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Biogeochemistry: its origins and development

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Abstract. The history of how aspects of biology, geology and chemistry came together over the past three centuries to form a separate discipline known as biogeochemistry is described under four major headings: metabolic aspects, geochemical aspects, biogeochemical cycles, and the origin of life. A brief chronology of major conceptual advances is also presented.

Message from home

> Do you remember, when you were first a child,
> Nothing in the world seemed strange to you?
> You perceived, for the first time, shapes already familiar,
> And seeing, you knew that you have always known
> The lichen on the rock, fern-leaves, the flowers of thyme,
> As if the elements newly met in your body,
> Caught up into the momentary vortex of your living
> Still kept the knowledge of a former state,
> In you retained recollection of cloud and ocean,
> The branching tree, the dancing flame.
> Kathleen Raine

Introduction

Biogeochemistry deals with control of the concentrations and cycling of elements in and above the earth's crust by the synthesis, death and decomposition of organisms, most of which capture their energy from the sun. (It must of course be recognized that organisms are themselves limited in varying degree by their physico-chemical environment). The term was coined by Vernadsky (1926) to cover a sub-discipline of geochemistry, that term having been coined by Schönbein (1838) almost a century earlier. The subject may be said to have come of age in the 1980's with, *inter alia*, the founding of two journals devoted to it, *Biogeochemistry* (1985) and *Global Biogeochemical Cycles* (1987), and following reviews such as those edited by Pomeroy (1974), Krumbein (1978), Trudinger & Swaine (1979) and Bolin & Cook (1983). It has long been linked to ecosystem science through studies of element cycling. Biogeochemical studies became an important part of limnology just before and during World War II (Einsele 1936; Mortimer 1941—42), and formed the basis for volume 1 of Hutchinson's (1957) classic treatise on limnology. They also became an important part of ecology after World War II (Odum 1953), and have been exemplified recently by the outstanding work of Likens et al. (1977) and Schindler (1985); see also reviews by Gorham et al. (1979) and Schlesinger (1989). Information about the distribution of the chemical elements in the environment and in organisms has been collated by Bowen (1979).

The roots of the subject can be traced to Greek concepts (Browne 1944), but its development accelerated sharply with the rise of modern science in the seventeenth century. During the mid-1600's, informal gatherings of persons with a scientific bent led to the formation of both the Royal Society of London and the French Académie des Sciences. At this time interactions between organisms and their environments became the subject of careful observation and experiment.

Major aspects of the development of biogeochemistry relate to early, diverse studies of

— photosynthesis and respiration,
— decomposition,
— the metabolism of nitrogen and sulfur,
— the inorganic nutrition of plants, and
— the weathering of rocks and soils.

These came together in the demonstration of biogeochemical cycles and the calculation of chemical budgets, eventually with the aid of isotopic tracers. The concept of the biosphere was formulated explicitly by Suess (1875), although Lamarck (1802), in a very confused and often mistaken way, viewed organisms as a major force of nature: "The action of living organisms now appears of basic importance for the establishment of a valid theory of the earth. This action, the natural result of their existence and of the remains left by their countless generations, continuously reworks the earth's external crust." The biosphere concept was given a thorough biogeochemical foundation by Vernadsky (1924, 1926; see also Hutchinson 1948), who viewed it as a geological entity powered by solar energy and equal qualitatively to the lithosphere, hydrosphere and atmosphere. In recent years scientists have become interested in the biotic regulation of biogeochemical cycles on a global scale, leading in the last decade to controversy concerning the "Gaia hypothesis" (Lovelock 1972, 1979; Boston 1989), Gaia being the Greek personification of earth as a goddess. We have also become greatly concerned with human disturbances of biogeochemical cycles by means of artificial fertilizers, acid rain, the greenhouse effect, destruction of the stratospheric ozone layer by chlorofluorocarbons, etc.

Human perturbations of the biosphere have become so powerful (Vernadsky 1924) that scientists in the twentieth century have been led to new concepts of the noösphere (LeRoy 1927; Vernadsky 1945) and sociogeochemistry (Hanya & Akiyama 1987). These describe the ways in which human beings — exploiting their mental powers — are seen in their totality as a geochemical force of major importance, operating on a global scale as foreshadowed by Buffon (1779) and Marsh (1864). It has even been suggested by Brown (1954) that humans will continue to exploit ores of lower and lower grades until, in the distant future, they will be forced to rely upon raw materials obtained from crustal rocks, the sea and the air. At that stage of development, any major disruption of the global industrial network might well — according to Brown — be irreversible and cause a catastrophic return to an agrarian existence. The castastrophe could, however, come much earlier according to other scenarios. For instance, McElroy (1976) speculated that: "The terrestrial atmosphere contains within itself the seeds of an instability" and asked whether positive feedbacks between anthropogenic "greenhouse gases" and oceanic evaporation could develop a runaway "terrestrial greenhouse of Venusian proportions"? The question of such a positive feedback remains of great interest (Cess 1991; Marston et al. 1991). Hern (1990) has very recently suggested that human beings, through uncontrolled exponential growth of population, may be capable of "terminal derangement of the global ecosystem" (Hern 1990).

Eventual "derangement" of the biosphere by advanced civilization may even be viewed as inevitable, either on earth or elsewhere in the universe (Drake 1962; Sagan 1980; but see Tipler 1981; Ornstein 1982), given that the social sciences by which technology must be managed are far more complex than the physical sciences on which it is based (Gorham 1990). If our understanding of human and societal responses and interactions cannot, therefore, keep pace with the technical innovation that — with enormous capacity for both good and ill — continually threatens the stability of both society and the biosphere, then catastrophe may be the most likely result of humanity operating on nature's own scale.

A major offshoot of biogeochemistry has been the search for the origin of life (Oparin 1924; Haldane 1929), following the overthrow of earlier theories of spontaneous generation by Pasteur (1861a). Scientists have, in this context, become concerned with determining the fitness of diverse environments for such an origin (Koene 1856; Chamberlin & Chamberlin 1908; Henderson 1913; Chang et al. 1982), and with the factors controlling the subsequent evolution of diverse life forms (Berkner & Marshall 1965; Cloud 1968, 1983; Schopf 1983). More recently, attention has focussed on the detection of life on other planets (Hitchcock & Lovelock 1967).

In this review I trace the development of biogeochemistry from its earliest origins. The treatment must inevitably be somewhat idiosyncratic, at least with regard to minor figures and after World War II, when the literature burgeoned enormously. Throughout the past few decades in particular I have cited only papers that seemed to me especially apposite; others might make distinctly different choices.

Readers wishing to know more about the major figures concerned may consult the Dictionary of Scientific Biography, published by Scribners in 16 volumes from 1970 to 1980. It also provides numerous citations to the primary literature of publications by the individual and the secondary literature about him. The latter in particular can help to indicate the connections among various scientists and the ways in which their scientific ideas developed, both of which are beyond the scope of this review and await the attention of professional historians of science.

Metabolic aspects

Photosynthesis and respiration, decomposition, microbial metabolism of nitrogen and sulfur, and inorganic nutrition are all important aspects of the interactions between organisms and their environment.

