BIOGEOCHEMICAL CYCLING OF MACRONUTRIENTS

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Contents

Summary

Life on Earth is composed of a number of elements. The major elements that support life are called macronutrients. They are hydrogen, carbon, oxygen, sulfur, nitrogen, phosphorus, calcium, sodium, potassium, and magnesium. Organisms exchange material (elements) and energy with the environment. That is, they incorporate and discharge elements. Plants produce organic compounds from simple inorganic compounds, carbon dioxide, and water. Animals eat plants for their sustenance. Dead bodies of plants and animals are decomposed by fungi and bacteria. This process is called the food chain. The elements are moved among the organisms through the food chain. The entire assembly of the organisms on Earth is called the biosphere.

Earth is divided into atmosphere, hydrosphere, lithosphere, and biosphere. The hydrosphere consists of oceans, lakes, and rivers. The lithosphere is the solid part of Earth, soil and the crust at the surface, and the mantle and core inside. All these spheres are made of chemical substances that are made of elements. Elements are constantly moving (cycling) through the atmosphere, hydrosphere, lithosphere, and biosphere. This movement is called biogeochemical cycling.

This chapter outlines the major biochemical processes, the distribution of elements in

the four spheres, the correlation between the elemental distribution in the organisms and the surroundings, the geochemical cycling, and the effects of the biosphere on the geochemical cycling. This chapter discusses the biogeochemical cycling at the global level of all the macronutrient elements (except for hydrogen) as quantitatively as possible. The next chapter discusses the biogeochemical cycling of other elements.

1. Introduction

Life on Earth supports itself using the resources available around it. No significant amount of carbon and other materials has been introduced to Earth from outside since life started here on Earth. Therefore, we should assume that the resources life has used and uses are only those available on this planet. There is an absolute limit to the quantities of the resources on Earth. (It is believed, however, that a significant amount of carbon came to the young Earth in the forms of meteorites, asteroids, and other debris, before life started on Earth.)

An organism is an open system. That is, the organism exchanges both energy and material with its surroundings. Life is sustained by assimilation of energy and material. The ultimate source of energy utilized by organisms on Earth is the Sun. Heat generated by radioactive material within Earth also contributes a little.

The entire community of organisms (i.e., the biosphere) is also open like an individual organism. It exchanges energy and material with its surroundings. In this manner, the biosphere is intimately interacting with its surroundings. The organisms in the biosphere are also interdependent on each other. An important interdependency among organisms is the so-called food chain. Simply put, plants and algae produce food from inorganic compounds using energy from the Sun, and we animals eat them to sustain our lives. Some microorganisms eat dead bodies of plants and animals, and they eventually decompose the organic compounds to simpler inorganic compounds.

The surroundings are conveniently divided into atmosphere, hydrosphere, and lithosphere. The hydrosphere consists of rivers, lakes, and oceans. The lithosphere can further be subdivided into soil, crust, and the inner solid (mantle and core) of Earth. Only the soil and the crust will be considered as the lithosphere in this article and the next, though the mantle and the core are involved in the cycling of elements over a very long geological time scale. The biogeochemical cycling of elements deals with the interactions between the biosphere and the surroundings in the form of cycling of each individual element through these different spheres. It is to be noted, however, that elements interact with each other and the cycling of one is influenced by other elements.

What will be discussed in this article and the next is the biogeochemical cycling of elements at the global level. The geochemical movements of elements at the local level such as a savanna area of Australia, Siberia tundra, a forest in Pennsylvania, the Black Sea, or your own backyard may not be exactly like those discussed in these articles. The situation in each of these special local segments of the globe needs separate treatment beyond the scope of these articles.

2. The Elemental Compositions of the Atmosphere, Hydrosphere, and Lithosphere

First let us take a look at the magnitudes of the constituents of Earth. Table 1 gives that data. It is pointed out here only that the biosphere (about 2 x 10^{16} kg as whole bodies including water) is miniscule compared to the surroundings: lithosphere, hydrosphere, and atmosphere (whose combined mass is 2.6 x 10^{22} kg). Yet, the biosphere contributes substantially to the geochemical cycling of certain elements, particularly that of carbon, oxygen, nitrogen, sulfur, and phosphorus. Geochemical cycling of other elements can also be influenced significantly by the biosphere in some segments of Earth. A single species, *Homo sapiens*, now contributes significantly to the geochemical cycling of many elements, as human civilization uses elements such as iron, nickel, lead, and others. This issue of the impact of human activities will be discussed briefly in Biogeochemical Cycling of Micronutrients and other Elements.

