BIOGEOCHEMICAL CYCLING OF MICRONUTRIENTS AND OTHER ELEMENTS

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Summary

The biogeochemical cycling of several elements, essential or toxic, is discussed. The reader is referred to Biogeochemical Cycling of Macronutrients for the significance of biogeochemical cycling of elements. Included in the discussion in this article are micronutrients: silicon, iron, manganese, copper, and zinc; and toxic elements: mercury, lead, and arsenic. The biogeochemical cycling of these elements is, perhaps, representative of all other elements, and hence suggests the general schemes for biogeochemical cycling of other elements. Quantitative data are scarce, and only very rough estimates can be given.

The dynamic aspects of elemental distribution (biogeochemical cycling) have changed over geological time since Earth's formation. The major causes for the change were the emergence of life and the subsequent production of free oxygen by photosynthetic organisms. This article includes a brief survey on how these changes have affected the biogeochemical cycling of elements.

Since the Industrial Revolution, humankind has been using an increasingly larger amount of material. Hence the human (anthropogenic) contribution to the cycling of

elements has become significant and perhaps has started to disrupt the previously balanced state of the cycling of elements. This disruption has been manifested in many situations including the increase of the greenhouse gases and incidences of pollution by toxic elements.

1. Introduction

All the elements that are naturally present on Earth are very likely present in all the organisms including humans. The reason for this is that an organism is an open system. However, some elements are present at such a low level that, at this writing (2002), current (and perhaps even the more sophisticated of the future) techniques may not be able to detect them. Some of the more significant elements other than those dealt with in the previous article will be discussed in this article. Included are silicon, iron, manganese, copper, zinc, mercury, lead, and arsenic. The first five elements (silicon, iron, manganese, copper, and zinc) are essential to a wide variety of organisms, and the last three (mercury, lead, and arsenic) are toxic. In addition, two topics will be discussed; one is the historical change of the biogeochemical cycling of elements over the entire period of Earth's history, and the other is the impact of human activities on the biogeochemical cycling of elements.

2. Biogeochemical Cycling of Silicon

Silicon is one of the most abundant elements on Earth. Hence it is also found universally in organisms. However, it turned out that the quantity of silicon tends to vary widely from one individual to another, suggesting that silicon ingestion depends heavily on diet and environment. The biological functions of silicon in the human body have not been clearly delineated, though there is every indication that it is essential to human lives and many other organisms. Silicon in the human body is found bound mostly with connective tissues. It has been suggested that silicic acid $(Si(OH)_4)$ binds covalently with muco-polysaccharides (such as chondroitin-6-sulfate and hyaluronic acid) of connective tissues. Silicon has also been found bound with collagen, a protein in connective tissues. Silicon is also bound with pectin in citrus fruits and alginic acid in plants. A suggestion has been made that silicic acid cross-links these polymers and thus maintains the structure and integrity of connective tissues.

Some land and oceanic organisms have an absolute requirement for silicon. Silicon is often deposited as an amorphous silica gel in the shoots of vascular plants, particularly grasses, bamboo, rice, barley, oats and horsetails. On a dry-weight basis, the silica content of these plants ranges from 3% to 5%, though values higher than 20% have been reported for some grasses. A horsetail, *Equisetum arvense*, collapses when grown on a silicon-free nutrient solution but is normally erect when sodium metasilicate is added to the growth medium. Silicic acid $(Si(OH)_4)$ dissolved in water in the soil is absorbed by plant roots and then carried by the transpiring system.