Photosynthesis and respiration

The earliest scientific view of how plants interacted with their environment was that they derived their substance by the transmutation of water, as shown by the famous experiment of van Helmont in the sixteenth century (Hoff 1964). In the seventeenth century Plattes (1639) claimed that "all fruits are compounded of a double substance, the one terrestriall and the other aethereall, and for the most part, the want of the terrestriall part causeth ill successe". Later in the century Hooke (1687) came to a similar view, interpreting studies by Thomas Brotherton of reduced growth in pruned trees to mean that plants draw nourishment from the air as well as from water in the soil. This view was shared by Hales (1727), but not by Woodward (1699), who believed that plants grew only from the vegetable and mineral matter contained in the water they took up. Still another opinion was expressed by Tull (1733), a famous agriculturist who claimed that minute, earthy particles of soil were the source of plant nourishment. Home (1757) believed that plants are probably fed by air, water, earth, salt, oil (organic matter), and fire in a fixed state.

We get closer to modern biogeochemistry with the work of Priestley (1772). His experiments upon the restoration by plants of the air's capacity to support breathing and burning have cyclic implications that he saw clearly, stating that plants: "receive nourishment by their leaves as well as by their roots," and also: "it seems to be extremely probable that the putrid effluvium is in some measure extracted from the air, by means of the leaves of plants, and therefore that they render the remainder more fit for respiration". Finally, it is: "highly probable, that the injury which is continually done to the atmosphere by the respiration of such a number of animals, and the putrefaction of such masses of both vegetable and animal matter, is, in part at least, repaired by the vegetable creation". Of this scheme, which clearly implies a concept of the balance of nature, Benjamin Franklin wrote to Priestley: "That the vegetable creation should restore the air which is spoiled by the animal part of it, looks like a rational system. . . ." Most interested scientists, however, continued to believe that plants were nourished mainly through the roots by soluble organic compounds released from dead organic matter, especially manures, even after the role of atmospheric carbon dioxide was recognized. Both Thaer (1810) and Davy (1813) held to this view, which continued to the time of Liebig (1840). They did, however, recognize the essentiality of specific chemical elements; Thaer's list is as follows: C, H, O, N, P, S, earth bases, and some salts.

Concerning the role of air in respiration and combustion, studies by Boyle, Hooke, and others in the seventeenth century showed that it contains an ingredient necessary both for breathing and burning (Dampier 1948). A century later, in 1778, Lavoisier showed that breathing consumes — and requires — "eminently respirable air" (oxygen), while carbon and hydrogen are oxidized to "fixed air" (carbon dioxide) and water (Guerlac 1973).

By the end of the century Ingenhousz, Senebier and others had carried the above-mentioned studies forward. In particular, Ingenhousz (1779) demonstrated that only green plants placed in the light can purify the air, in a process by which "fixed air" (carbon dioxide) apparently is converted to "dephlogisticated air" (oxygen) and carbon. He, like Priestley, was aware of the global significance of the process. According to Browne (1944), Ingenhousz laid down the rule that: "the surest way to find out the real nourishment of organized bodies seems to be, to inquire what is the substance, without which they inevitably perish". Early in the next century de Saussure (1804) developed, from a series of quantitative experiments, a general theory of nutrition in which plants acquire their carbon by breaking down the traces of carbon dioxide in the atmosphere, emitting oxygen derived from the same source. Water is incorporated from the soil during this process, along with the nitrogen and mineral elements that are essential for growth. A useful flow sheet connecting the various investigations, along with appropriate references and translations of key passages, has been provided by Nash (1957).

The view that oxygen released during photosynthesis comes from the carbon dioxide that is fixed was opposed during the 1780's by Berthollet (Nash 1957), who believed it to originate by the breakdown of water molecules. It was not until the twentieth century that Berthollet's view came to be accepted through the work of van Niel (1930), Hill (1938) and, most conclusively, Ruben et al. (1941). The comparative biochemistry of photosynthesis has been reviewed comprehensively by van Niel (1949).

Organic decomposition

The processes of decomposition, leading not only to the release of carbon dioxide but also to the geochemically important formation of humus, are mediated largely by microbes and fungi, whose roles were elucidated chiefly during the second half of the nineteenth century (Brock 1961; Le Chevalier & Solorotovsky 1965; Collard 1976). A first step in understanding the process came with the recognition by MacBride (1764; see also Priestley 1772) that the fermentation and putrefaction of organic matter produced "fixed air" (carbon dioxide). Somewhat later Volta, in 1778, investigated "inflammable air from marshes" (chiefly methane), said also to have been discovered slightly earlier by Franklin (Heilbron 1976). Later still Jameson (1800) became aware of emissions of carbonetted hydrogen (methane) as a decay product in peatlands, and Rennie (1810), in his study of peat and peatlands, observed that although carbon dioxide was the major product of organic decay, ammonia was another. Moreover, where peat accumulated owing to anoxia in waterlogged depressions, sulphuretted hydrogen (hydrogen sulfide) was also evolved, along with methane and phosphine. None of these investigators had any notion of microbial involvement.

The role of microbes was demonstrated clearly by Schwann (1837), who described them as nourished by the organic substances that they destroyed by putrefaction, or the sugar that they fermented to alcohol. Cagniard-Latour (1838) discovered, independently of Schwann, the role micro-organisms (yeast cells) play in fermentation. Their work was discredited, however, because the great German chemist Liebig (1839) claimed that decomposition was simply a chemical oxidation at low temperature. Liebig's strictly chemical view of decomposition was finally controverted by Pasteur (1857), who published a classic series of papers on the aerobic and anaerobic metabolism of yeast and other microbes.

Nitrogen metabolism

Digby (1669) claimed to have grown barley luxuriantly by watering it with a weak solution of nitre (potassium nitrate). Although Davy (1813) later expressed some suspicion about Digby's results, he himself found carbonate of ammonia to be an excellent fertilizer. De Saussure (1804) also observed from his experiments that plants require nitrogen for growth. However, it was Liebig (1840) who upset traditional agriculturists by demonstrating conclusively that plants can grow from wholly inorganic sources: carbon dioxide, water, ammonia, and certain mineral elements — whether made available by the decay of organic manures or provided initially as inorganic compounds. There were, however, complications. Liebig himself was led, mistakenly, to view atmospheric ammonia as the main source of plant nitrogen. Furthermore, Boussingault's (1838) experiments indicated that unlike wheat and oats, clover and peas could grow in the absence of inorganic salts of nitrogen if air was admitted to the plant chambers, but not if it was excluded and an artificial source of carbon dioxide was utilized. Unfortunately, Boussingault's later experiments cast doubt upon his original conclusions that the legumes were fixing free nitrogen from the atmosphere, as did the careful studies of Lawes et al. (1861) on plants grown in ignited soil (hence free of an inoculum of *Rhizobium*) with ammonia-free water and air free of combined nitrogen. Legumes had, however, been known since Roman times as extremely valuable green manures (Wilson 1940). Atwater (1884—85, 1886) carried out experiments similar to those of Boussingault much later, but was uncertain as to whether microbes or atmospheric electricity were the agents of fixation. Fixation of free atmospheric nitrogen by the microbes inhabiting nodules on legume roots was demonstrated experimentally by Hellriegel & Wilfarth (1887). They noted that cereals, being without such nodules, must depend wholly on nitrogenous salts in the soil.