Constituent	**Mass (kg)**	**Flux (kg y^{-1})**
Total	5.976×10^{24}	
Core	1.881×10^{24}	
Mantle	4.068×10^{24}	
Lithosphere (continental and oceanic crust)	2.51×10^{22} *2 × 10^{22} continental crust* *7 × 10^{21} oceanic crust* *2 × 10^{21} sediments* *2 × 10^{17} soils*	2×10^{13} continental weathering
Hydrosphere (ocean and sea)	1.41×10^{21}	4×10^{16} river runoff 3.9×10^{17} precipitation 4.3×10^{17} evaporation
Atmosphere	5×10^{18}	
Biosphere	1.5×10^{16} living bodies 8.3×10^{14} living (as carbon)* 4.5×10^{15} dead (as carbon)*	4.8×10^{13} terrestrial* 4×10^{13} oceanic*

*, Flux of carbon in the biosphere is shown as primary production, or the amount of carbon sequestered by autotrophs from the lithosphere and atmosphere.
Values in italics are subdivisions of other values given. For instance, the value given for the mass of the continental crust is included in the total value for the lithosphere.

Table 1: Magnitudes of the constituents of Earth
Source publications include: Chameides, W.L. and Perdue, E.M. (1997), *Biogeochemical Cycles—A Computer Interactive Study of Earth System Science and Global Change*, 224 pp, Oxford, UK, Oxford University Press.

Next let us look at the overall distribution of elements as found (on average) in the current atmosphere, hydrosphere, and lithosphere. Table 2 gives a list of the components in the atmosphere, as currently found. Oxygen (O_2) is a crucial substance for the majority of living organisms on Earth. Nitrogen (N_2) is also a critical element, but it is not easily utilized as such by most of the organisms. Carbon dioxide is mainly consumed by photosynthesizing organisms, for instance, plants and algae, that convert carbon dioxide (CO_2) to carbohydrates (simplified as CH_2O; example: glucose ($C_6H_{12}O_6$)) which is utilized by all the other organisms as the energy source. The atmospheric content of carbon dioxide is increasing as a result of human activities. Otherwise, the atmospheric composition does not seem to have changed significantly over the past 200 Ma or so. The historical change of the oxygen content of the atmosphere will be discussed in the next article.

Compounds	**Formula**	**Concentration**	**Total mass (kg)**
Major constituents		(%)	
Nitrogen	N_2	78.084	3.87×10^{18}
Oxygen	O_2	20.946	1.19×10^{18}
Argon	Ar	0.934	6.59×10^{16}
Minor constituents		(ppm)	
Carbon dioxide	CO_2	360	2.8×10^{15}
Neon	Ne	18.2	6.49×10^{13}
Helium	He	5.24	3.70×10^{12}
Methane	CH_4	1.75	4.96×10^{12}
Krypton	Kr	1.14	1.69×10^{13}
Hydrogen	H_2	0.510	1.82×10^{11}
Nitrous oxide	N_2O	0.311	2.41×10^{12}
Xenon	Xe	0.087	2.02×10^{12}

Table 2: Global mean concentrations of atmospheric constituents
Source: Schlesinger W.H. (1997), *Biogeochemistry, An Analysis of Global Change*, 588 pp, San Diego, Academic Press.

The elemental compositions of contemporary seawater and Earth's crust are shown in Figure 1. This figure is not meant to imply any correlation between the two sets of data, and the correlation, if any, is a complicated issue. However, it may be pointed out that some elements in higher oxidation states such as iron (+3, III), titanium (+4, IV), and aluminum (+3, III) tend to be present in low concentrations in contemporary seawaters, as indicated by line (B) in the figure. The reason is that the elements in high oxidation states tend to form insoluble hydroxides in seawater. The elements that usually exist in the II (+2) oxidation state are clustered along line (A). This implies that the elemental composition of seawater is commensurate with that in Earth's crust in the case of these elements. An implication is that the iron content of seawater on ancient Earth (before about 2 000 Ma) might have been much higher than it is in today's seawater. This is because the atmosphere is supposed to have been anoxic in that earlier time, and hence the iron must have been in the form of Fe(II).

