations of the concentrations of the components are presented on Figure 1. In the orogenic period CO₂, coming from the subduction zone, fills the “atmosphere-hydrosphere” system and reaches its maximal concentration. Note, that because of the equilibrium in the system [8]



other inorganic species are described by the same curve as CO₂.

In the subsequent geosynclinal period due to photosynthesis the CO₂ concentration falls down reaching minimal meaning by the end of the period. The corresponding variations are described by exponential curve what is typical to the chemical reactions.

The changes of O₂ and organic matter are presented by the antiphase curves relative to CO₂ curve, since they are the products of the reaction (1) whereas CO₂ is the substrate. It should be also underlined that we have replaced the total “living matter” in the reaction (1) by the sedimentary organic matter, since the residence time of the sedimentary organic matter within the carbon cycle, is greater than the life time of the “living” matter.

Isotopic Variations of Organic Matter in the Course of Orogenic Cycles

To illustrate the special role of carbon isotope data in substantiation of the redox carbon cycle model, additional information on carbon isotope fractionation in photosynthesis is needed.

As known, photosynthesis consists of two reciprocal processes: CO₂ assimilation and photorespiration. From recent works it was found that each of these processes is accompanied by carbon isotope fractionation with the effect of opposite sign. The CO₂ assimilation results in ¹²C enrichment of biomass, whereas photorespiration leads to the accumulation in biomass of ¹³C. Thus carbon isotope composition of the total biomass is determined by both isotope effects. The above processes are in reciprocal relations, i.e., the strengthening one of them is accompanied by the weakening of the other. Contribution of each process into isotope composition of biomass depends on the CO₂/O₂ concentration ratio in the environment, since intensification of photorespiration leads to the enrichment of biomass in ¹³C, whereas intensification of CO₂ assimilation leads to ¹²C enrichment. The last is especially meaningful bearing in mind that with photosynthesis emergence average O₂ concentration in the atmosphere steadily grew up. The O₂ concentration growth occurred also within geosynclinal period of orogenic cycle.

Taking the above into consideration, one should conclude that in orogenic period the “living matter”, and hence the buried organic matter has maximal enrichment in ¹²C, whereas in geosynclinal

period of the cycle organic matter is gradually enriched in ¹³C reaching maximal ¹³C enrichment by the end of the cycle.

One more important notion is the following. Considering the actualism principle [8], the carbonates can be regarded as analog of the carbon dioxide in the past atmosphere, whereas coeval sedimentary organic matter can be considered as analog of the “living” matter. Following this logic, the difference between carbon isotope composition of carbonates and that of coeval organic matter maybe regarded as analog of ¹³C isotope discrimination in the past photosynthesis. It was designated as ε parameter [9].

Taking into account that isotope ratio of carbonates doesn't depend on O₂ concentration; it is convenient to use the ε parameter variations to analyze the impact of CO₂/O₂ ratio within the cycle. Within the cycle ε parameter varies from the maximal value in orogenic period, when CO₂/O₂ ratio is maximal, to the minimal value by the end of geosynclinal period when CO₂/O₂ ratio reaches minimal meaning (Figure 2).

Another important relation may be deduced from the assumed depletion of inorganic pool of CO₂ in geosynclinal period. The depletion of the inorganic pool is accompanied with an isotope effect

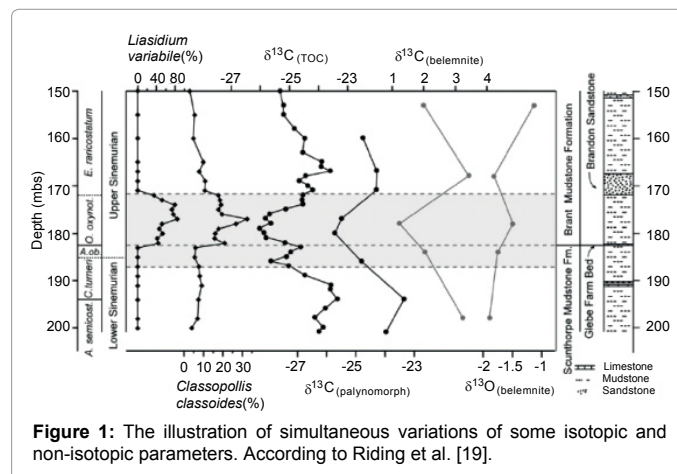


Figure 1: The illustration of simultaneous variations of some isotopic and non-isotopic parameters. According to Riding et al. [19].

