

## BIOGEOCHEMISTRY

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### Summary

Biogeochemistry tries to combine biology and geochemistry to achieve a deeper understanding of the whole complex of chemical transformations occurring in nature, in the continuous interactions between its biotic and abiotic components. The biotic metabolism involves redox reactions that can affect the global distribution of elements that are important to life, and of some elements that are not. Many of the essential elements occur at low concentrations in the environment. Others, like copper, zinc, cobalt, and nickel, exist as trace elements but are essential constituents of specific enzymes. In this review of biogeochemistry we will focus on carbon, oxygen, sulfur, and iron. The global cycling of these four elements is as interdependent today as it has

been throughout earth's history. It is fundamental to life, and also affects the world's climate.

The origin of life on earth, and the emergence of different microorganisms, are fields of great interest to biogeochemists. If mankind is to understand the many issues relating to the origin of life, it will be possible only through the achievements of biogeochemistry.

## 1. Introduction

Biogeochemistry straddles three disciplines, *biology*, *geology*, and *chemistry*. It is clearly an interdisciplinary science. Semantically, the root of the term biogeochemistry is chemistry, and above all chemistry related to geoscience: *geochemistry*. In Goldschmidt's view, the discipline geochemistry includes three major areas:

- Establishment of the terrestrial abundance and relationships among elements.
- Accounting for the terrestrial distribution of elements in the geochemical spheres.
- Detection of laws governing the abundance relationships and the distribution of the elements.

Adding the prefix *bio* to geochemistry implies that biogeochemistry is concerned with the activities of living organisms in the migration, distribution, dissipation, and concentration of chemical elements. The two central processes of the organic aspects of biogeochemistry are photosynthesis and respiration.

Depending on a particular process, the role of biota in geochemistry is best explained in one of the following ways. In some cases it involves catalysis of geochemical reactions by specific enzymes. The catalysis increases the reaction rate significantly over what it would be in the absence of the catalyst. In some other cases, specific biota excrete metabolic products in significant quantity, which are abiotically very reactive with susceptible geochemical substances, resulting in chemical change in geochemical substances that would be much slower or non-existent in the absence of the metabolic product. In other cases again, specific biota may consume a substance in the environment which can, for instance, result in a significant change in pH or redox potential, and thereby accelerate or slow down a geochemical reaction that would otherwise occur in the absence of the biota. Geochemical reactions in which biota participate may result in the formation of inorganic solids, or in the dissolution of such solids. The inorganic solids in such biota forms may become structural components of their cells (as in CaCO<sub>3</sub>-containing cell walls of some algae), or they may accumulate in the bulk phase (for example, metal sulfide in some reducing sediments). The net effect of biota in geochemistry, whatever the mechanism of their action, is therefore on geochemical reactions, with biota controlling certain chemical reaction rates. It should be emphasized that biota participate effectively in geochemical reactions only if these reactions are not in a state of chemical equilibrium.

In the search of life on other planets, a study of their atmospheres (if they have one) may provide clues as to whether or not life exists on them. The atmosphere may reflect the equilibrium state of a planet. This is because the atmosphere of a planet is the region

with lowest mass and shortest residence time. Lovelock (1988) used this fact when NASA first investigated the possibility of life on Mars. The components of the Martian atmosphere are very close to chemical equilibrium, indicating a low probability for the existence of life. An extra-terrestrial observer of the earth, on the other hand, would find that the components of its atmosphere exist in a condition which lies far from chemical equilibrium. This, in itself, would offer strong evidence for the existence of life on our planet. The biosphere itself is using feedback mechanisms, thereby interfering with the chemical equilibria. The sustainability of our environment is dependent on the rate of these feedback reactions in comparison with the rate of changes created by mankind. The burning of fossil fuels leads to an increase of carbon dioxide in the atmosphere, at a rate higher than the uptake by photosynthesis. Lovelock hypothesized in *The Ages of Gaia* that our whole planet should be regarded as a “living organism.” He also states in his book: “in Gaia we are just another species, neither the owners nor the stewards of this planet. Our future depends much more upon a right relationship with Gaia than with the never-ending drama of human interest.”