(In this article oxidation states are expressed by Roman numerals as illustrated. See Biogeochemical Cycling of Micronutrients and Other Elements for a discussion on this implication.)

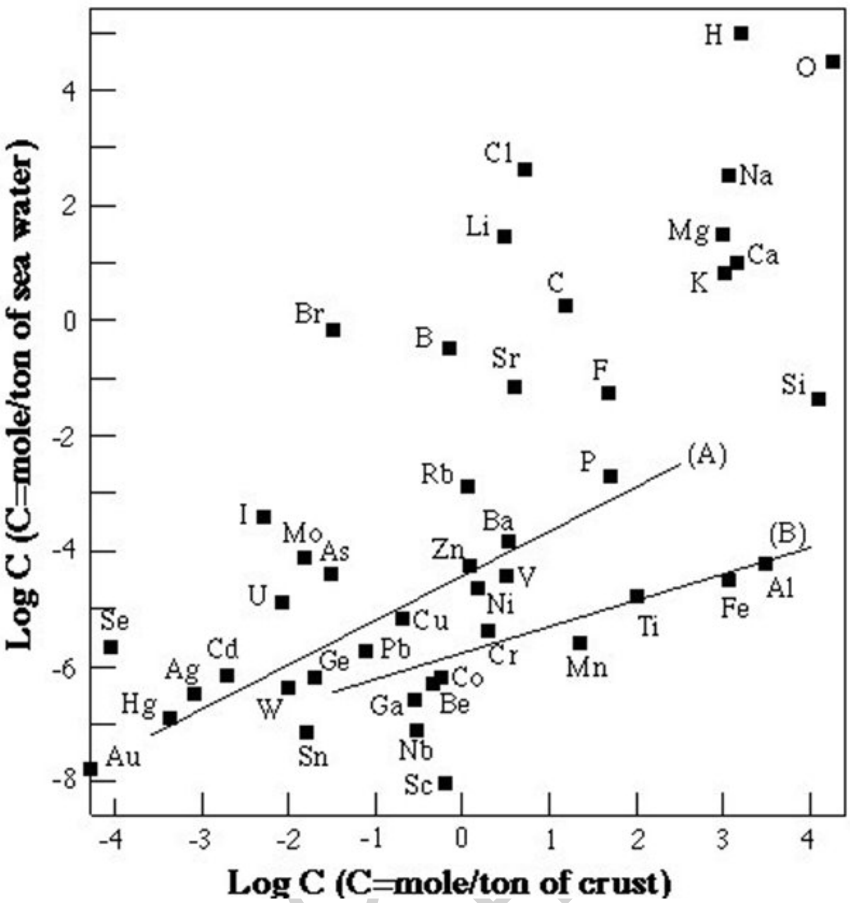

Figure 1. Elemental distribution in Earth's crust and seawater, measured in moles of atoms. Data for Earth's crust are taken from Mason, B. (1966), *Principles of Geochemistry*, 3rd ed., 329 pp, New York, John Wiley and Sons. Data for seawater from Henderson P. (1982), *Inorganic Geochemistry*, 353 pp, London, Pergamon Press.

Other elements including alkali metals (I), alkaline earth metals (II), halogens (-I), sulfur, and molybdenum are rather concentrated in the seawater relative to their abundance in Earth's crust. The ions of the first three categories have high solubility in water. Sulfur and molybdenum are in the form of oxyanion (SO_4^{2-} and MoO_4^{2-}) which is quite soluble. These are the reasons for the relatively high abundance of these elements in seawater. (It is noted that an Arabic numeral, for example, 2-, is used to indicate the electric charge of the entity, as in MoO_4^{2-}, while the oxidation state of molybdenum here is expressed with a Roman numeral, Mo(VI).)

3. Life's Need for Elements—Logic of Life on Earth

Living organisms require a number of elements; the exact number has not been determined and varies slightly from one species to another. However, the chemistry of the major portion of living systems is very consistent. Any living system requires: (a) energy or chemical substances that can be converted to energy, (b) building material, and (c) genetic material. The energy source in all organisms is a compound called adenosine triphosphate (ATP).
There are essentially two different types of organisms on Earth. One kind of organisms

can produce carbohydrates from inorganic compounds alone, i.e., carbon dioxide (CO_2) and water (H_2O), and can produce also the energy carrier ATP. These organisms are called autotrophs. One class of such organisms uses sunlight for the production of carbohydrates and ATP. That is, they conduct photosynthesis, and these are called photoautotrophs. Plants with green leaves are examples of photoautotrophs. The other major photoautotrophs are algae and blue-green algae (cyanobacteria). By the way, a few photoautotrophs use hydrogen sulfide (instead of water) as the source of hydrogen. These organisms are called sulfur bacteria.

