

# The Distribution of Elements

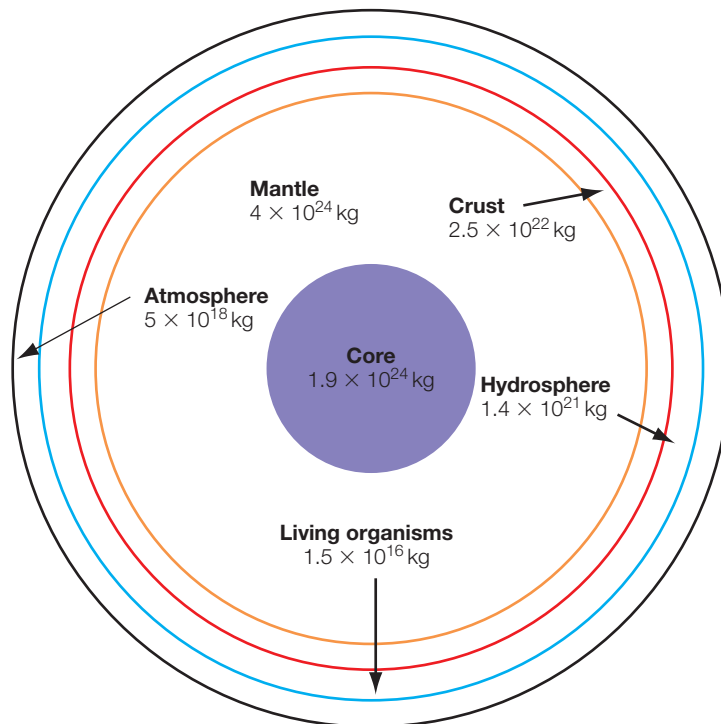
## 1.1. THE DISTRIBUTION OF ELEMENTS IN THE EARTH'S CRUST, SEAWATER, AND ORGANISMS

The material in the universe is composed of about 100 elements, which have been created through different nuclear reactions since the time of the Big Bang. The cosmic distribution of elements hence reflects these processes, and also the relative nuclear stability of different nuclides. The distribution of elements on Earth is significantly different from that in the overall universe. This fact reflects the way the Earth was formed, and the constraints due to its size. Against this background, organisms originated on Earth, and evolved through its long history.

It is convenient to regard the established Earth as consisting of several components: the core, mantle, crust, atmosphere, hydrosphere, and biosphere. The magnitudes of these components are shown in terms of their masses in Figure 1.1. The biosphere is tiny compared with the nonorganic components. The quantity of living organisms presented in this diagram may well be an underestimation, because the deep ocean is now recognized to harbor a significant proportion of living organisms, which have not been evaluated. In addition, the ecology of these organisms may be quite different from those on land and in shallow water.

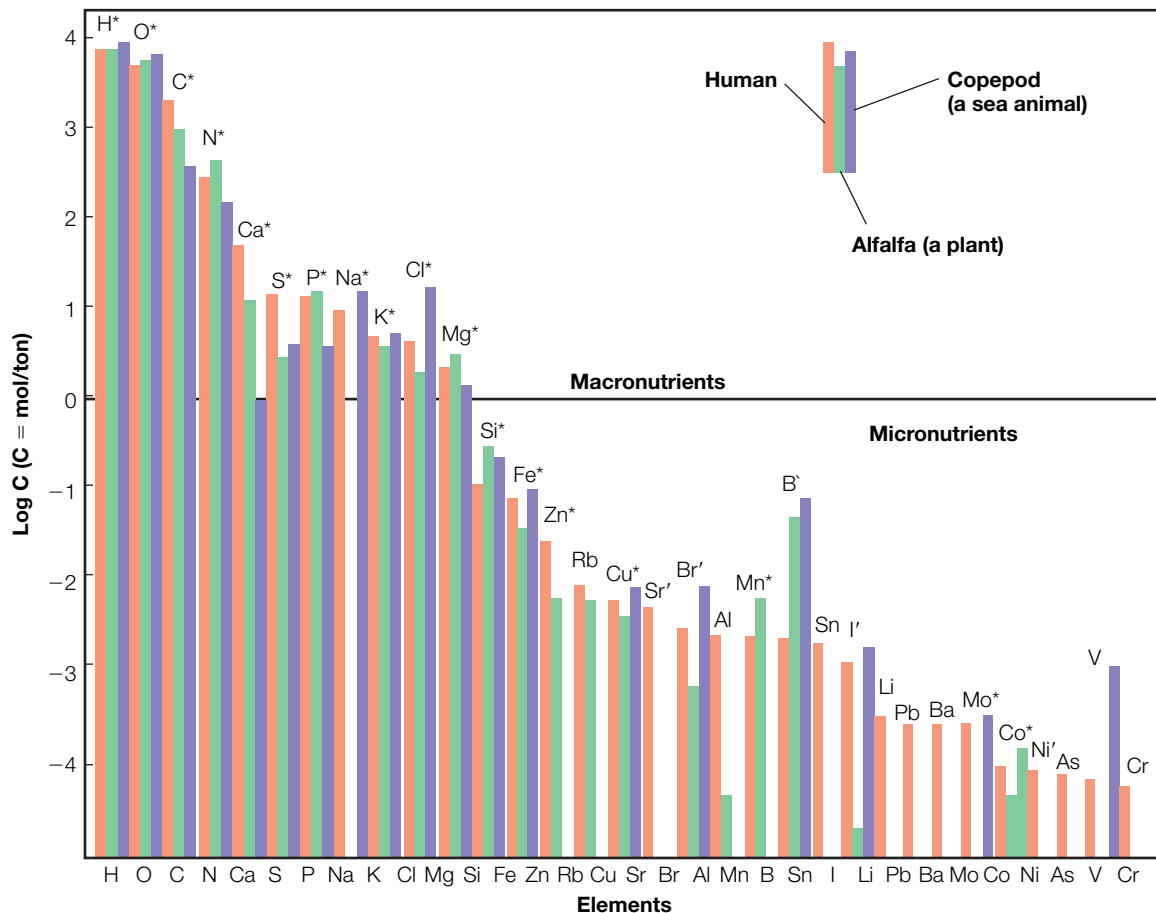
From a thermodynamic standpoint, an organism, whether unicellular or multicellular, is an open system. Therefore, it will exchange energy and material with its surroundings. An implication is that organisms will ingest, utilize, and hence contain all the elements present in their surroundings.