Interest in nitrogen fixation by free-living soil microbes was also growing at this time. Jodin (1862) observed active growth of "mycoderms" in a solution containing only mineral phosphates and various sources of carbon. At the same time he demonstrated a loss of nitrogen from the atmosphere above his cultures. Later, when Joulie (1885) found that cultivated soils exposed to the air, but not to rain and dustfall, fixed substantial amounts of atmospheric nitrogen, he was uncertain about whether microbes or vascular plants were involved. In the same year Berthelot (1885) showed a similar fixation, in which he did state that microbes were the causal agent. However, it was not until Winogradsky (1893) demonstrated fixation in anerobic cultures of *Clostridium* that the matter was finally settled. A few years later Beijerinck (1901) demonstrated fixation in aerobic cultures of *Azotobacter.*

The roles of other microbes in the nitrogen cycle were also being investigated during the latter half of the nineteenth century, subsequent to the demonstration by Smith (1849) that nitrogenous organic matter introduced into natural waters was oxidized to nitrate. Following a suggestion by Pasteur that nitrification be re-examined in the context of germ theory, Schlösing and Müntz (1877) trickled diluted sewage through soil and found that its ammonia was converted to nitrate, but only when microbial activity was permitted; the process ceased upon sterilization. Winogradsky (1890) pursued the subject, and found that "the nitrifying organism is able to synthesize completely its cell substance from carbonic acid and ammonia" in the dark, the first instance of chemosynthesis (Brock & Schlegel 1989). Warington (1891) soon found that nitrification is a two-step microbial process, converting ammonia to nitrite and the latter to nitrate, but it was Winogradsky (1891) who isolated and cultured the organisms responsible for both conversions. Marchal (1893) remarked that in the production of ammonia from organic nitrogen, bacteria are important in alkaline arable soils that are poor in organic matter, whereas fungi predominate in acid soils rich in organic matter.

Lawes et al. (1861) remarked that "free nitrogen is given off in the decomposition of nitrogenous organic matter, under certain circumstances". According to Reed (1942), studies of sewage in 1867 by R. A. Smith indicated similar losses. In the same year Schönbein stated that nitrates are reduced to nitrites. Schlösing (1868, 1873) observed that during microbial fermentation nitrates could be converted to NO_2, NO or N_2, often in mixture. Meusel (1875) described microbial reduction of nitrate to nitrite, and pointed out that nitrates are useful not only for the nitrogen they contain, but also for their oxygen, with which the bacteria can break down cellulose. Warington (1891) observed that soils could both convert nitrate into nitrite and destroy the latter, and in the following year Gayon and Dupetit (1882) isolated nitrate-reducing bacteria and coined the term denitrification.

More recently, the highly local and extreme concentration of nitrogen (and phosphorus) in guano excreted by sea-birds has been discussed exhaustively by Hutchinson (1950) as a biogeochemical phenomenon.

Sulfur metabolism

Sulfur was one of the elements regarded by Thaer (1810), in his treatise *Principles of Rational Agriculture*, as necessary for plant growth. In the same year Rennie (1810) observed that it was released as hydrogen sulfide from decaying, anoxic peat. Schwann (1837) discovered the evolution of hydrogen sulfide during microbial putrefaction. Its evolution from coastal waters in West Africa was ascribed by Daniell (1841) to the mixing of large quantities of river-borne organic matter with sea water rich in sulfate. Volcanic sources could be ruled out, and Daniell was able to verify his conclusion experimentally. A major contribution to our understanding of the sulfur cycle came with Winogradsky's (1887, 1889) identification of the colorless sulfur bacteria able to oxidize hydrogen sulfide as a source of energy (see also Winogradsky 1949; Brock & Schlegel 1989; Zavarzin 1989). Shortly thereafter Beijerinck (1895) identified microbes responsible for sulfate reduction.

The role of sulfate-reducing organisms in the oceanic part of the sulfur cycle was described by Forchhammer (1865), who ascribed to them the precipitation of iron as ferrous sulfide as well as some release of free hydrogen sulfide. Much later, Conway (1942) suggested that emission of volatile sulfide is an important part of the global sulfur cycle, a hypothesis confirmed by the sulfur-isotope studies of Jensen and Nakai (1961). The role of microorganisms in the formation of sulfur deposits was noted by Hunt (1915; see also Butlin & Postgate 1954).

Inorganic nutrition

The discovery of various chemical elements in living organisms has been chronicled by Vinogradov (1953), who compiled extensive information (see his Table 1, pp. 7—10) about the elementary composition of marine organisms. De Saussure (1804) was the first person to show experimentally the biological need for specific elements contained in plant ash, finding that more fertile soils supplied them in greater amounts. Davy (1813) observed that plants contain in their tissues fifteen elements, many of which he regarded as essential: C, H, O, N, P, S, Cl, K, Na, Si, Al, Ca, Mg, Fe, and Mn. He was, however, uncertain as to the roles of most of them. According to Browne (1944), Sprengel (1839) reiterated Davy's list as being essential, and suggested that a number of elements not yet found in plants (e.g., F, I, Br, Li, Cu) might also be found to be essential even if present only in minute amounts, i.e., as trace elements. Browne (1942) pointed out that Sprengel anticipated, in his text *Die Bodenkunde* (1837), Liebig's (1855) famous Law of the Minimum, stating that even a soil otherwise favorable for plant growth "may often be unproductive because it is deficient in one single element that is necessary as food for plants".

Liebig (1840), in promulgating his theories of inorganic plant nutrition, taught that the soil was the source of most necessary elements, such as potassium, calcium, sulfur, and phosphorus. The problem of which chemical elements are truly necessary for plant growth was investigated further by Salm-Horstmar (1856), who invented the minus-experiment to test for both essentiality and function, omitting elements one by one from a complete nutrient solution and observing the growth response of the plant.

The selectivity of plants for nutrient elements was demonstrated by Liebig (1859), who observed that when *Lemna* was cultured in pond water: "The soluble mineral constituents were taken up by the plant in various degrees required for its vital processes, in no way proportional to the amount present in the fluid." The extraordinary degree to which certain organisms may concentrate specific elements from the environment was remarked by Vernadsky (1924), who noted that recent experiments had shown some to concentrate strontium, others barium, and yet others phosphorus, magnesium, or zinc. The Noddacks (1940) were among the first to investigate spectrographically the enrichment of numerous elements in organisms as compared to their environment, finding the average vanadium enrichment to be unusually high in marine animals, more than 280,000 times its concentration in sea water. Demonstration of the biomagnification of element concentrations along food chains awaited the use of radioisotopes in field studies after World War II (Krumholz 1956; Hanson & Kornberg 1956).