The minute oceanic algae, diatoms, and zooplanktons called radioralia, are the most important in terms of silicon biogeochemical cycling. The cell walls of photosynthetic diatoms consist of siliceous frustule (box) in an organic coating. An enormous number of diatom species are known, each of which produces a varied, intricate, often

beautifully crafted silicon box (frustule). One cell is in a box and another in its lid. The silica is similar to silica gel ($SiO_2 \cdot nH_2O$). The protein of the coating seems to provide nucleation sites for silicate to crystallize. Many radiorialans have shells made of silica that are beautifully crafted like a work of art. Sponges use either calcium carbonate or silica crystals to increase the rigidity of their bodies. The dead bodies of these organisms sink to the bottom of the ocean quickly. In due course the organic compounds are mostly decomposed and lost. The siliceous ooze thus formed has been estimated to cover a large area of the ocean bottom (38 million km^2, about 10% of the ocean bottom) in the temperate to cold seas. Such siliceous ooze is believed to be the origin of non-clastic siliceous sediments, cherts. Because of the biological activity, the silicon content in the ocean surface is virtually zero, though the overall average silicon content of the seawater is about 2 μg g^{-1}(ppm).
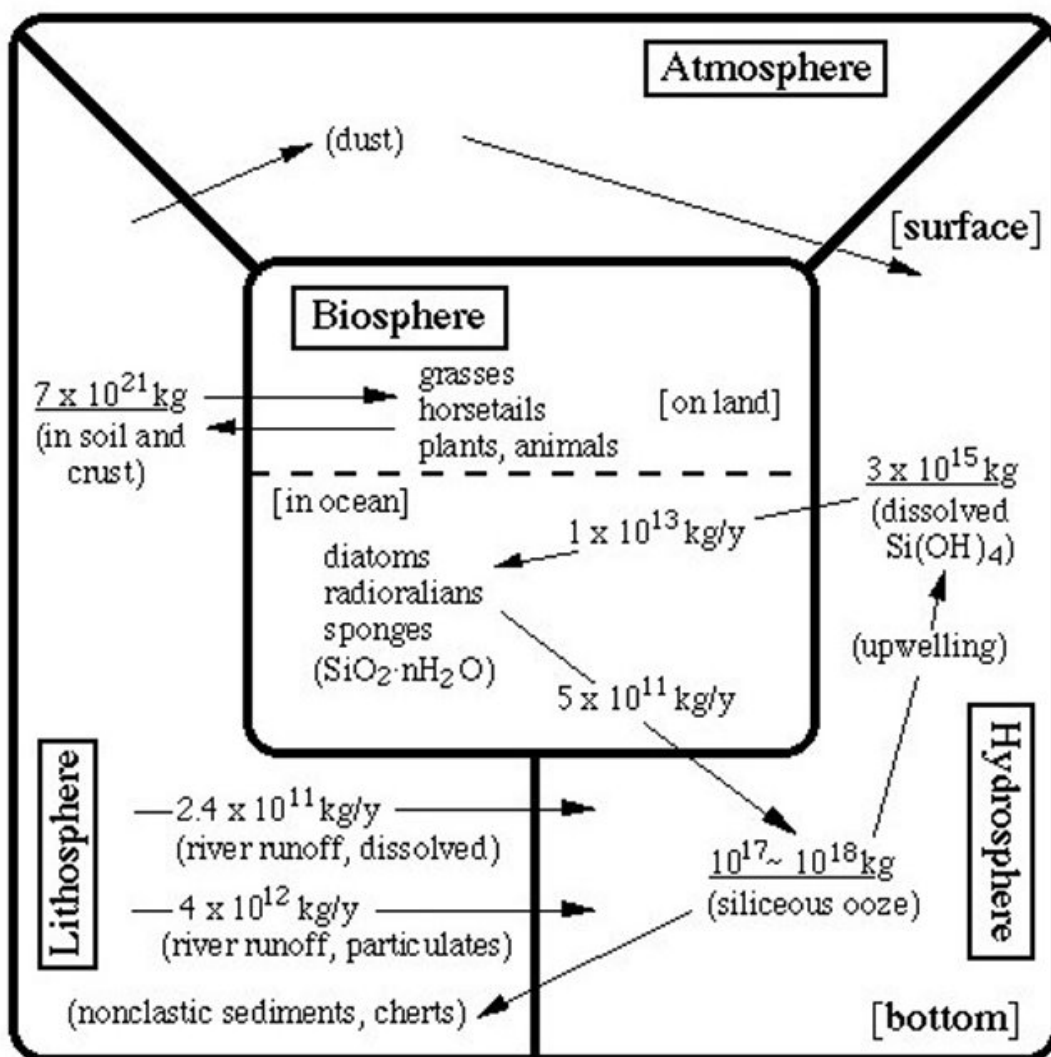

Figure 1: The biogeochemical cycling of silicon
See the note below (2.1) for an explanation.