■ **Figure 1.1.** The magnitudes (in terms of mass) of components of the Earth.



A set of elemental compositions of the human body, alfalfa (plant) and copepod (seawater crustacean), is given in Figure 1.2. Of course, the elements are not distributed uniformly in the body. The data for humans in Figure 1.2 were obtained for an organ (the liver), collected from a number of different literature sources. It is also not expected that different individuals would show a numerically similar distribution of elements. Hence, such a set of data as presented in Figure 1.2 can be considered to represent average or “ballpark” figures. It is obvious that living organisms contain all kinds of elements in addition to the four elements that constitute the bulk of the organic compounds. Many of these elements are essential to the organisms, and their behaviors in the organisms are essentially the subject of bioinorganic chemical studies.

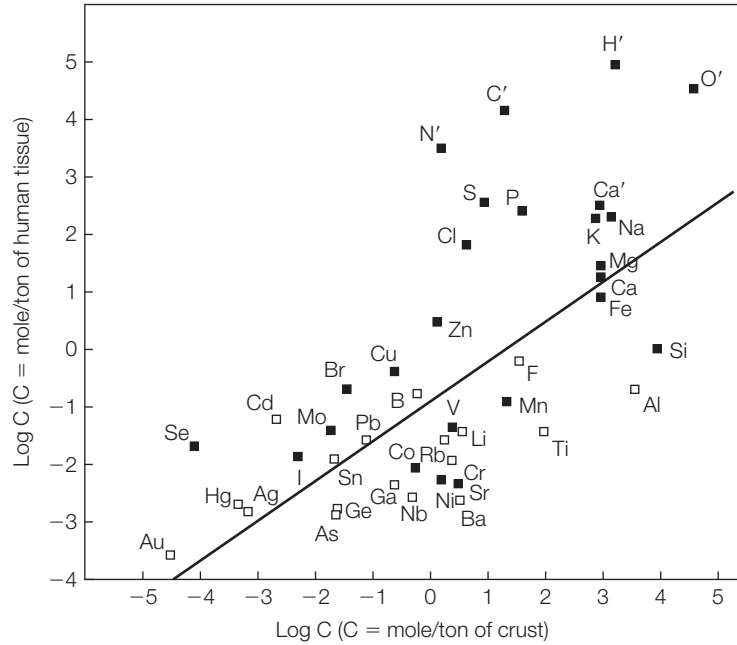
As an organism is an open system, its elemental composition may reflect that of its surroundings. It is expected that some elements are actively taken up by the body and others may simply enter inadvertently. Hence there is not necessarily a very high correlation between



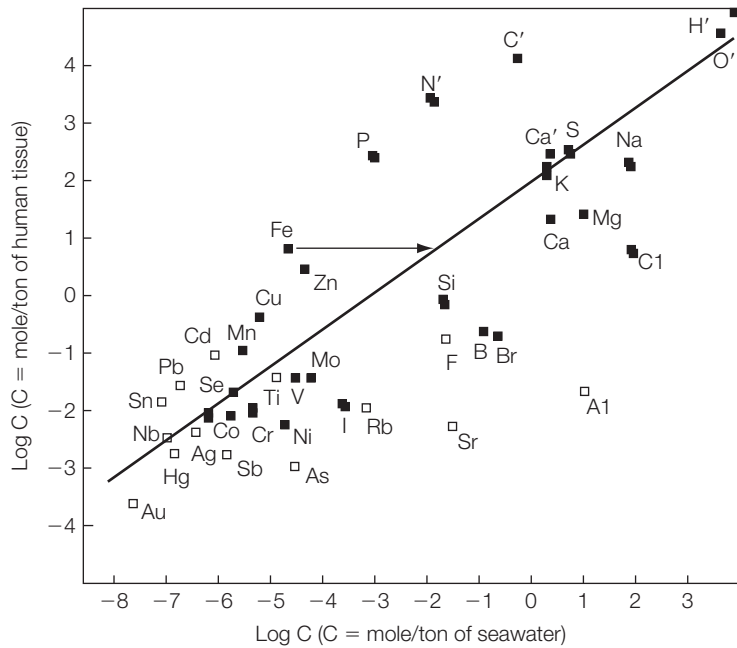
■ **Figure 1.2.** The elemental composition of representative organisms: human, copepod, and alfalfa (from Ochiai, 2004a).