One of the most thorough explorations of plant uptake in biogeochemical terms was Hutchinson's (1943) account of aluminum (and related elements) in the biosphere. The history of geobotanical and biogeochemical prospecting for various elements has been reviewed by Brooks (1972). According to Kovalevsky (1987), biogeochemical exploration for mineral deposits began in the USSR in the 1920's, when S.P. Aleksandrov discovered unusually high concentrations of vanadium, uranium and radium in ash from plants growing on a deposit of vanadium and uranium.

It may be remarked here that Goldschmidt (1954) theorized that life in the sea was possible only because of the removal of toxic trace elements (e.g., Cu, Zn, Pb, As) by adsorption on sedimenting clays and oxidates, with precipitation as sulfide also involved in some cases. He also noted the capacity of soil humus layers and coal deposits to concentrate trace elements (Goldschmidt 1934; Swaine 1988).

Geochemical aspects

Related to the metabolic aspects of biogeochemistry are the geochemical processes of rock and soil weathering, and the calculation of chemical budgets.

Rock and soil weathering

Until nearly the beginning of the nineteenth century soil formation was ascribed to processes of physical weathering by water, as outlined for example by Home (1757) and Hutton (1795). However, once the chemical nature of carbon dioxide produced so abundantly in the soil by organic decay (MacBride 1764) was understood, including its power to dissolve in water to form carbonic acid, the role of chemical weathering became apparent. Cavendish (1767, see also Bergman 1779—80) was the first to recognize that carbon dioxide dissolved in water formed an acid that could dissolve calcareous earth and magnesia. A little later Lane (1769) showed that iron could also be dissolved. Thaer (1810) and Davy (1813) both recognized that carbonic acid could dissolve calcium carbonate and form clays from minerals composed of silicon, aluminum and iron. By the mid-nineteenth century the brothers Rogers (1848) had shown experimentally that carbonic acid released elements from pure minerals in proportions very different from those in the minerals themselves.

Bischof (1854), in the first real textbook of geochemistry, *Elements of Physical and Chemical Geology*, published a half-century before the classic *Data of Geochemistry* by Clarke (1908), ascribed the predominance of "carbonate of lime" in most river waters to the major role of carbonic acid in the breakdown of rocks and soils. Julien (1879) further implicated in the weathering process a whole series of organic acids, ranging from minute amounts of simple organic acids to the crenic and apocrenic acids separated operationally by Mulder (1840) from the "humus acids" first identified by Sprengel (1826); for a recent review see Tan (1986). Complex organic acids were also envisaged by the great Russian soil scientist Dokuchaev, and his followers in the last quarter of the nineteenth century, as playing an important role in the development of diverse types of soil profile, with their genetically related but physically and chemically distinctive horizons of leaching above and deposition beneath (Joffe 1931). The general role of acid leaching in the development of such soil profiles was clearly appreciated before the middle of the nineteenth century; Johnston's (1843) *Lectures on Agricultural Chemistry and Geology* described differences between the surface soil (top 12—15 inches), subsoil (next 12—15 inches) and the almost unaltered subjacent mass. These were said to be caused by the accumulation of dead organic matter in the surface soil, and to a much lesser degree in the subsoil, and to the washing downward into the subsoil of salts of sodium and potassium, carbonates of calcium, magnesium and iron, and fine clay particles, together with some soluble organic matter.

The significance of long-term acid leaching for differential ecosystem acidification and floristic impoverishment throughout the post-glacial period was first recognized by Salisbury (1922), who was also the first scientist (1925) to follow the time-course of leaching, by showing calcium depletion and hydrogen-ion increase in a dated sand-dune chronosequence. Historical aspects of the scientific understanding of ecosystem acidification have been dealt with by Gorham (1989). Recently Schwartzman and Volk (1989) have considered quantitatively the strong biotic enhancement of weathering and its effects upon global climate and the habitability of the planet.

Chemical budgets

Chemical input/output budgets have become a major feature of biogeochemistry today, whether for individual catchments (Likens et al. 1977) or the global ecosystem (Bolin & Cook 1983). The basic idea behind such budgets was formulated long ago by Plattes (1639) as follows: "The Land flouds doe carry away the fatnesse" (fertility) "from the arable land, and all high grounds, in huge quantities into the sea". Plattes also noted that some of the "fatnesse" was deposited and enriched the meadows of low-lying ground, the prime example being that of the Nile River and its delta. Later in the century, Boyle (ca. 1673) concluded that the sea owes its high salinity to the leaching of salt from the land in dilute streams and rivers over long periods of time. This view was adopted by Halley (1715), who believed that it might offer a method of dating the age of the earth if oceanic salinity could be determined on two widely separated dates. The idea was later pursued quantitatively by Joly (1899; see also Becker 1910) with reference to the rate of sodium weathering from rocks. Conway (1943) continued along this line, and suggested a volcanic source for the chloride balancing the sodium (see also Rubey 1951). Livingstone (1963) carried the matter further, more to elucidate details of the sodium cycle than to compete with the superior radiometric measurements of geological time developed after World War II (see Cloud 1968). Recent developments suggest a more complicated picture of the chemical evolution of the ocean (Degens 1989).

On a more local basis, Reade (1876—77) estimated that annual runoff from England and Wales carried 8.5 million metric tons of dissolved material to the sea, or 56 tons per square kilometer. The level of the land was lowered thereby one meter in 43,000 years. At the same time Ebermayer (1876) was studying related problems on an even smaller scale, measuring annual litterfall and its composition under a variety of forest types of differing productivity in order to see whether litter removal as then practised was likely to decrease productivity.

Inputs were studied as well as outputs by Lawes and Gilbert (1882), who compared the amount and chemical composition (chloride, nitrogen) of rain and drainage waters from permanent, unmanured and uncropped grass plots at Rothamsted. They observed that inputs and outputs of chloride were similar, but that outputs of combined nitrogen were much greater than inputs. Much later Viro (1953) compared the amounts and chemical composition of both atmospheric precipitation and river discharge over the whole of Finland. He found substantial weathering losses of most elements, but chloride (as expected) was in approximate balance. Nitrogen falling in precipitation was, however, about three times that carried by rivers to the sea. Presumably the remainder was largely bound in actively increasing forest biomass, although some must have been denitrified to the atmosphere. For a review of the literature on environmental factors controlling ionic inputs to inland waters, with special reference to atmospheric deposition, see Gorham (1961).

In calculating global chemical budgets it is important to be able to estimate plant productivity over the earth as a whole. An early figure for terrestrial productivity was given by Schroeder (1919). Almost two decades later Noddack (1937) attempted to include both terrestrial and marine components, but with grossly inadequate information concerning the latter. Riley (1944) incorporated many more marine data, and estimated a global photosynthetic efficiency of 0.2%. His data for unproductive areas of the ocean were believed by Steeman-Nielsen (1952) to be too high; the criticisms were rebutted by Riley (1953). Earlier attempts to estimate much more locally the energy efficiency of plants were made by Becquerel (1868) and, in modern times, by Transeau (1926). It is worth noting in this connection that human beings have now coopted or lost almost 40% of terrestrial and 25% of global net primary production (Vitousek et al. 1986).