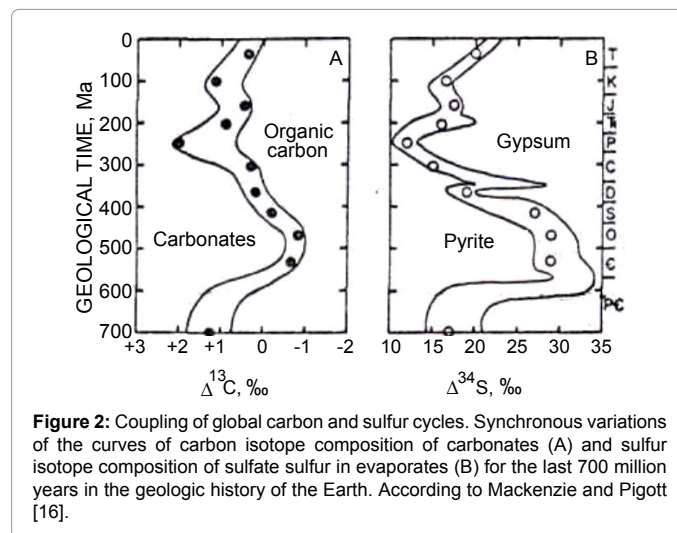


Figure 2: Coupling of global carbon and sulfur cycles. Synchronous variations of the curves of carbon isotope composition of carbonates (A) and sulfur isotope composition of sulfate sulfur in evaporates (B) for the last 700 million years in the geologic history of the Earth. According to Mackenzie and Pigott [16].

of photosynthesis and hence it should give rise to the so-called Raleigh effect. It means that in the course of geosynclinal period the residual CO₂ in the “atmosphere-hydrosphere” system and the newly produced “living” matter are consistently enriched in ¹³C. The “heaviest” organic carbon is produced by the end of geosynclinal period.

Note that in geosynclinal period there is O₂ growth in the atmosphere what stimulates photorespiration and results in additional accumulation of ¹³C in organic matter. At the same time a decrease of CO₂ concentration in the system results in the temperature drop on the Earth surface. It achieves the minimal meaning by the end of the geosynclinal period and causes glaciations. Thus high oxygen concentration, low temperatures (glaciations) and ¹³C enrichment of organic matter are three traits, indicating the end of the cycle.

The Arguments In Favor of the Redox Carbon Cycle Model; The Dependence of Carbon Isotope Composition of Sedimentary Organic Carbon on O₂ Concentration

Hayes et al. [9] who examined carbon isotope ratio of sedimentary organic matter in Precambrian and Phanerozoic along the geologic scale found the sequential ¹³C enrichment of organic matter, what corresponded to the growth of O₂ in the atmosphere.

The examination of sedimentary organic matter at three successive periods has discovered that during the Neoproterozoic: from 800 to 750 Ma δ¹³C values of organic carbon were greater than 32‰; from 685 to 625 Ma δ¹³C were between 32‰ and 28‰, and in Phanerozoic up to the Early Oligocene interval the values were less than 28‰, reaching up to 22‰.

Average O₂ concentration in this interval grew up from some percent in late Proterozoic [10] to approximately 20-25% in Late Paleocene [11,12].

The oils show the same tendency (Figure 3) [13,14]. There are three successive steps of ¹³C enrichment corresponding to the growth of the average concentration of O₂ in geologic time. This phenomenon is explained by the fact, that oils are the derivatives of organic matter and inherit its carbon isotope composition from them. It also relates to all oil fractions.