the elemental composition in humans and that of the surroundings. The correlation between the elemental composition of the human body and that of the upper crust is shown in Figure 1.3, and that between the human body and the seawater on the current Earth is shown in Figure 1.4. The elemental composition of humans in these diagrams is that in the liver except for C, H, N, O, P, S, and Cl; the figures for the latter elements are those in the total body. In Figure 1.4, the estimated level of iron (as Fe(II)) in ancient seawater also is indicated. The correlation appears to be better with this corrected distribution in seawater. No matter how they are looked at, these figures imply that the living organisms are open systems that interact intimately with their environments.

■ **Figure 1.3.** The correlation of the elemental compositions of human tissue (liver) and of the crust (from Ochiai, 2004a).



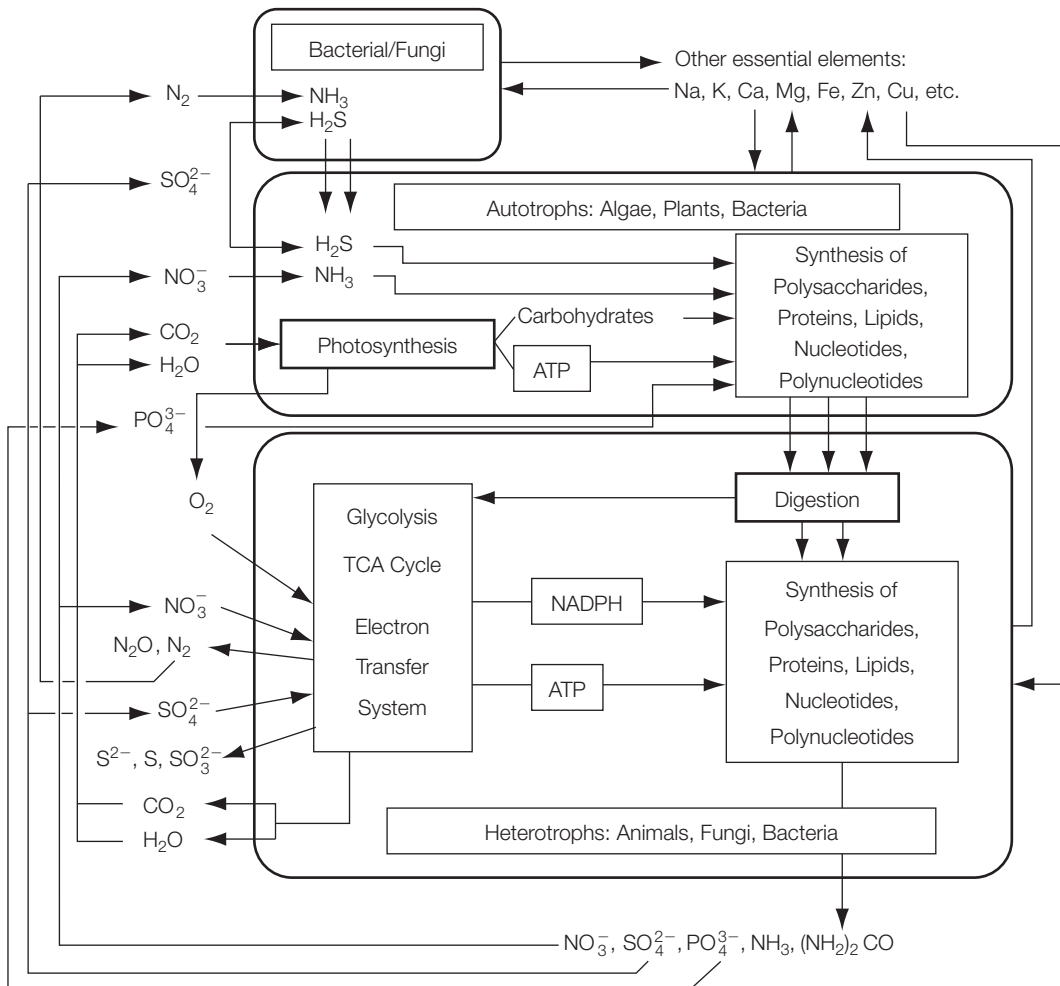
■ **Figure 1.4.** The correlation of the elemental compositions of human tissue (liver) and of seawater (on the present Earth); the position shown by an arrow represents an estimated concentration of iron in seawater on the anoxic Earth (from Ochiai, 2004a).