Liquid water is an absolute prerequisite for life. Earth is the only celestial body in our solar system that has water in liquid, solid, and gaseous form. Liquid water is important to life because it represents a major part of a living cell (73–91 percent in bacteria). The remainder of the cell includes compounds of carbon (including nucleic acids, proteins, carbohydrates, and lipids), as well as some inorganic substances. These cell components are important to cell structure and/or function. The organic components are produced by cellular metabolism from organic and/or inorganic nutrients. The gaseous form of water is a prerequisite for the hydrological cycle, which is the driving force of weathering and transport of solutes and particulates from the continents.

The biosphere has no effect on the endogenic (interior) geochemical processes of the earth but it actively affects exogenic (exterior) processes, which occur between depths of a few kilometers within in the crust and heights of a few kilometers in the atmosphere. The deep biosphere of the crust was unknown until quite recently. It is now thought to contain a volume of biomass of the same order of magnitude as the surficial biosphere.

## **2. Ancient Biogeochemistry**

### **2.1. Origin of Life**

Several hypotheses of how life originated on earth have been proposed by natural scientists. One is the hypothesis of *panspermia*, according to which life arrived from outer space. The interstellar media is supposed to contain all essential molecules required for the origin of life. This material was deposited in our solar system in protoplanetary bodies that collided with each other to form the inner planets. It was also deposited in meteoritic bodies that collided with the earth. Dependent on the size of the colliding body(ies), some of this organic material survived the heat from the impact energy. It has been estimated that the time period when events disruptive to chemical and early biotic evolution became less frequent, and life might have evolved, was 3.7–4 Ga ago. The hypothesis also assumes that some bacterial spores originated on another planet and were ejected into interstellar space, either as a result of collision between the life-bearing planet and a meteorite, or due to a supernova explosion. To survive the interstellar environment during the timespan necessary for travel to earth, the spores

would have had to be surrounded by some kind of shell. Their survival possibility during the entry through earth's atmosphere would have been higher when the atmosphere was anoxic. Unfortunately, the panspermia hypothesis avoids the obvious question of how life arose from non-living matter.

Most scientists believe that life on earth arose *de novo*. An older idea was that it arose in an "organic soup"—also called "broth"—in an oxygen-free environment. The energy necessary for its generation was provided by electrical discharge from lightning, heat and/or light. Certain wavelengths of UV light are fatal to cellular life, so the UV light must have been filtered through some kind of material (for example, a water column) to allow survival of cells. Mineral surfaces, like those on clays, could have acted as catalysts for the formation of large, self-reproducing organic molecules in the pre-cellular stages of life.

It is highly probable that the building blocks from which cellular polymers were formed existed in the early stages, but the formation of large polymeric molecules from the components in the "organic soup" is still not clearly understood. According to the organic soup hypothesis, the first organisms that arose were *heterotrophs*: that is, they used organic molecules available in their surrounding environment to build new cell material. Only later did *autotrophs* emerge: these beings transformed carbon dioxide into organic cell material, using chemical or light energy to drive the process. The chemical energy could have resulted from the oxidation of hydrogen, for instance, or from reduced sulfur. The organic soup theory has been criticized for being incompatible with thermodynamics, for being chemically and geochemically implausible, and as discontinuous with biology and biochemistry. Nevertheless, it has been retained as accepted dogma.

In 1988, Wächtershäuser published a new hypothesis that avoids the above-mentioned drawbacks, and which today is one of the favored theories among many scientists studying the early stages of life on earth. It assumes that the concentration of dissolved organic constituents in the water-phase is negligible, and that the early stages of life, represented by so-called surface metabolists, were autotrophic and took place on a mineral surface as a two-dimensional metabolic process. An oxidative redox-process involving the conversion of ferrous sulfide (FeS) and hydrogen sulfide into pyrite provided the energy needed for carbon fixation. These early forms of life favored positively charged surfaces like those of pyrite, because the proposed building blocks from which surface metabolists were constructed bore a negative charge. Consequently negatively charged surfaces, such as those of clays, were not favored by surface metabolists. In time, the first two-dimensional life on mineral surfaces produced isoprenoid lipids, and eventually became covered by lipid membranes (protocells). The next step was the complete enclosure of surface metabolists by a membrane, thus producing the first cells.