It was also disclosed [9] that organic matter related to the “ice house” period was always enriched in ¹³C as compared with that related to the interglacial periods.

Isotopic Data on Precambrian Carbonates

Figure 4 presents carbon isotope data on Precambrian carbonates. Data were taken from work of Derry et al. [15], who gathered all the available data at that time. They disclosed great isotopic variations which could be explained in the frame of the suggested model. Two narrow peaks, corresponding to the abrupt negative excursions, according to the model, correspond to two short-term orogenic periods of two different orogenic cycles. Negative sign of the excursions within short-term intervals correspond to “greenhouse effect” typical to orogenic periods. Additional support for the explanation is a proximity of each peak to two glacial episodes: the Sturtian (ca. 780 Ma) and Varangian (ca. 600 Ma) correspondingly. In accordance with the model, abrupt cooling always proceeded by orogenic period.

Carbon and Sulfur Cycles Coupling Source of CO₂

Here we illustrate how isotopic data and non-isotopic arguments prove one of the most important model’s assertions: CO₂, produced in

oxidation of sedimentary organic matter by means of thermochemical sulfate reduction, occurs in subduction zones in the orogenic period. It was also shown that sulfate reduction is the point of coupling of carbon and sulfur natural cycles.

Temporal curves on Figure 5 demonstrate synchronous isotopic variations of carbon and sulfur in marine carbonates and gypsum (sulfates) in geologic time [16]. 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 the authors, to indicate minerals of sedimentary rocks that were mostly spread at the corresponding periods. Carbonates and pyrites correspond to the humps in the lower parts of the secular curves. Organic matter and gypsum correspond to the humps in the upper part of the curves respectively.

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

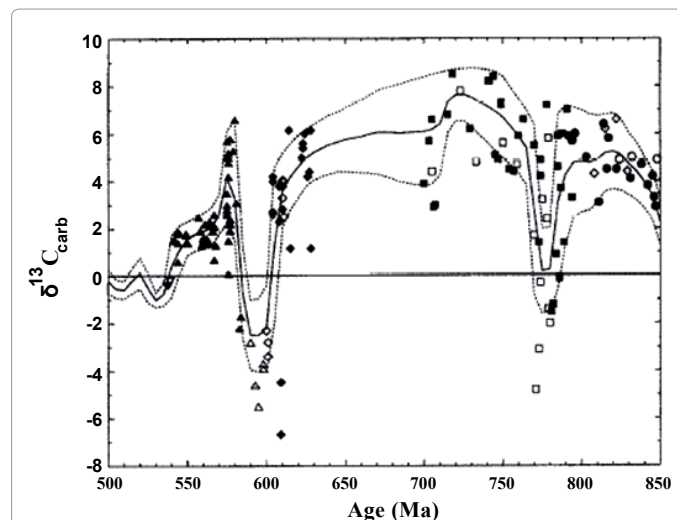


Figure 3: Secular variations of ¹³C of Late Proterozoic marine carbonates from different stratigraphic groups. Negative excursion in δ¹³C curve, according to the model, correspond to the onset of “greenhouse” period. According to Derry et al. [15].