Whether iron was in the form of Fe(II) or Fe(III) in ancient seawater is not known, but it can be related to the atmospheric oxygen content at the time. This issue has not been settled among the geochemists. The most recent account of the controversy is found in *Science* (2005; 308, 1730–1732). The prevailing notion championed by Holland (1984) is that the atmosphere was quite low in free oxygen content from the beginning of the Earth (i.e., about 4.6 billion years ago) until about 2.2 to 2.4 billion years ago and then rose rapidly to the current level (i.e., 0.2). An alternative idea proposed (by Ohmoto and Felder, 1987; Ohmoto *et al.*, 2006) asserts that the oxygen content of the ancient atmosphere went up quickly in the early stage (4 billion years ago) to reach the current level, where it has remained throughout the rest of the Earth's history. If the atmosphere was anoxic as the prevailing hypothesis asserts, the iron in the ancient seawater was in the form of Fe(II), which is soluble, and consequently the iron content was much higher, perhaps as much as a thousand-fold more than that in today's seawater. This seems also to be consistent with the formation of the so-called BIF (banded iron formation) that is the predominant source of today's iron ores, and is believed to have formed in the period about 3.0 billion to 2.0 billion years ago, peaking at 2.2 to 2.0 billion years ago. If all these hypotheses are reasonable, then the iron content in living organisms is commensurate with the iron content in the ancient seawater (see Fig. 1.4). This issue will be discussed again later.

## 1.2. THE ENGINES THAT DRIVE THE BIOCHEMICAL CYCLING OF THE ELEMENTS

Living systems are open and exchange material and energy with their environments. The major life processes are: (a) production of reduced carbon compounds (mostly carbohydrates) from carbon dioxide and water (and hydrogen sulfide in some organisms) through photosynthesis and chemosynthesis, (b) oxidative metabolism of reduced carbon compounds to extract their chemical energy (production of ATP), and (c) metabolic processes that produce all the other necessary compounds; many such chemical reactions require negative free energy in the form of hydrolysis of ATP. In accomplishing these processes, living organisms make use of a number of other elements; these are partially shown in Figure 1.2. An element is taken up by an organism, incorporated, and eventually released back to its surroundings. That same element may be directly incorporated into another organism, in the predator–prey relationship. This includes decaying processes,

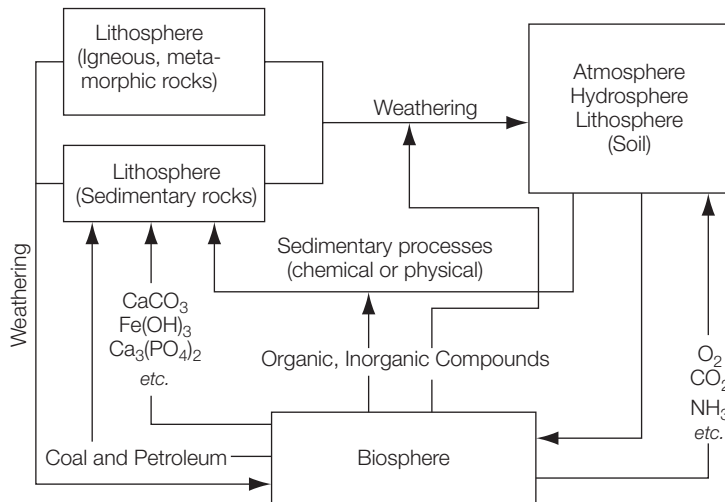


■ **Figure 1.5.** The life process on Earth, and the movement of elements associated with life (from Ochiai, 1992).

and is the generalized food chain. The life processes, being dynamic, thus move the elements. An outline of life processes on Earth and the movement of associated elements are given in Figure 1.5.

### 1.3. FLOW OF THE ELEMENTS—BIOGEOCHEMICAL CYCLING

The elements and their compounds are constantly being moved by natural nonbiological forces as well as biological systems. The major

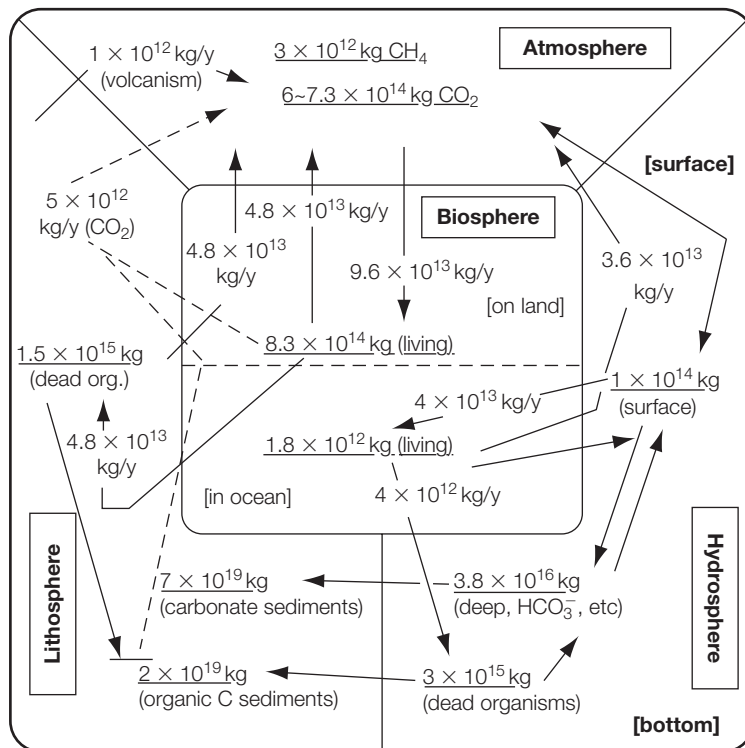


■ **Figure 1.6.** An outline of biogeochemical cycling of elements (from Ochiai, 1997).