Another group of organisms obtains energy for the production of carbohydrates and ATP from oxidation of such compounds as ammonia (NH_3) and iron (Fe(II)). They are called chemoautotrophs. A variety of chemoautotrophs are known and they are playing important roles in the biogeochemical cycling of elements.

The other kind of organisms are heterotrophs. They include animals, fungi, and some bacteria. These organisms cannot produce their own food (carbohydrates) from inorganic compounds, and hence have to eat autotrophs or their derivatives (other heterotrophs). They can be further divided into herbivores (plant eaters), carnivores (meat eaters), omnivores (mixed food eaters), and decomposers.

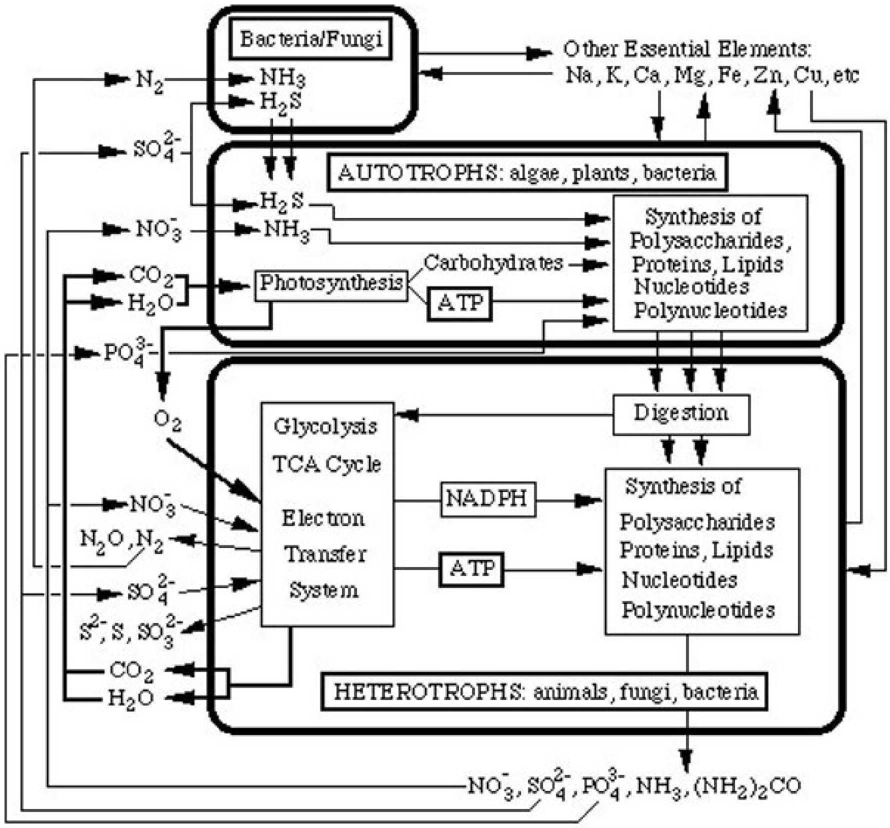

Figure 2: Biochemical logic of life on Earth

Source: Ochiai, E-I. (1997), Global metabolism of elements. *J. Chemical Education*, **74**, 926–930.

The major chemical compounds and biochemical reactions involved in the functioning of these organisms can be depicted in a single diagram (Figure 2). Carbohydrates are the immediate product of photosynthesis (shown in the middle portion of the diagram), but plants (and other autotrophs) produce from carbohydrates other crucial organic compounds such as proteins and nucleic acids (plus minor compounds such as vitamins). Plants are eaten by animals, which metabolize the contents of plants. In the process the animals produce energy (ATP) and the necessary building chemicals. The metabolic processes in the heterotrophs are shown in the bottom half of the diagram. The diagram omits an important group of organisms: chemoautotrophs. This omission is made only because the inclusion of such a group will complicate the diagram.