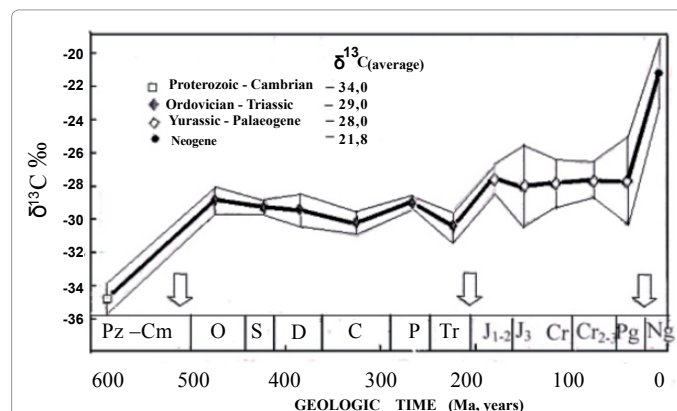
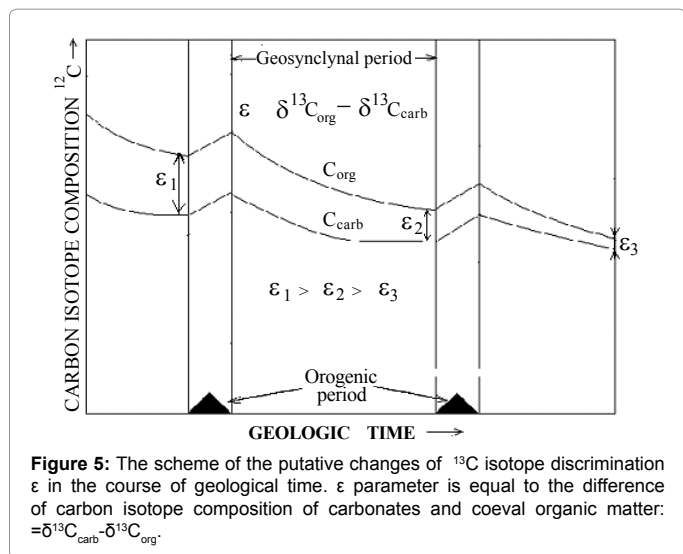


Figure 4: Change of the average carbon isotope composition (δ¹³C, ‰) for saturate fraction C₁₅* of crude oils. Vertical bars are standard deviations, which increase with decreasing age. Arrows indicate Cambrian-Ordovician, Triassic-Jurassic, and Paleogene-Neogene boundaries where ¹³C enrichment occurs. According to Andrushevich et al. [14].



reaction products, whereas the substances, corresponding to the upper humps on the curves coincide with the reaction substrates. It explains the opposite directions of the humps.

Analysis of the isotopic changes of carbon and sulfur proves that the coincidence is not accidental.

Prior to the analysis of the dynamics of carbon and sulfur isotopic variations presented by the curves on Figure 5, firstly, we should note that thermochemical sulfate reduction is followed by sulfur isotope fractionation [17,18]. Secondly, due to periodic character of the reaction, the substrate pool of sulfates is periodically depleted. The depletion is followed by the 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 . The enrichment of sulfates in ^{34}S evidences in favor of high extent of sulfate conversion. At the same time high extent of sulfate conversion proves that another reaction product CO_2 should be also produced in a considerable amount. The produced CO_2 inherits its “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 to be “lighter” due to the chemical isotope exchange between species.

Quite opposite picture one can deduce from the analysis of the 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 are the results of sulfate reduction process occurring in the subduction zones.

An indirect argument in favor of sulfate reduction in subduction zone was the great abundance of sulfide oxidizing bacteria in Precambrian. It evidences for significant inflow of the reduced sulfur forms (sulfides and hydrogen sulfide) onto the Earth surface. This was favored by low oxygen concentration in the Earth’s atmosphere at that time. The sulfide oxidizing bacteria were so widely disseminated that gave grounds for Hayes et al. [9] to conclude that these bacteria were the main source of organic matter in rocks in the Proterozoic.

Some other arguments evidencing in favor the assertion that CO_2 is formed in sulfate reduction in orogenic period are given in our previous works.

Ecological Compensation Point

Global photosynthesis is the key element of carbon turnover. With emergence of photosynthesis its product oxygen has begun to accumulate in the “atmosphere-hydrosphere” system. At first oxygen was a poison and destructive to the photosynthesizing organisms, but in the course of evolution they found the way to make use of oxygen having created photorespiration, which began to increase with photosynthesis development [8]. Thus, evolution worked out feedback mechanism to compensate the growing impact of oxygen. The growth of oxygen forced the organisms to evolve in direction to their compensation point. It is the state when the contribution of CO_2 assimilation became equal to that of photorespiration. Below this point physical existence of organism is impossible.