processes are summarized in Figure 1.6. Weathering erodes rocks through physical and chemical processes. Weathered material is carried by streams to the oceans, and is laid down there, eventually being turned into sedimentary rocks. The eroded material can also be carried through the atmosphere by wind. Living organisms and the biosphere as a whole contribute to these processes. As suggested in Figure 1.6, some minerals are produced by organisms. Examples include calcite ( $\text{CaCO}_3$ ) and limonite ( $\text{Fe(OH)}_3 \cdot x\text{H}_2\text{O}$ ). The latter is formed as a result of chemoautotrophic process of such microorganisms as *Arthrobacter siderocapsulatus* and *Gallionella*. Some microorganisms help weathering processes; for example, some sulfur bacteria oxidize copper sulfide to leach out copper in a soluble form.

Hence elements are constantly being cycled throughout the entire Earth. This process partially involves the biosphere, and is called *biogeochemical cycling*. Figure 1.7 is a schematic representation of the biogeochemical cycling of the basic element, carbon (Ochiai, 2004). Carbon, in the form of carbon dioxide, is incorporated into organic compounds such as carbohydrates through photosynthesis in plants; they are then cycled among organisms through the food chain in the biosphere. When living organisms die, carbon will be deposited in the hydrosphere and lithosphere. It is also partially turned back to carbon dioxide in the atmosphere. Overall, it cycles among these four spheres of the Earth. The quantities underlined in the figure

■ **Figure 1.7.** The biogeochemical cycling of element carbon; the figure underlined represents the quantity (kg) of C currently present in each of the atmosphere, hydrosphere, lithosphere, and biosphere. The figure (kg/y) along a solid line (arrowed) is the flow of C; the figure (kg/y) along a dotted line (arrowed) represents the flow caused by anthropogenic activities (from Ochiai, 2004a).

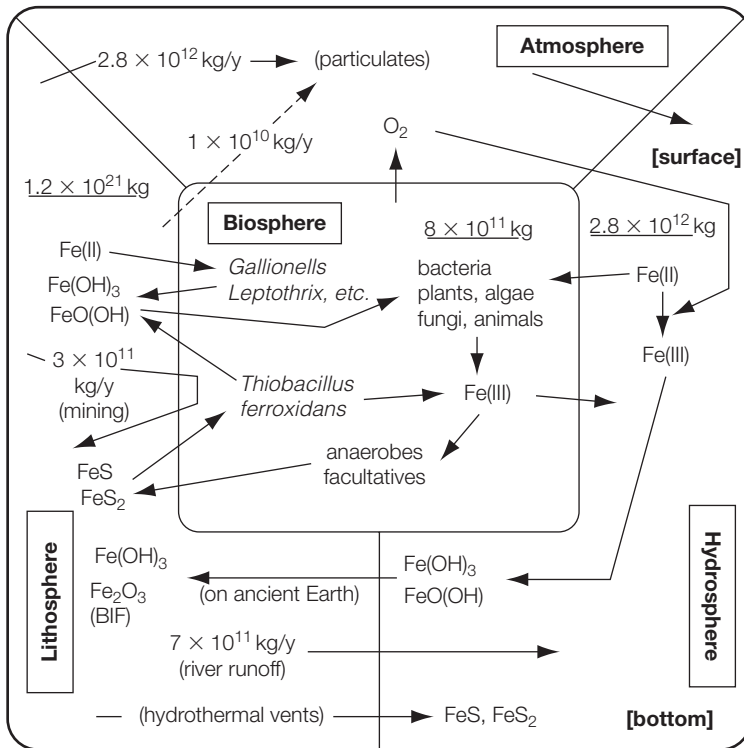


give the steady state quantities of carbon in various segments of the planet. Figure 1.7 also gives some quantitative estimates of the quantity and the flow (among different spheres) rate in units of kg/year. The broken lines indicate the anthropogenic flow of carbon and its compounds, particularly carbon dioxide. The combustion of fossil fuel (organic carbon sediment) is seen to be contributing significantly to the increase in the atmospheric carbon dioxide content.

The quantity and the flow rate of carbon in living and dead organisms (i.e., the biosphere) have been estimated (see, for example, Chameides and Perdue, 1997), though no very accurate evaluation is possible. The quantity and the flow rate of other elements in the biosphere are more difficult to estimate. Nonetheless, some estimates have been attempted. Similar diagrams of the biogeochemical cycling of nitrogen and sulfur are found in the Appendix (A.1 and A.2).

Similar estimates have been made for other elements (Ochiai, 1997, 2004b). Figure 1.8 depicts the biogeochemical cycling of iron.





■ **Figure 1.8.** The biogeochemical cycling of iron; figures underlined and figures along arrows represent quantities and flows as in Figure 1.7 (from Ochiai, 2004b).