Among the earliest attempts to compare the various pools of carbon in the biosphere was that of Vernadsky (1924). He reported that crustal carbon totalled about 8×10^{16} metric tons, of which about 3.1×10^{16} tons were in the form of chalk deposited by organisms. About 1×10^{14} tons were present in the ocean, about 5×10^{13} to 5×10^{14} tons in living matter, and 2.2×10^{12} tons in the atmosphere. Oil deposits were estimated at 2.2×10^{13} tons. Vernadsky remarked on the great excess of carbon tied up in calcareous, biogenic sediments over that currently present in living matter.

Current estimates of carbon inventories (Hunt 1972; McElroy 1976) are surprisingly similar to those of Vernadsky with the exception of living matter, which he overestimated by more than two orders of magnitude. For recent estimates of global chemical budgets for the more biophilic elements, readers may consult Bolin et al. (1983a).

Biogeochemical cycles

The concept of cycles, whether hydrological, geological or biological, is an old one, although the linkage of all three types into biogeochemical cycles took place only within the past two centuries.

Early descriptions of cycles

The basic idea, which implies the balance of nature, can be traced back to the Greeks Democritus, who lived from about 460 to 350 B.C., and Epicurus, who lived from 341 to 270 B.C., as set forth by their Roman disciple Lucretius (~ 95—50 B.C.):

> "Finally, all of us spring from a seed that descends out of heaven;
> All of us have the same Father, by whom the life-giving Earth-Mother,
> When she has taken from him the liquid droplets of moisture,
> Brings forth out of her womb goodly crops, joyous trees, yea, and mankind;
> Bears all the beasts of the field; provides them with food for their bodies,
> So that they lead joyful lives, and multiply each his own offspring:
> For this reason she rightly is given the title of Mother.
> That too which erstwhile came from the earth returns thither again, and
> That which was sent from the sky's far shores is upward translated,
> And is again received back to the habitations of heaven.
> Death indeed destroys things, but does not annihilate atoms;
> For it but severs their union, and joins them anew with each other.
> Thus it ensues that all things change their outward appearance" . . .

The compartments through which materials cycle were foreshadowed by Empedocles (483—424 BC), who described the basic indestructible elements of the universe as air, water, earth, and fire. Lambridis (1976) has described the antecedents of his ideas. Nowadays these elements would be called atmosphere, hydrosphere, lithosphere, and energy (the driving force), respectively, to which we would add as a living component the biosphere (see Suess 1875; Degens 1989).

Shortly after the middle of the sixteenth century A.D., Palissy ascribed the principal benefit of manures to the salt they contain, which restores that removed by crops but can also be washed away by rain (Browne 1944). A century later Home (1757) stated that in decaying vegetation "The oils and salts, from being fixed, are volatilized, carried up into the air, and descend again to fructify the earth, which was lately robbed of them. Corruption, then, is the parent of vegetation". It "carries on that beautiful circle, which nature is commanded, by her author and constant supporter, to move in".

The role of plants in the circulation of water also received attention. Woodward (1699) noticed that plants evaporate most of the water taken up from the soil through pores in the leaves, especially during warm weather, and Hales (1727) carried out rather sophisticated experiments on plant transpiration. The water budget of an ecosystem is of course essential to the calculation of its chemical budget. Therefore the quantitative calculations by Halley (1687, 1691, 1694) that validated globally the long-known concept of the solar-powered hydrological cycle (see for example the Roman Lucretius, undated) were a vital prerequisite to the eventual calculation of chemical budgets. The role of plant evapotranspiration in the general hydrological cycle was remarked by de la Methiére (1797).

On a more strictly geological note, the recurrent cyclical nature of mountain building and erosion, foreshadowed by Hooke (1705, see also Ranalli 1982), was postulated by Hutton (1785, 1795) as necessary to provide continuously the fresh soil necessary for the growth of plants (and indirectly that of animals) according to the grand design of the Creator. He also noted the biogenic origin of calcareous sedimentary rocks, which, "though at present in the most solid state, appear to have been formed by the collection of the calcareous *exuviae* of marine animals." This statement reflects an earlier view of Linnaeus, who said that "fossils are not the children, but the parents of rocks" (Anonymous 1875, who said in turn that . . . "life has been the means, not the end, of the earth's development").

The modern view of biogeochemical cycles

Although the idea of biogeochemical cycles and the balance of nature was foreshadowed by the work of Priestley (1772) discussed earlier, a clear, thorough description of such cycles and their generating force did not come until the publication of a classic paper by Dumas (1841) that reflected also the views of his close friend Boussingault (Dumas & Boussingault 1844). This paper can fairly be regarded as marking the real beginning of biogeochemistry, eight decades before Vernadsky coined the term and well over a century before it became well established as a separate discipline. The major importance of this paper can easily be appreciated from 15 lines of its 25 pages:

> "Thus closes this mysterious cycle of organic life at the surface of the globe. The air contains or engenders oxidized products, as carbonic acid, water, nitric acid, oxide of ammonium. Plants, constituting true reducing apparatus, possess themselves of their radicals, carbon, hydrogen, azote, ammonium. With these radicals they form all the organic or organizable matters which they yield to animals. These, forming, in their turn, true apparatus for combustion, reproduce carbonic acid, water, oxide of ammonium and nitric acid, which return to the air to produce anew and through endless ages the same phenomena.
>
> . . . Add to this picture, already, from its simplicity and its grandeur, so striking, the indisputable function of the solar light, which alone has the power of putting in motion this immense apparatus, this apparatus never yet imitated".

Given that carbonic acid and other acids released into the soil solution by organisms, and especially by organic decay, are also major agents of rock weathering and soil formation that liberate a variety of elements to be taken up by organisms, we are even more impressed by the vital role of organisms in diverse biogeochemical cycles.

It should be pointed out here (see also Hutchinson 1948) that the role of solar energy in determining purely physical phenomena such as the temperature and motion of the air, as well as the temperature and counter-current systems (surface and deep) of the oceans, was also clearly apprehended at this time (Mayer 1848). Moreover, its role in driving the hydrological cycle had long been known (Halley 1687).

A small-scale example of the global balance of nature elaborated by Dumas was described a decade later by Warington (1851), who prepared an aquarium with fish, snails, pondweeds and algae that he was able to maintain with considerable stability for almost a year, when he submitted his article. Aquaria have since become important tools in biogeochemical studies.