The biogeochemical cycling of silicon is outlined in Figure 1. The major inputs of silicon to the ocean are river runoff (at a rate of 4.2 x 10^{12} kg y^{-1} total), upwelling, and

transportation of dust by wind. The particulate materials transported by rivers and wind form clastic rocks such as sandstone, or mud (clays that contains silicates) turns into shale. The major chemical species in the ocean is silicic acid ($HSiO(OH)_3$ and its dissociated form $SiO(OH)_3^-$). The total amount of dissolved silicon in the ocean can be estimated at 3×10^{15} kg, assuming a concentration of 2 μg g^{-1}. The total amount of silicon in the ooze at the ocean bottom is difficult to estimate. The value in Figure 1 is simply an indication. No estimate can be made for the quantities of silicon in living organisms, as they are varied so much. In any case, silicon is not an element that limits the growth of most organisms. The growth and number of diatoms, however, are regulated by the availability of silicon in the ocean surface.

2.1. Notes on the Diagrams of the Biogeochemical Cycling of Elements

The format of the diagrams (Figures 1–7): The entire space is divided into four spheres: the biosphere (at the center) and the atmosphere, hydrosphere, and lithosphere surrounding it. The total quantity of an element in a sphere (e.g., the lithosphere) is given in kg and the number is underlined. The rate of transfer (flux or flow) from a sphere to another is given in terms of kg per year (kg y^{-1}) and the value is inserted in an arrow showing the direction of transfer. Some major chemical forms of elements (i.e., minerals, chemical compounds, etc.) are also indicated, if appropriate. Human, or anthropogenic, activities now also move some elements at significant rates. An anthropogenic transference is indicated by a dashed line that goes through the biosphere.

The quantity of an element: The quantity of an element is given as the mass of the element contained in all the compounds containing it. It is very difficult to estimate the quantity of an element in the biosphere. The best studied is carbon (C) because the carbon is the major constituent of organisms. Yet estimates by various researchers do not quite agree with each other. The values used in this article are those that this author deems to be reasonable based on many literature values for carbon. The estimates for other elements are much less accurate, but can be considered accurate within (plus or minus) one order of magnitude.

The rate of transfer (flux or flow): This estimate is also very difficult for both the natural and the anthropogenic transfer. Some data are provided by literature as indicated in the tables and the captions for figures, but others are estimates by this author, as explained in the next paragraph.

Estimation: No estimates of the quantities and fluxes were available in the literature for many of the elements dealt with here. Estimates were based on known data about the elemental composition of river water, seawater, Earth's crust, and some representative organisms, and the total quantities of the Earth's crust, seawater, the biosphere, river flow, and annual gross primary production. Other simplifying assumptions are (a) that the organic composition of an organism can be approximated as CH_2O, and (b) that the water content of organisms is about 80% on average.