The interaction between iron sulfides and organic material for the origin of life has made the "black smokers" of the mid-ocean ridges a potentially very interesting environment for scientists studying Wächtershäuser's hypothesis. The hydrothermal vents of the mid-ocean seafloor-spreading ridges, where new oceanic crust is being formed by erupting magma, support an ecosystem including microorganisms,

invertebrates, and vertebrates which is driven by heat rather than light energy. Seawater penetrating into the ocean crust to depths as great as three kilometers reacts with the basalt of the crust, under the influence of heat diffusing from underlying magma chambers. This reaction with the basalt generates hydrogen sulfide from seawater sulfate, and liberates metals in the form of ferrous iron, manganous manganese, cupric copper, zinc, and lead from the basalt. The resultant acidic hydrothermal solution is forced through cracks and fissures to the surface of the ocean crust, and emerges as hot hydrothermal solution. Its encounter with cold seawater results in rapid precipitation of most of the metals as sulfides: the manganous manganese is an exception because it is relatively soluble. The metal precipitates form chimneys at the mouth of the vents. Unreacted sulfide, and to a limited extent manganous manganese, become the primary energy source for the ecosystem that develops around the mouth of the vents. The sulfide is exploited by appropriate sulfide-oxidizing autotrophic bacteria. These share some of the carbon they fix at the expense of this oxidation with invertebrate forms of life, which have an absolute dependence on this source of carbon. Indeed, some of these invertebrates form an obligate symbiosis with the sulfide-oxidizing bacteria. These ecosystems may offer a model of how life evolved on the early earth. (See Figure 1.)

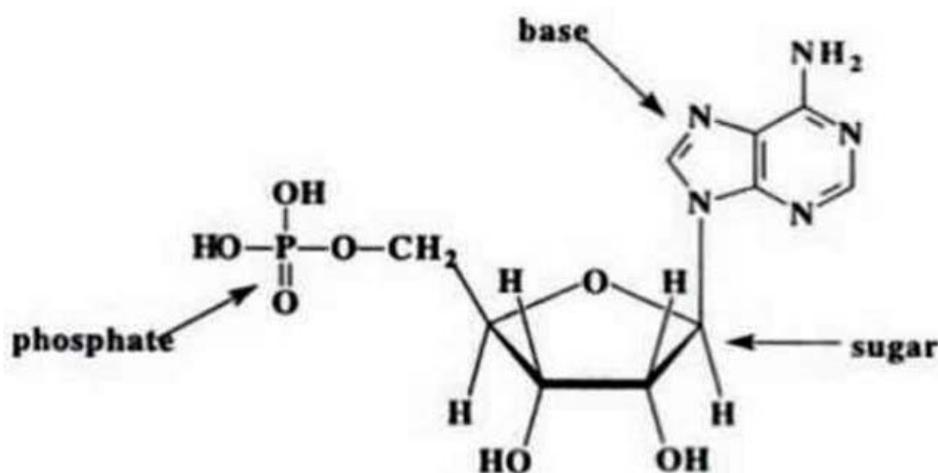


Figure 1. Structure of a typical building block of RNA

One of the most fascinating organic molecules is that of nucleic acid. There are two principal types of nucleic acids: RNA (ribonucleic acids), and DNA (deoxyribonucleic acids). They are composed of three moieties: the four bases adenine, guanine, cytosine and uracil that are the carriers of the genetic codes in all living systems; the sugar ribose forming the backbone of the molecule; and the phosphate group that is the link to the neighbor in the nucleic acid chain. All these organic molecules are supposed to have existed in the prebiotic environment on earth. How, and why, they transformed into nucleic acids is the great mystery. There appears to have been quite a wide gap between the chaotic prebiotic chemistry and the first "living" system. The origin of information and genetic code must be better understood in exploring the path from non-living matter to biological life. We know from experiments that non-biological chemistry containing cyanogroups (CN) gives rise to purine bases and amino acids, but to very little pyrimidine. The hypothetical formation of coded peptides on templates of purine monolayers (primarily adenine and hypoxanthine) on mineral surfaces would allow the