Another major contributor to the idea of biogeochemical cycles was Cohn (1872), who postulated that bacteria and fungi (ignored by Dumas) were the agents by which the complex molecules synthesized by plants were broken down in the soil, releasing their chemical elements to allow a new cycle of plant uptake and growth. Although, in the words of Lipman (1926): "... it had been clearly established before the end of the nineteenth century that microorganisms are directly concerned in the migrations of carbon, hydrogen, nitrogen, sulfur and of a number of mineral ingredients of the earth's surface", during the first quarter of the twentieth century soil scientists laid stress chiefly on the importance of bacteria mediating the nitrogen cycle (e.g., Russell 1912; Hilgard 1921). By the 1930's it had become apparent that the microorganisms maintaining the oxidation-reduction cycles of sulfur and nitrogen, and those operating on other elemental cycles as well, are of an importance equal, in terms of biologically driven cycles, to that of the green plants and the microbial and fungal decomposers driving the carbon cycle (Waksman & Starkey 1931; see Deevey 1970a, b, 1973 for more explicit statements). It must be granted, however, that green plants do trap most of the energy that drives biogeochemical cycles.

Local examples of biogeochemical cycles were readily demonstrated in the metabolism of lakes, first by Hoppe-Seyler (1895) and a decade later by Birge (1906; Birge & Juday 1911). The early history of limnology has been outlined by Berg (1951). Redox cycles between sediments and water in lakes were described much later, for instance by Einsele (1936), Sugawara (1939), and Mortimer (1941, 1942). Recently biomethylation has been recognized as a process important in the aquatic parts of the cycles of some trace elements (Jensen & Jernelöv 1969; Wood 1974).

Stratigraphic examination of the chemistry of sediment cores from aquatic and peatland ecosystems has become a powerful tool for investigating their biogeochemical ontogeny. Among the earliest investigations of the inorganic chemistry of lake sediment cores was that of Hutchinson and Wollack (1940); Vallentyne (1954) and Vallentyne and Swabey (1955) added the study of organic chemistry by analyzing fossilized plant pigments (see also Züllig 1955). For a recent review of paleolimnology, see Binford et al. (1983). Cores from marine sediments (Arrhenius 1952) and peat deposits (Mattson et al. 1944; Mattson & Koutler-Andersson 1954) have been examined in a similar way.

An attempt to define the limits of biologically suitable environments in terms of redox potential and pH was made by Baas Becking et al. (1960). The formation of reduced iron in bogs, and its oxidation in the springs issuing from them, was described much earlier (Johnson 1866) and implicated in the formation of bog-iron ore. The role of microorganisms such as *Gallionella ferruginea* in the formation of these ores was described even earlier by Ehrenberg (1836).

After World War II biogeochemical cycles became important in ecosystem ecology, receiving considerable attention in successive editions of Odum's (1953) pioneering textbook. The role of the atmosphere in such cycles was thoroughly reviewed by Hutchinson (1954).

The full flowering of biogeochemistry was first seen in Vernadsky's (1924) book, *Geochemistry*, in which the role of "living matter" was given great emphasis throughout, not only with regard to the biophilic elements carbon and nitrogen, but also such lithophilic elements as silicon, calcium, and manganese. In this connection Forchhammer (1865) had, much earlier, remarked on the great ability of organisms to alter the chemistry of river waters after they entered the sea, precipitating calcium, silica, and iron (as a sulfide following sulfate reduction).

Geochemistry was followed by another book, *The Biosphere* (Vernadsky 1926), in which Vernadsky first described two "biogeochemical" principles. These are as follows: (1) "The biogenic migration of chemical elements in the biosphere tends towards a maximum of manifestation", and (2) "The evolution of species, in tending toward the creation of new forms of life, must always move in the direction of increasing biogenic migration of the atoms in the biosphere". Thus: "a newly evolved species will survive in the biosphere only if it is sufficiently stable and sufficiently active in furthering the migration of atoms". In ecological terms this can be translated to mean that evolution leads to increasing biodiversity, with new species exploiting ever more effectively the earth's resources of light, water, nutrients and space (the ecospace of Cloud 1989), thereby increasing the biomass of the biota, and increasing and altering the circulation of chemical elements.

Modern views of the interactions of biogeochemical cycles are given by Bolin et al. (1983b) and by Schindler (1985).

Isotopic tracers

In the 1940's and 1950's powerful new tools, in the form of radioisotopes, came to be employed in identifying the pathways of biogeochemical cycles. Although Joly (1922) had suggested the use of radioactive radium salts to measure the flow of water in a river, it was not until the late 1940's that Hutchinson and Bowen (1947, 1950) used ^{32}P to investigate the phosphorus metabolism of Linsley Pond. Hayes applied the same technique independently to a Nova Scotian lake slightly later (Coffin et al. 1949; Hayes et al. 1952). At about this time Steeman-Nielsen (1952) employed ^{14}C to measure oceanic photosynthesis more sensitively than could be done using oxygen in the classic light-and-dark-bottle technique of Gaarder and Gran (1927).

Under the aegis of the U.S. Atomic Energy Commission in particular, and analogous agencies elsewhere, radioactive isotopes from atomic explosions also came into vogue for tracing diffusion in the sea (Munk et al. 1949; Miyake et al. 1955; Miyake & Sugiura 1955), downstream transport by rivers (Foster & Rostenbach 1954), and bioaccumulation along food chains (Krumholz 1956; Hanson & Kornberg 1956). At about the same time, radioactive ^{14}C came into use as a tool for dating (Libby et al., 1949; Arnold & Libby 1949; Libby 1952).

Stable isotopes were employed as well, the pioneering work of Nier (Nier & Gulbranson 1939; Murphy & Nier 1941) on carbon isotopes and Thode et al. (1949, 1953) on sulfur isotopes being good examples. Carbon-isotope studies now suggest that prolific microbial life existed shortly after the formation of the earth, beginning about 3.5—3.8 billion years ago (Schidlowski 1988).

Biotic regulation

Although biotic participation in geochemical cycles was made abundantly clear by Dumas (1841), and local examples such as the circulation of elements between forests and their soils were well known (Ebermayer 1876), the idea that the biota had a large-scale regulatory role in geochemistry took a long time to develop. Henderson (1913), in his classic book *The Fitness of the Environment*, remarked that: “the regulation of the ocean in general bears a striking resemblance to a physiological regulatory process, although such physiological processes are supposed to be the result of organic evolution alone”. His remarks related to temperature regulation by evaporation and regulation of alkalinity by the bicarbonate buffer system. Recently, Walker et al. (1981) have suggested that the temperature of the earth’s surface may be buffered against the steady increase in solar luminosity over geologic time by a negative feedback mechanism involving the rates of silicate weathering and deposition of carbonate sediments interacting with the “greenhouse effect” of atmospheric carbon dioxide.

The possibility of biotic regulation was examined by Redfield (1934), who noticed the remarkable regularity of the ratios of certain biophilic elements one to another in the ocean. Eventually he published (Redfield 1958) an influential review of the subject entitled: “The biological control of chemical factors in the environment”, dealing with the role of biogeochemical cycles in controlling the chemistry of both the ocean and the atmosphere (see also Redfield et al. 1963). At the same time Goldberg (1958) wrote another excellent review: “The processes regulating the composition of sea water”, in which biogeochemical processes were shown to have an important role (see also Lowenstam 1974). The roles of marine microbes in oceanic biogeochemistry have been described from a historical perspective by Zobell (1946).