3. Biogeochemical Cycling of Iron

Iron is one of the most important micronutrients that are required by almost all organisms. Its biogeochemical cycling is outlined in Figure 2. Iron can exist in the form of either Fe(II) or Fe(III) under ordinary conditions. Fe(III), however, is relatively unstable in nonacidic media, precipitating out as $Fe(OH)_3$ (iron (III) hydroxide). Because of this property, iron presently on Earth's surface, being exposed to the oxidizing air, is usually in insoluble form, particularly $Fe(OH)_3$ or $FeO(OH)$. Iron, therefore, is relatively difficult for organisms to obtain. It is especially so for those at the bottom of food chains, for they have to extract it directly from the environment, from the insoluble forms such as $Fe(OH)_3$, Fe_2O_3, and FeS_2. (In this article oxidation states are expressed by Roman numerals.)
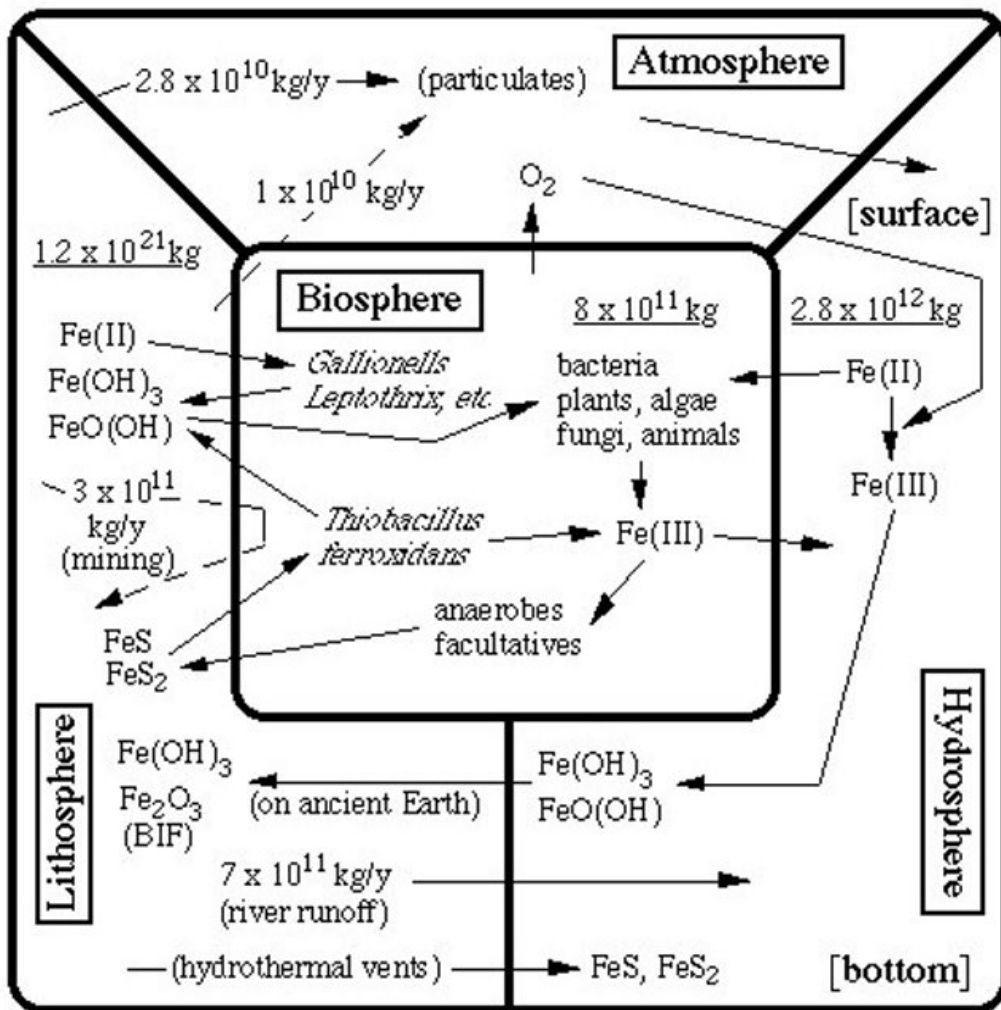

Figure 2: The biogeochemical cycling of iron

Some microorganisms, bacterial species such as *Bacillus* and *Aerobacter*, and fungi such as *Aspergillus*, *Neurospora*, and *Actinomyces*, invented strongly chelating agents called "siderophores". They excrete these chemical agents into the surroundings. Siderophores act as an iron-capturing devise but also act in certain cases as antibiotics against the other microorganisms in their vicinity. Several types of siderophores have been recognized. Siderophores of the cathechol or hydroxamate type bind Fe(III)

inordinately strongly, and the chelates are then ingested by the organism. Examples of siderophores include aerobactin, enterochelin, and rhodotoluic acid.