Some other diagrams of the biogeochemical cycling are found in the Appendix (A.3 for Ca and A.4 for Hg), and more extensively in Ochiai (2004a, 2004b).

#### 1.4. HISTORICAL CHANGE IN THE BIOGEOCHEMICAL CYCLING OF ELEMENTS

The biogeochemical cycling described so far is that on the present Earth. The conditions on Earth have changed drastically since its formation. The major changes have been brought about by the emergence of life and also by the production of free oxygen by water-decomposing photosynthetic organisms. In addition, the geological changes involving the surface (plate tectonics, glaciation, etc.) and the interior of the Earth have influenced profoundly the geochemical cycling of elements over geological time. A brief survey will be given here on the historical change over geological time regarding the biogeochemical cycling of elements.

The elements were cycled by physical and chemical forces alone before the emergence of life. Sunlight and the internal energy source (such as heat created by radioactivity, gravity, and mantle movement) were the driving forces (as on the present Earth). It is believed that lightning and the bombardment of meteors and asteroids occurred more frequently and more severely on the ancient Earth, and that these events would also have contributed to the cycling of elements. As on the present Earth, water flow could dissolve material, and dislodge and carry particulate matter, and the wind transported material.

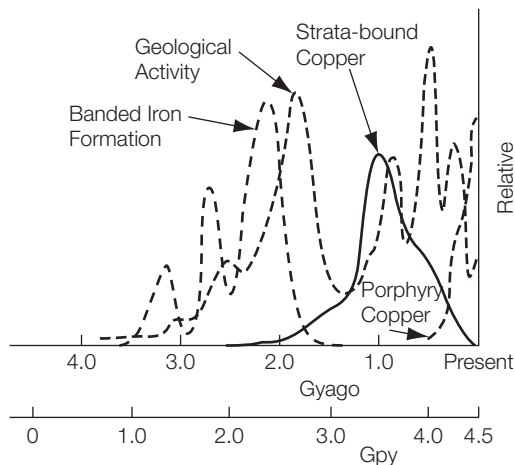
In the earliest period, the atmosphere contained a significant level of carbon dioxide (from volcanoes) but it was devoid of free oxygen (dioxygen). It is assumed that oxygen, being reactive, was consumed by reacting with oxidizable substances in the process of the formation of the Earth and the atmosphere, and that, as a result, little oxygen remained in free form in the atmosphere, according to the standard model (Holland, 1984).

Life is believed to have emerged under such an anoxic condition, and is now widely believed to have originated in hydrothermal vents at the ocean floor (see Ochiai, 1995b for several ideas on origin of life). Wächterhäuser and his coworkers have produced some experimental evidence for the formation of some crucial compounds such as pyruvate involving the Fe-Ni sulfide type of metallic compounds (Wächterhäuser, 2000). The original organisms thus are believed to be chemoautotrophs. There is some indication that such chemoautotrophs evolved as early as 3.5 billion years ago, based on S-isotopes fractionation data (Thamdrup, 2007; Philippot *et al.*, 2007).

The first water-decomposing photosynthetic organisms are believed to have been cyanobacteria (blue-green algae), and it has been suggested that they appeared about 3.0 to 2.5 billion years ago. Free oxygen ( $O_2$ ) is produced as a byproduct of the photosynthetic process:  $CO_2 + H_2O \rightarrow CH_2O$  (carbohydrates) +  $O_2$ . Photosynthetic oxygen caused no significant increase in the overall oxygen level in the atmosphere until about 2.2 to 2.4 billion years ago, because the oxygen was consumed by oxidizable material. A rise of the atmospheric oxygen now is believed to have started at 2.45 to 2.22 billion years ago (Bekker *et al.*, 2004; Kaufman *et al.*, 2007). The largest of such oxygen sinks was iron (Fe(II)) in the ocean. Iron is oxidized readily by oxygen and changes to Fe(III), which precipitates as iron hydroxide in seawater. Perhaps this was how the vast amount of iron

oxide sediments known as the Banded Iron Formation (BIF) formed. The formation of BIF sediments started about 3 billion years ago and ended about 1.8 billion years ago (see Fig. 1.9). The iron oxide ores formed thereafter are of different types. This suggests that the iron in the ocean was exhausted by then, and also a sufficient level of atmospheric oxygen had formed. This changed the conditions of formation of the iron oxide minerals.

Nitrogen is another essential element. Almost all nitrogen is present as the inert form  $N_2$  in the atmosphere. Ammonia is not and was not present at any significant level in the atmosphere at any time in the history of the Earth. Other usable forms (i.e., usable by organisms) are nitrite and nitrate,  $NO_2^-$  and  $NO_3^-$ . These compounds can be produced in lightning and other natural processes, but the quantity was never sufficient for organisms. Hence organisms must have developed their *nitrogen fixation* capability at earlier stages, perhaps from the very beginning of life. Nitrogen fixation (formation of ammonia) requires an enzyme, nitrogenase, which requires molybdenum. Molybdenum is and was relatively abundant in seawater in the form of molybdate  $MoO_4^{2-}$  even when the atmospheric oxygen level was very low. This assertion can be made on the basis of the reduction potential of  $MoO_4^{2-}$  and the potential ( $E_h$ ) of seawater as related to oxygen pressure (Ochiai, 1978b). This suggests that molybdenum was amply available to organisms from the earliest stage of their evolution.