The left half of the diagram shows the processes characterized as oxidation and/or reduction reactions. Photosynthesis is a kind of reduction reaction (carbon dioxide (CO_2) is reduced to carbohydrates: CH_2O in short). Nitrogen (N_2) (and or nitrate (NO_3^-)) needs to be reduced to ammonia (NH_3) in order for the nitrogen to be utilized by organisms. Likewise sulfate (SO_4^{2-}) has to be reduced for some uses. Carbohydrates are oxidized in heterotrophs and the energy released is converted into the form of ATP. This process is called respiration. Respiration also takes place even in plants and algae when they are not producing energy (ATP) by photosynthesis (i.e., during the night). The right half of the diagram represents the processes of producing the building material for the body and the genetic material.

The other point that this diagram shows is that all the elements involved are circulated among organisms and also through the surroundings. The most important one is that of carbon. CO_2 is used (along with water) by plants and is converted into carbohydrates (CH_2O) which are then taken up by animals and oxidized back to CO_2. Oxygen (O_2) is produced as a byproduct in the photosynthesis of plants, and is consumed by animals (and other aerobes, or oxygen respiring organisms) to oxidize their food. Other elements also are ingested by organisms and released back into the surroundings. Such important elements include nitrogen (N), sulfur (S), phosphorus (P), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), and so forth (the biologically essential elements). Therefore the biosphere functions as an engine to move various elements and contributes to the geochemical cycling of the elements.

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Bibliography

Chameides, W.L. and Perdue E.M. (1997), Biogeochemical Cycles—A Computer-Interactive Study of Earth System Science and Global Change, 224 pp, Oxford, UK, Oxford University Press. [This provides a useful summary of data of cycling of elements (C, N, O, S, and P).]

Ehrlich, P.R., Ehrlich, A.H., and Holden, J.P. (1977), *Ecoscience—Population, Resources, Environment*, 1051 pp, San Franciscov W.H. Freeman and Co. [This is one of the most comprehensive reference for the topic of environment; see especially chapter 3, on nutrient cycles.]

Ochia, E-I. (1997) , Global Metabolism of Elements. *Journal of Chemical Education* **74**, 926–930. [The format of biogeochemical cycling diagram used in this chapter is taken from this paper.]

Scientific American. (1970), The Biosphere, September 1970 Special Issue, 266 pp. [This entire issue is devoted to the cycling of the important elements: C, N, O, S, and P.]

Scientific American. (1983), The Dynamic Earth, September 1983 Special Issue, 201 pp. [This issue gives a number of articles pertinent to the cycling of elements on the global scale; in particular the chapter "The Biosphere" by Cloud P. is useful.]

Schlesinger W.H. (1997), *Biogeochemistry—An Analysis of Global Change*, second edition, 588 pp, New York, Academic Press. [This modern textbook provides detailed information on the elemental cycling in ecological systems such as land, freshwater, wetlands, rivers, estuaries, and oceans.]

Trudinger, P.A. and Swaine, D.J., ed. (1979), Biogeochemical Cycling of Mineral-forming Elements, 612 pp, Amsterdam, Elsevier. [This is the most authoritative account of the cycling of some elements.]

Westbroek, P. (1991), *Life as a Geological Force—Dynamics of the Earth*, 240 pp, New York, W. Norton and Co. [This is an interesting little book that emphasizes the importance of Emiliania.]

Biographical Sketch

Ochiai, E-I., *(emeritus)* is a native of Japan, graduated from a Japanese high school, and obtained all his degrees (BS, MS, and Ph.D.) from the University of Tokyo. His undergraduate training was in applied chemistry, and his M.S. and Ph.D. were in chemistry. His research interest was first in homogeneous catalysis by metal complexes, and later shifted to biological catalysts: enzymes that are dependent on metallic elements. His research efforts on these kinds of issues have culminated in the interdisciplinary research area of bioinorganic chemistry. Ochiai has contributed to the development of the field by publishing original papers as well as several reference books on the subject. His interest has expanded to include all phenomena associated with interactions between biological systems and inorganic elements, and inevitably has come to encompass geological aspects as well. He is also interested in the origin and evolution of life, particularly the bioinorganic aspects, i.e., how the inorganic environment affected the emergence and evolution of organisms. His other research interests include nonlinear phenomena. He has taught at the University of Tokyo, the University of British Columbia, the University of Maryland, the University of Toronto, and Juniata College (since 1981). He also spent some time at the University of Umea (Sweden) and the University of Stockholm.