Plant roots secrete organic acids that solubilize and/or chelate Fe(III). Some plants such as rice produce specific iron-chelating agents like mugineic acid and avenic acid. Heterotrophs higher in the food chain can usually obtain enough iron from food. The total amount of iron contained in the organisms on Earth (in the biosphere) is on the order of 10^{12} kg, an estimate based on the mass of the biota and its mean iron content of 40 μg g^{-1}.

Iron is oxidized or reduced by specific organisms. The oxidation of Fe(II) by dioxygen can take place with or without the aid of organisms. The process, however, can be promoted by specific microorganisms. Some of these are chemoautotrophs and use the energy obtained to synthesize carbohydrates and ATP. *Thiobacillus ferroxidans* is the best-known bacterium that oxidizes Fe(II) enzymatically using O_2 as the ultimate electron acceptor. This oxidation (Fe(II) to Fe(III) by O_2) produces ΔG^0 (standard Gibbs free energy change) of -27 kJ mole–1 (at pH 3). The optimal pH for this oxidation seems to be quite acidic (pH 3–3.6). Because of the relatively small ΔG^0 value and the low efficiency, about 100 moles of Fe(II) must be oxidized to fix one mole of CO_2. *T. ferreoxidans* seems to contain both a sulfur-oxidizing system and an iron-oxidizing system. The oxidation of pyrite (FeS_2) contained in coal can take place slowly without organisms, but is catalyzed by the sulfur-oxidizing system: $2FeS_2 + 3O_2 + 2H_2O$ $\rightarrow 2Fe(II) + 4SO_4^{2-} + 4H^+$. The resulting Fe(II) is then oxidized by the iron-oxidizing system. The overall result is the production of sulfuric acid and Fe(III), and this is largely responsible for acid mine drainage, when coal contains pyrite. Other microorganisms that oxidize Fe(II) chemoautotrophically at an acidic pH include *Sulfolobus acidocaldarius*, *Leptospirillum ferreoxidans*, and *Metallogenium*.

Some bacteria, such as *Gallionella ferruginea*, oxidize at a neutral pH, forming limonite. Bacteria such as *Leptothrix*, *Crenothrix*, *Clonothrix*, *Arthrobacter siderocapsulata*, and *Lieskella bifida* form an iron-deposited sheath. Whether the iron oxidation occurs autotrophically is not well established for these organisms. The sheath may somehow promote the air-oxidation of Fe(II) and deposition of $Fe(OH)_3$ or it may simply promote precipitation of ferric hydroxide or oxides by adsorbing them on its surface.

The course of anaerobic metabolism of *Bacillus polymyxa* can be altered and the ferric iron is reduced when Fe(III) is added to the growth medium under anaerobic conditions. Other bacteria, including *Bacillus circulans*, *Escherichia freundii*, *Aerobacter aerogenes*, and *Paracolobactrum*, can also reduce Fe(III) to Fe(II) under anaerobic conditions. Some fungi have also been observed to reduce hematite (Fe_2O_3).

Fe(III) can be chemically reduced to FeS by H_2S formed by sulfate-reducing bacteria (*Desolfovibrio*), and S^{2-} also directly binds Fe(II) to FeS. Under certain circumstances, Fe(III) reduction can lead to the formation of pyrite FeS_2. The chemical reaction that takes place is: $2FeO(OH) + 3H_2S \rightarrow FeS + FeS_2 + 4H_2O$. Pyrite is the predominant species in relatively anoxic conditions.

By far the most significant contribution of the biosphere to iron geology is the so-called banded iron formation. It is believed that Fe(II) in the ancient marine environment was oxidized by dioxygen produced by photosynthesizing cyanobacteria and algae, leading to the precipitation of $Fe(OH)_3$ that turned to oxides. The layer structure of banded iron formation may be due to the seasonal change in the photosynthetic activities.

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Biographical Sketch

Ochiai, E-I. is a native of Japan, graduated from a Japanese high school, and obtained all his degrees (BS, MS, and PhD) from the University of Tokyo. His undergraduate training was in applied chemistry, and his M.S. and PhD 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.