information in the monolayers to have a putative proto-biological meaning. It would allude to a binary pre-RNA translation mechanism with potential relevance to the origin of life. On certain minerals, the monolayers are enantiomorphic (cannot be superimposed on their mirror images), even though they are composed of achiral molecules that can be superimposed on their mirror images. A resulting symmetry break could be related to the peculiar property of these biological systems in using only left-handed amino acids.

Thanks to the information contained in the structure of nucleic acids, organisms can biosynthesize different types of proteins and reproduce themselves. Proteins are the main components of muscles, skin, hair, and other body elements. They are biosynthesized from amino acids. As minerals can set the redox state of geochemical environments, they also provide the reducing energy necessary for the construction of life precursors such as amino acids. Minerals of different kinds have therefore been invoked in many models for the origin of life. (See Plate 3.)

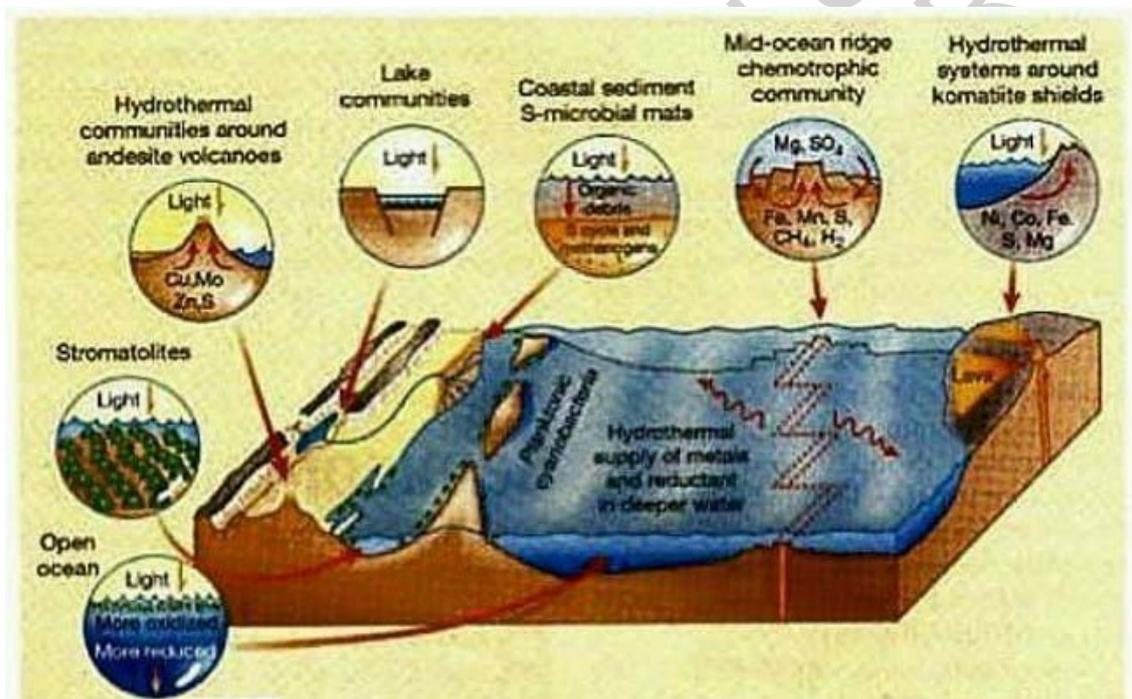


Plate 3. A map of Archaean ecology: places where early life flourished. Among such settings are mid-ocean ridges. New findings also point to deep-water hydrothermal systems as habitats for life. The atmosphere at this time would have been rich in carbon dioxide and nitrogen, with minor amounts of, for example, methane. Source: Nisbet (2000).