The influence of organisms upon the chemistry of the present atmosphere was examined in some detail by Hitchcock and Wechsler (1972). Shortly thereafter McElroy (1976) discussed chemical processes in the solar system, with special attention to the role of life on earth. In this connection, Hitchcock and Lovelock (1967) had already suggested that analysis of the planetary atmosphere should permit the detection of life (if it exists) on Mars.

The role of the biota in regulating chemical budgets over the course of terrestrial ecosystem succession has been described at length by Gorham et al. (1979). A formal, logical flowchart for the axioms and theorems of biogeochemistry has been presented in an ecosystem-related context by Reiners (1986).

Within the past few years Redfield's ideas have been expanded (see Morel & Hudson 1985; Schindler 1985), even to the point of claiming adaptive regulation of planetary biogeochemistry by the evolving biota in such a way as to perpetuate and magnify its own existence — the "Gaia hypothesis" of Lovelock (1972, 1979, 1990; Lovelock & Margulis 1974; Margulis & Lovelock 1974, 1988). In its original formulation Lovelock stated that: "Earth's living matter, air, oceans, and land surface form a complex system which can be seen as a single organism and which has the capacity to keep our planet a fit place for life". Again: "the biosphere is a self-regulating entity with the capacity to keep our planet healthy by controlling the chemical and physical environment".

According to Stoddart (1986), theories of the earth as an organism have a history going back to the early nineteenth century among geographers. One of the more explicit statements was that of Herbertson (1913), who saw the earth in terms of a series of geographical entities and anticipated Tansley's (1935) concept of the ecosystem in the following words: ". . . a plant association . . . is not complete in itself. A forest, for instance, is more than an association of trees and other plants. It has its foundation of rock, its floor of soil, its ambient air, the moisture which penetrates it and the sun's rays which play rhythmically on it. The concrete geographical entity comprises all of these. Without all, it is not complete. It is a continuous space on the outer limits of the solid layers of the Earth, with all it contains, solid and fluid, inorganic and organic.

There are no satisfactory terms for such entities . . . Each has its own form and its own activities . . .

It has been suggested that the term macroorganism should be given to this complex entity, . . ."

In 1988 the "Gaia hypothesis" was the subject of a meeting of the

American Geophysical Union (Lindley 1988) at which criticism led Lovelock to a somewhat weaker formulation: "that the non-living and living represent a self-regulating system that keeps itself in a constant state" (at least within a limited range of conditions, see Lovelock & Whitfield 1982). Whether or not the earth represents a stable or quasi-stable equilibrium that is biotically controlled, the concept of Gaia has been thought useful in stimulating both debate and study (Slingo 1988; Boston 1989; Mann 1991).

In opposition to the Gaian view, Veizer (1988a, b) notes that although life modulates and catalyzes earth processes and planetary evolution, it is constrained ultimately by the tectonic mountain-building processes that control rock weathering and nutrient supply — a remarkable restatement in modern terms of Hutton's original 18th century hypothesis. We may note that tectonic processes control global topography, and hence the distribution of land and sea. Thus, they also influence climate, in particular the distribution of atmospheric precipitation, and thereby exert a strong effect on biotic productivity.

Margulis apparently claims that even plate tectonics may be under Gaian control, along with a series of equally debatable speculations (Mann 1991). This reviewer inclines to the opinion of Cloud (1988), who has pointed out that shorn of its mysticism the Gaia hypothesis merely reflects the well known Le Chatelier principle, that a change in one of the conditions of a stable equilibrium (implied by the Gaia hypothesis) will alter that equilibrium in such a way as to restore the original condition. The principle is, of course, fundamental to homeostasis in organisms and to the topic of biotic regulation discussed above.

Major anthropogenic influences

The idea that humans can have a significant influence on how the world works is an old one. For instance, Aiton (1811) believed that the cutting down of forests could greatly influence climate (see also Marsh 1864).

Some effects of human activities upon biogeochemical cycles can be very local, as for instance in the drying up of the Aral Sea (Micklin 1988) and the cultural eutrophication (Hasler 1947; Shapiro 1988) of many lakes by phosphorus from sewage and detergents. Others are regional, as in the case of widespread use of artificial NPK fertilizers, pioneered by Liebig (1840) and followed up at Rothamsted by Lawes and Gilbert (1880, 1900); it sometimes leads to regional eutrophication. Acid rain, discovered in Manchester by Smith (1852, see also Smith 1872) and found a century later to have spread far from its urban/industrial sources (Barrett & Brodin, 1955; Houghton, 1955; Gorham 1955), is another regional example. Smith was a pioneer in the field of "chemical climatology" (Gorham 1982) and, incidentally, the prototype of the scientific civil servant (MacLeod 1965). The acidifying effect of acid deposition upon lakes was discovered by Mackereth (1957) and Gorham (1957, 1958; Gorham & Gordon 1960a, b). The history of our scientific understanding of acid deposition has been recorded by Cowling (1982).

Global examples of anthropogenic perturbations are the worldwide distribution through the atmosphere of radioactive fallout and synthetic organic biocides. The history of scientific studies of long-range transport and deposition of air pollutants has been reviewed recently by Gorham (unpublished manuscript, in revision). Yet another global example of such human influence, now viewed with great concern, is the "greenhouse effect" of carbon dioxide released to the atmosphere by combustion of fossil fuels and secondarily by land clearance and cultivation. It is expected to result, in combination with increases in other "greenhouse gases", in a very substantial warming of the earth's climate during the century to come (Hansen 1988), despite the moderating influence of oceanic absorption (Revelle & Suess 1957). As noted by Plass (1956) and Henderson-Sellers (1990), the "greenhouse" role of the atmosphere was pointed out long ago by Fourier (1827). The roles of carbon dioxide, and of water vapor and hydrocarbon vapors, were remarked by Tyndall (1861). Toward the end of the century Arrhenius (1896) took a much more quantitative look at the role of carbon dioxide in relation to atmospheric temperatures and periods of glaciation, and estimated that a doubling would raise global temperatures by 5—6 °C. He also noted the role of the ocean in regulating atmospheric carbon dioxide, and the possibility of human influence through fossil-fuel combustion, which he believed to be then capable of increasing atmospheric carbon dioxide by about 0.1% per year. Shortly thereafter Chamberlin (1897, 1898, 1899) elaborated on changes in carbon dioxide as a cause of climatic change. Nowadays, it is known that other "greenhouse gases" are also of importance, notably methane and nitrous oxide (Wang et al. 1976) and chlorofluorocarbons (Ramanathan 1975). The first two are produced by microbes, and are often influenced greatly by human activities; the third is produced by humans directly. Henderson-Sellers (1990) has provided a very recent review. Depletion of stratospheric ozone by chlorofluorocarbons is another example of global influence (Molina & Rowlandson 1974). The importance of pollution studies to the fundamental understanding of biogeochemical cycles has been emphasized by Goldberg (1974).