The similar feedback mechanism determines the evolution of the carbon cycle to the ecological compensation point. The latter corresponds to the state when the whole amount of the reduced carbon, produced in photosynthesis, becomes equal to the carbon returning into the oxidizing forms. At this point the system becomes very sensitive to the collisions of separate plates. The orogenic cycles became shorter and finally turned into short-term oscillations, termed climatic oscillations. The identical nature of orogenic cycles and climatic oscillations is supported by the same set of traits.

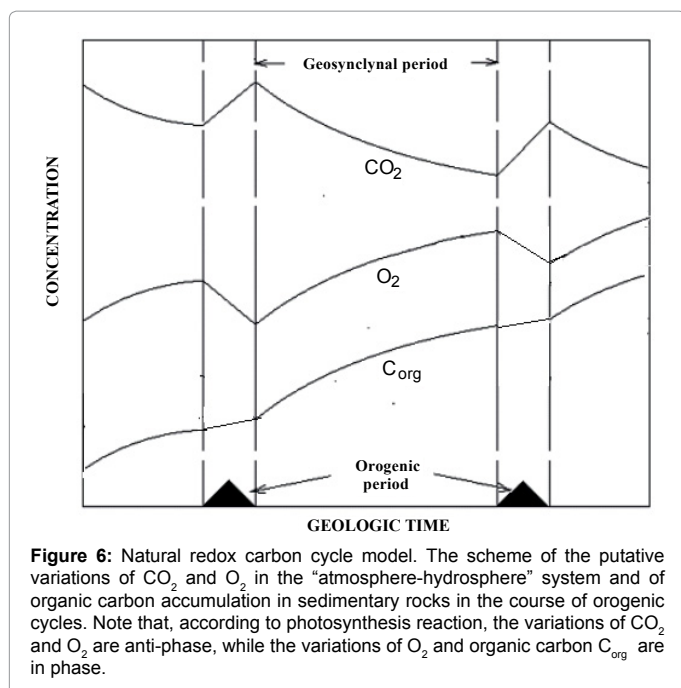
Both consist of two phase: warming and cooling. Warming phase is characterized by high CO_2 concentration and temperature, by low oxygen concentration. This phase is characterized by intense volcanism and magmatism, by sea level rise. In these conditions predominance of thermophilic organisms takes place.

On contrary, the cooling phase is characterized by low CO_2 concentration and temperature, by increased oxygen concentration, by the reduced tectonic activity. Volcanism and magmatism are replaced by strengthening of photosynthesis and weathering processes. Sea level drops. The transition from anaerobic to aerobic environment is followed by the emergence of aerobic organisms.

It should be stressed that the transition from cooling to warming phase, accompanying with dramatic changes in the environment, results in great biotic events, such as mass extinction. It stimulates the formation of deposits rich in organic matter. The transition is always followed by the simultaneous change of isotopic shifts of different elements. It correlates with the variations of non-isotopic parameters Figure 6 [19]. It allows clearly distinguishing the onset of warming period and carrying out stratigraphic correlations.

Conclusion

- The suggested redox carbon cycle model reveals the underlying mechanisms of interaction of biosphere and Earth crust processes. It was found that lithospheric plates’ movement exerts impact on photosynthesis development via periodic injections of CO_2 into “atmosphere-hydrosphere” system during plates’ collisions.
- The model corresponds well to the available experimental data. It allows explaining of many biosphere events in the geological past, such as climatic cycles, mass extinctions, the irregularity in stratigraphic distribution of deposits rich in organic matter, etc.



- Carbon isotope data on marine carbonates and coeval sedimentary organic matter play an important role in carbon turnover studies. The most effective use of isotopic parameters is to combine them with non-isotopic parameters and to find coherence.

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