## 2.2. Bioremnants as Fingerprints or Biomarkers

Some sedimentary rocks that are almost 4 billion years old contain traces of organic molecules, derived from specific compounds in living organisms trapped in sediments at the time of its deposition. If the provenance of these compounds is interpreted correctly, they can provide information about the ancient environment. Intact fossilized organisms

themselves, seen with the naked eye or a microscope, can also provide such information. As a rule of thumb, however, the older a sedimentary rock the fewer the fossils that it may contain. Organic molecules therefore provide our only remaining opportunity to study this early period. These organic molecules (for example hopanes, triterpenes) are extremely resistant to diagenetic alteration, and can be specific enough to act as fingerprints for different organisms. First referred to as “chemfossils” by Eglinton, they are now more commonly called *biomarkers*.

The syllable *bio* in biogeochemistry most often refers to microbiological phenomena. As an example, microbial biogeochemists apply the disciplines of microbiology and geochemistry in the interpretation of biomarkers left behind in ancient sedimentary rock by microorganisms present at the time of its formation. Like most other scientists looking back into the past, biogeochemists base their investigations on a *uniformitarian* approach. The term uniformitarianism was coined by Lyell in his publication *Principles of Geology* (1830). He defined it on the basis that “the present is the key to the past.” In interpreting the biogeochemistry of ancient sedimentary rocks, biogeochemists depend on results from studies of geochemical processes in modern sedimentary environments. It is assumed that microbes that lived in the Precambrian (1–4 Ga ago) acted in the same way that similar types do today.

Scientists who study organic paleochemists have generated information about biomarkers over the last three decades. Their study employs sophisticated analytical instruments that extract information from extremely small samples, 1 mg or less in size. At present, the significance of only a small number of biomarker compounds is understood. The source of the rest, and how they were formed, still remains to be unraveled. One example of possible proxies is derivatives of pigments like bacterial chlorophyll. These biomarkers can serve as indicators of eutrophic conditions, and high levels of hydrogen sulfide, in the photic zone of oceans. Algal lipids may serve as an indicator of paleotemperature. This inference is drawn from the ratio between two alkenones ( $C_{37}$ ), which has become one ( $U_{37}^K$ ) of the international standards for paleotemperature during the latest glaciations. It has, in some cases, been proven more accurate and more reliable than the use of oxygen isotopes.

One major theme has been the study of stereochemistry in sedimentary organic compounds. The thermal history of a sedimentary rock can be examined by determining the extent to which biosynthetically introduced stereochemistry has been preserved within the biomarkers in that rock. Using this technique, the history of a basin’s subsidence can be reconstructed, and the “thermal maturity” of any petroleum source rock can be determined quickly and securely. It has become a very important technique in oil prospecting.

### **2.3. Microbes and the Ancient Earth**

Prokaryotic microorganisms have existed on our planet for almost 4 Ga, whereas eukaryotic microorganisms did not appear until about 2 Ga ago. Multicellular eukaryotic organisms (higher forms of life) did not appear on earth until about 1 Ga ago. Some spectacular forms of life have evolved from them in the last 700 million years, among which the dinosaurs in particular have attracted much popular interest.

Prokaryotic microorganisms are grouped within two domains: Bacteria and Archaea. These diverged from a common ancestor very early in prokaryotic evolution. Their members can be distinguished on the basis of cell anatomy and biochemistry. In both domains, physiological types include heterotrophs and autotrophs. Heterotrophs depend on organic carbon as their source of energy, and on assimilable carbon. Autotrophs derive the energy they need for energy-consuming reactions from the oxidation of reduced inorganic substances such as hydrogen (H<sub>2</sub>), reduced forms of sulfur, ferrous iron, nitrogen, and other substances, or from sunlight. Typical photosynthesizers depend on a form of chlorophyll to transduce radiant energy from sunlight into chemical energy, which is used to assimilate carbon dioxide and to do other physiological work. They have been found only among members of the domain Bacteria. Some Archaea can transduce radiant energy into chemical energy with a rhodopsin-like pigment, instead of chlorophyll, but this system is not coupled to carbon dioxide assimilation, and these microorganisms are therefore not autotrophs. The carbon source of all autotrophs is carbon dioxide.