■ **Figure 1.9.** The age profile of (a) geological (magmatic) activity, (b) banded iron formation (BIF), and (c) strata-bound (sedimentary) and porphyritic (igneous) copper ore (production in 1974) (from Ochiai, 1983, 2004b). ((a) and (b): adapted from Eichler, 1976; (c) adapted from Bowen and Gunatilaka, 1977.)

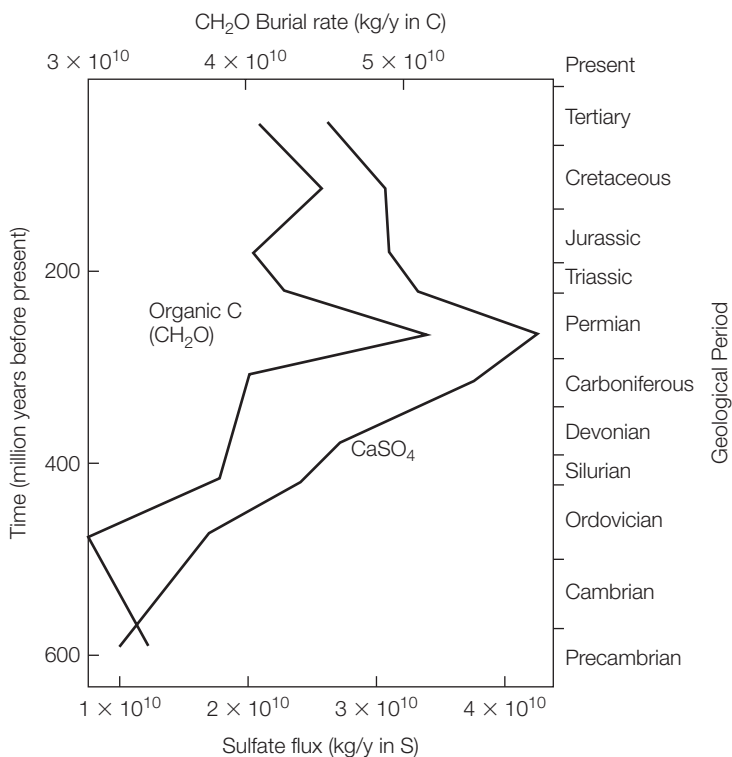
The free oxygen level in the atmosphere governs the oxidation-reduction potential in seawater and the potential governs the oxidation states of different elements. As in the case of iron, a given element can be in different oxidation states and hence will have different solubility in seawater. Therefore, the oxygen level in the atmosphere may determine the organisms' accessibility to the elements in seawater, as mentioned earlier with regard to molybdenum. If we knew the evolution of the atmospheric oxygen level throughout the history of the Earth, we would be able to deduce the change in the availability of different elements over geological time. The availability (i.e., solubility in seawater) influences the geochemical cycles involving the biosphere.

It may even have dictated biological evolution, because different species require different sets of elements. For example, an organism that requires copper for its survival would not have emerged when copper was not available to it. Copper has much higher reduction potentials (for  $\text{Cu(II)/Cu(I)}$ ,  $\text{Cu(II)/Cu(0)}$ ) than iron. This means that the metallic state of copper is much more stable relative to  $\text{Cu(II)}$  than that of metallic iron relative to  $\text{Fe(II)}$  or  $\text{Fe(III)}$ . In fact, copper is found often as copper metal in nature, whereas no significant amount of iron has been found in the metallic state in the Earth's upper crust. Copper, therefore, would not have become available to organisms in the soluble form of  $\text{Cu(II)}$  until the oxygen level in the atmosphere had become sufficiently high. Figure 1.9 shows the age profile of the quantity of strata-bound sedimentary copper ores. This suggests that organisms could not have been able to use copper before about 1.8 billion years ago; therefore those organisms that had appeared before that time did not use copper. Proteins and enzymes that depend on copper have been identified mostly in eukaryotic organisms, though they are found in a very few prokaryotes as well. Eukaryotes (i.e., higher organisms with a separate nucleus in cells) are believed to have emerged sometime between 2.0 and 1.5 billion years ago. This is consistent with the hypothesized evolution of  $\text{Cu(II)}$  availability. As far as copper geochemical cycling is concerned, the biosphere was not involved before about 1.8 billion years ago.

The same idea can be applied to all other elements, and employed to deduce the historical change of the biogeochemical cycles of elements over geological time (Ochiai, 1978a, 1983). To obtain a meaningful insight on this issue from such an analysis, however,

more detailed and definitive data on atmospheric oxygen and its change and geological activities are required. Unfortunately, these critical data are still lacking (see earlier).

A little more data are available for the more recent past; that is, the last 600 million years since the end of the Precambrian period. At the beginning of this period, atmospheric oxygen is estimated to have reached a few percent of the present level. It increased rapidly, reaching the present level 550 million years or so ago, and it seems to have remained steady since then. The data were isotope ratios of  $C^{13}/C^{12}$  and  $S^{34}/S^{32}$  of the rocks over this period of time. The significance of such data cannot be discussed here, but it suffices to note that they can indicate biological activities. From the isotopic data, Garrels and Lerman (1981) attempted to deduce the change in the rate of organic carbon burial and that of the formation of gypsum  $CaSO_4$  over a period of time, from 600 million years ago to the present. Their results are shown in Figure 1.10.