Microorganisms can be found nearly everywhere on the earth's surface, and in the upper crust. They have survived all catastrophic events on earth over geologic time. They play an active role in all kinds of environmental processes. Several types are genetically adapted to live in very extreme types of environments. Some of these have been found living at temperatures as low as about -10 °C, or as high as about +120 °C; at salinities as low as 0‰, or as high as 230 ‰; at oxygen concentrations as low as 0 percent, or at the concentration found in normal air. Some microorganisms play a role in the formation of fossil fuels like peat, oil, and gas, and in the formation of some type of ores. The oldest known microbial fossil identified with certainty is 3.5 Ga old. The oldest known sedimentary rock on earth is 3.8 Ga old. It contains organic remains with a structure that some scientists interpret as having been derived from bacteria. The fossil record shows that microbes existed at a very early stage in the history of the earth, but it does not tell us anything about how they evolved, their activities, or their influence on geochemical processes.

One of the means of studying the influence of microorganisms on the geochemistry of the early earth is through examination of stable isotope ratios in the geological record. This record shows clear evidence of biological isotope fractionation, which began very early in earth's history. Study of this record leads to the conclusion that the cycles of carbon, sulfur, and oxygen were governed mainly by the biosphere over geological time. When microorganisms attack a molecule to extract energy, they have to break chemical bonds. In most cases the strength of the bond is dependent on the mass of the atoms forming the bond. The larger the mass, the stronger the binding forces. Different elements may exist as isotopes having different masses, because of the different numbers of neutrons in their nuclei. Some of these isotopes disintegrate spontaneously and are called *radioactive*, whereas other isotopes are stable. If stable isotopes are involved in metabolism then microorganisms preferentially attack the lighter of two stable isotopes, especially at suboptimal metabolic rates. For example, microbial transformation of an element such as sulfur from one redox state to another can lead to an enrichment of atoms with low mass (<sup>32</sup>S) in the reaction product, and an increased

number of atoms with higher mass ( $^{34}\text{S}$ ) in the unmetabolized residue. Such a process is termed isotope fractionation.

Carbon is stored in two main forms: as oxidized inorganic carbon, usually carbonate; and as organic carbon, which generally contains carbon in a reduced state. The isotopic  $^{13}\text{C}/^{12}\text{C}$  ratios of carbon ( $\delta^{13}\text{C}$ ) in the sedimentary record exhibit a difference between carbonate-carbon and organic carbon, with organic carbon being enriched in  $^{12}\text{C}$  by 20 to 30‰ on average. The organic carbon is richer in the lighter carbon because autotrophic bacteria discriminate against heavy carbon ( $^{13}\text{C}$ ) during carbon fixation. Schidlowsky found carbon isotope ratios in sedimentary rocks starting with the oldest known, which are 3.8 Ga old. These exhibited great variation, especially with respect to the carbonate data. Although the ratio display large variations, the average isotopic data from rocks younger than 3.5 Ga display a stable trend with a fractionation between inorganic and organic data sets, which is about  $-25\%$ . This has been taken as evidence that photoautotrophy was quantitatively the most important process of biological carbon fixation from 3.5 Ga, and possibly from 3.8 Ga. (See Figure 2.)

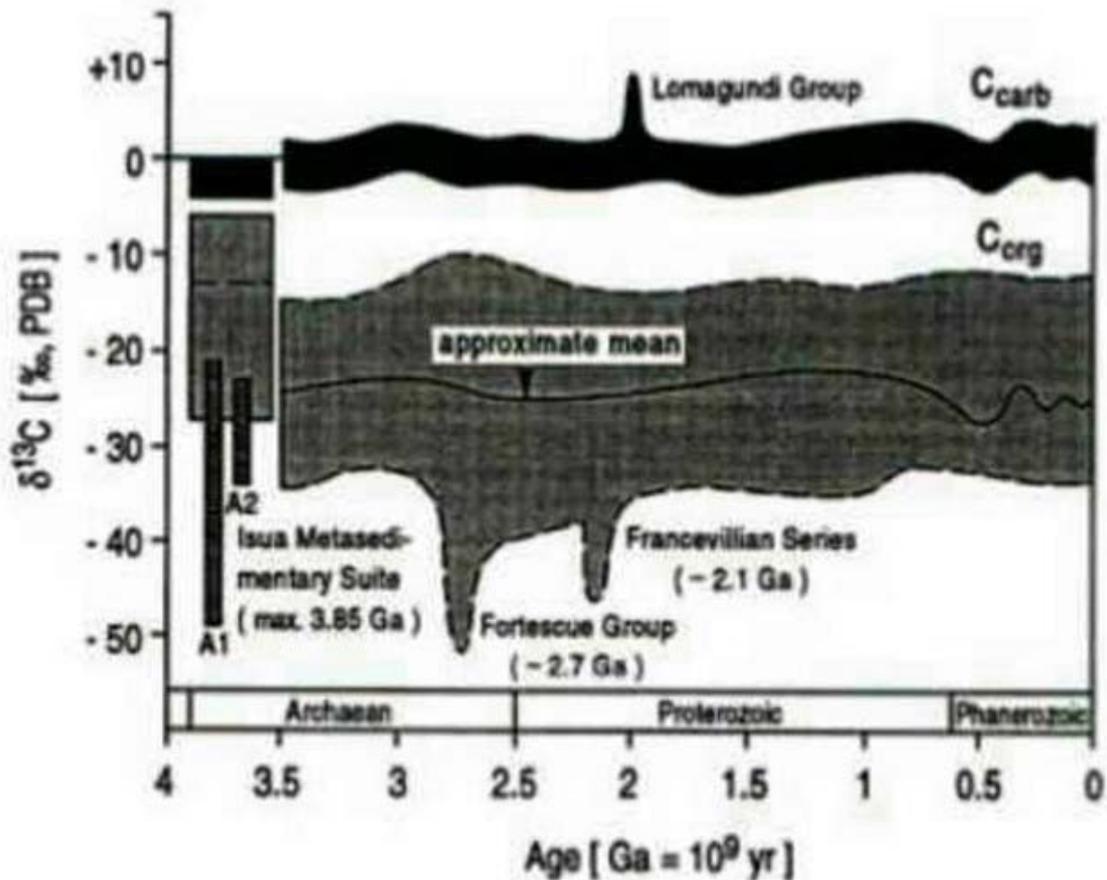


Figure 2. Isotope age functions of organic carbon ( $C_{org}$ ) and carbonate carbon ( $C_{carb}$ ). The negative spikes at 2.7 and 2.1 Ga indicate a large scale involvement of methane in the formation of respective kerogen precursors. The discontinuity at the beginning of the record is due to isotopic re-equilibrium of  $C_{org}$  and  $C_{carb}$  as a result of metamorphism. The average isotopic fractionation between the two components has remained fairly constant through geologic time.

The reason for this stable trend is that most of the organic carbon was oxidized and recycled back to carbon dioxide. Had all organic carbon formed by the biological systems been preserved and not been recycled to carbon dioxide, the two datasets would have deviated sharply with very high numbers for  $\delta^{13}C$  of inorganic carbon, as its amount of  $^{12}C$  would have been diminished by the biological activities.

Some stable isotope ratios can also serve as indicators of specific paleoenvironmental conditions. Stable isotope determination is presently the only available method for identifying biogeochemical phenomena that occurred more than 700 Ma ago, before microfossils became abundant.

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### Biographical Sketch

**Rolf Hallberg D.Sc.** is Professor at the Department of Geology and Geochemistry, Stockholm University. He is a fellow of the Royal Swedish Academy of Sciences. His interests emphasize biogeochemistry, especially with regard to the cycling of sulfur, global paleoclimate, interactions between metals and organic matter, bioleaching of sulfide ores, biomineralization, and soil restoration. He has nearly forty years' experience in the field of biogeochemistry.