■ **Figure 1.10.** The change in the organic carbon burial rate and the gypsum formation rate over the last 600 million years. (After Garrels, R. M. and Lerman, A. 1981. Phanerozoic cycles of sedimentary carbon and sulfur. *Proc. Natl. Acad. Sci., USA* **78**, 4652–4656.) (Modified from Fig. 1.2 (p. 6) of Schlesinger, W. H. 1997. *Biogeochemistry*. Academic Press, San Diego.) (Ochiai, 2004b)

The figure clearly shows that the fluxes of organic carbon and gypsum formation were interrelated over this time period. That is, when more organic carbon was buried, more gypsum formed. When organic carbon is buried without being subjected to oxidation (respiration), the oxygen is not consumed and its level in the atmosphere would go up. The oxygen (unused by respiration) would then oxidize sulfide, particularly pyrite  $\text{FeS}_2$ , producing sulfate that would end up in gypsum. Hence the oxygen content would not go up as high as the burial of organic material would allow. These two processes, if coordinated as indicated by the figure, would control the level of the atmospheric oxygen. It is inferred that the net production rate of the organic carbon had not been quite matched, as on today's Earth, by the rate of consumption by the heterotrophs and its removal rate by burial, until about 200 million years ago.

It is interesting to note that a very large quantity of organic carbon was buried in the period about 300 to 200 million years ago (see Fig. 1.10). This is the period from which most of the coal originates. This suggests that the biosphere might have consisted of more producers (plants) than consumers (animals, fungi, and bacteria) in this period, compared to the present biosphere. Besides, somehow the environment was such that plants were rapidly buried in marsh during this period. A more recent data on the atmospheric  $\text{O}_2$  content (Berner *et al.*, 2007) shows a curve similar to that of Figure 1.10, with a maximum of about 30% of  $\text{O}_2$  content (as compared to about 22% in the current one) at around 280 million years ago.

## REVIEW QUESTIONS

1. Convert the masses of various portions on the Earth (core, mantle, crust, hydrosphere, atmosphere, and biosphere) to ratio (e.g., set the core to be  $10^6$  million and express others accordingly). See how small the biosphere is.
2. Why is iron (Fe) a prominent element on the Earth as well as in the universe? This requires a little knowledge of nuclear chemistry, which you can obtain from a basic chemistry textbook.
3. Figures 1.3 and 1.4 indicate that the elemental composition of the human body correlates better with that of seawater than with that of the crust. What is the implication of this fact? Discuss.

- Pick one or two elements and elaborate the biochemical and biogeochemical cycling, referring to Figures 1.5, 1.7, and 1.8, identifying, if possible, special (meaning other than humans, mammals, common plants, etc.) organisms that deal (absorb, utilize, or otherwise) with it.
- A greenhouse gas  $\text{CO}_2$  is believed to be contributing to global warming. Figure 1.7 gives a rough estimate of quantities of C in several segments of the Earth and the rate of cycling among segments. It also gives an estimate of the contribution of anthropological activities to the C cycling (in the form of  $\text{CO}_2$ ). Calculate, using the numbers in Figures 1.1 and 1.7, (1) the current content of  $\text{CO}_2$  in the atmosphere in units of ppm (molar) and (2) the rate of annual increase of  $\text{CO}_2$  (per the current quantity) due to human activities.
- Oxygen ( $\text{O}_2$ ) is essentially toxic, and therefore, it caused very severe pollution problems for those organisms that had lived in an essentially anoxic atmosphere, when the atmospheric oxygen became significant. What was the response of the biosphere for this emergence of toxic atmospheric oxygen?

## PROBLEMS TO EXPLORE

- Investigate how an element (pick one from among Fe, Cu, Zn, Mo, Ca) was made into ores, and how organisms contributed to their formation, if any.
- Figure 1.5 contains a lot of information other than that given in the text. It is intended, for example, to show that the biochemistry of the entire life system can be divided into two groups. In the figure they are separated into the left half and the right half. It must be pointed out, though, that such separation cannot be done perfectly. The left half can then be divided into upper half and lower half. Try to extract as much information as possible from the figure and discuss.
- An interesting element in terms of abundance is uranium. The natural abundance of uranium in the Earth's crust is on average similar to those of molybdenum and tungsten, and even higher than that of mercury. All the isotopes of uranium are alpha-particle emitters. What is the implication of this fact for health effects of uranium? Investigate and discuss.

4. Many elements, particularly those of transition metals, readily change the oxidation states. As presumed, the atmospheric oxygen content varied very much over the course of the Earth's history, and that would have affected the oxidation states of the elements present in the ocean and the upper part of crust. That in turn would affect the availability of the elements to organisms, because organisms would utilize elements readily available in dissolved state. This has an implication that the variation of the atmospheric oxygen, hence that of the readily available elements, might have had significant effects on the evolution of various organisms. Explore the idea.