The origin of life

An interesting early view of the origin of life was expressed almost two centuries ago by Buffon (1779). According to Roger (1973), Buffon claimed that organic molecules (his name for the ultimate building blocks of organic matter) were born through the action of heat on aqueous, oily, and ductile substances suitable to the formation of living matter. The physicochemical conditions that made such formation possible were peculiar to that period of the earth's history; consequently spontaneous generation of living matter and organized living creatures could no longer occur. Darwin (1871) expressed a similar view in rather more detail, by pointing out that if organic molecules prerequisite to the origin of life were formed spontaneously today, they would inevitably be scavenged immediately by already living organisms:

> "It is often said that all the conditions for the first production of a living organism are now present, which could ever have been present. But if (and oh! what a big if!) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, &c., present, that a proteine compound was chemically formed ready to undergo still more complex changes, at the present day such matter would be instantly devoured or absorbed, which would not have been the case before living creatures were formed".

At almost the same time Cohn (1872) speculated that life on earth may have originated from a bacterium transported under intense cold from elsewhere in space; this was his alternative to Wyville Thompson's suggestion of transport to earth by meteorite.

The conventional scientific view during the early part of the nineteenth century was that organic compounds required for their formation some kind of "vital force". In considering the origin of life, therefore, it was important to know whether this was true, or whether organic compounds could be formed readily from inorganic precursors. The first major discovery in this area is often said to be the formation of urea from its inorganic isomer ammonium thiocyanate by Wöhler in 1828 (Teich 1970), but many historians of science dispute this as not representing a true synthesis (Keen 1976). Partington (1948), for instance, cites the making of acetic acid by Kolbe in 1844 as the first true organic synthesis. According to Le Chevalier and Solorotovsky (1965), it was Berthelot's (1860) textbook entitled *Organic Chemistry Founded Upon Synthesis* that "dealt a lethal blow to the theory of vital force". A thoughtful analysis of the "vital force" issue has been made by Brooke (1968). Buchner's (1897) discovery that yeast extract could convert sugar to alcohol, as an organic catalyst or enzyme acting outside a living organism, made it even more plausible that organic life could arise from non-living molecules.

In the early twentieth century Henderson (1913) stated that "a half century has greatly diminished the number of substantial biologists who look forward to (life's) scientific explanation, and the greatest chemists have ever shared such a view". Nevertheless his classic book, *The Fitness of the Environment*, took up scientifically a pre-Darwinian theological theme that the universe and its properties had been formed (by the Deity who created it) to be suitable for vegetable and animal life (Whewell, 1834; see also Dumas 1841). He thus prepared scientists to think again about such matters as the origin of life. Indeed, as Wald (1958) has said: "this is a book about the fitness of the environment for the origin of life".

Henderson focussed chiefly on the properties of water and various chemical elements that made them particularly suitable for the development of living systems. He did not concern himself with the sort of atmospheric chemistry that would both favor life and be changed by it, as did Koene (1856) before him and Oparin (1924) and Haldane (1929) after him. He did, however, foresee that: "a possible abode of life not unlike the earth apparently must be a frequent occurrence in space" (see also Lucretius undated, Book II). At about the same time the Chamberlins (1908) were speculating about conditions early in planetary history that might have favored the synthesis of organic molecules prerequisite for living organisms. The known environmental limits for present-day life on earth have been described by Vallentyne (1963).

The first substantial speculations about the origin of life were those of Oparin (1924) and, independently, Haldane (1929; see also Slater 1951). They considered not only the prebiotic synthesis of simple organic compounds to form a primitive "soup" that was eventually fed upon heterotrophically by the first organisms, but also the formation of polymers and possible primitive forms of cellular organization. A reasonably plausible prebiotic synthesis of diverse, complex organic molecules was first accomplished by Miller (1953), following a line suggested by his mentor Urey (1952). Cloud (1968) has summarized evolutionary interactions among biosphere, atmosphere, lithosphere, and hydrosphere on the primitive earth, and Kvenvolden (1974) has compiled a collection of bench-mark papers.

Alternatively, Chamberlin & Chamberlin (1908) suggested — on the basis of the likely chemistry of infalling planetesimals as well as the organic content of carbonaceous meteorities — that extraterrestrial sources may have been important as a source of prebiotic organic matter on planet Earth. This view is still given serious consideration (Anders 1989; Zhao & Bada 1989; Chyba et al. 1990). In addition, a quite different theory has recently been put forward: that pyrite formation from hydrogen sulfide and ferrous ions may have been the energy source for a chemo-autotrophic instead of a heterotrophic origin of life (Wächterhäuser 1988a, b; see also Popper 1990, and Russell, Hall & Gize 1990).

Pasteur, in the same year that he refuted earlier ideas of spontaneous generation (1861a), made an observation that was to be highly relevant to later studies on the origin of life, by demonstrating that microorganisms can live in anaerobic environments entirely lacking in oxygen (1861b). Such a reducing atmosphere has generally been considered a prerequisite for prebiotic organic synthesis. Five years earlier, Koene (1856; see also Phipson 1893) had suggested that the primitive atmosphere was lacking in oxygen and that the first organisms must have been photosynthetic anerobes. Over vast periods of time these organisms prepared the surface of the earth for higher forms of life by releasing oxygen to the atmosphere, and at the same time lowering greatly the concentration of atmospheric carbon dioxide by the deposition of vast amounts of fossilized carbon.

Even earlier Spencer (1844) — after reading Dumas (1841) — had suggested that much of the atmosphere's oxygen must have come from the excess, over geologic time, of photosynthesis over respiration, given the storage of vast amounts of carbon in coal and other geological deposits. The role of oxygen, released by the gradual development of the earth's vegetation, in the oxidation of iron in all but the earliest rock formations was noted briefly by Phipson (1893) and later in much more detail by Lane (1917) and Macgregor (1927); see also Cloud (1983). The production of a steadily more oxidizing atmosphere by photosynthetic autotrophs, accompanied by the locking up of vast amounts of carbon in sediments and coal deposits, was not assessed quantitatively until more than a century after Spencer and Koene (Berkner & Marshall 1965).

Johnston (1843) suggested that human use of coal deposits would lead eventually to an increase in atmospheric carbon dioxide, and Phipson (1893) implicated forest clearance as well. Neither recognized, as did Arrhenius (1896), and Callendar (1938, 1949) almost half a century later, that this would cause climatic warming.

Another source of oxygen to the evolving atmosphere could have been the photolytic dissociation of water molecules in the uppermost atmosphere, with the lighter hydrogen escaping to space. This was mentioned by Berkner and Marshall (1965); according to Broecker (1985) its importance relative to biotic oxygen production still cannot be assessed. Veizer (1988b) has suggested yet another possibility, that a decline in the supply of reductants such as divalent iron and manganese from the earth's mantle may have been a significant contributor to the early build-up of atmospheric oxygen.

Major conceptual advances — a chronology

In the long series of conceptual advances involved in the development of biogeochemistry, the following are among those of greatest significance:

1. the nature of the hydrologic cycle (Halley 1687);
2. the role of carbonic acid in rock and soil weathering (Cavendish 1767; Thaer 1810; Davy 1813);
3. the interactive roles of plants and animals in gaseous metabolism on a global scale (Priestley 1772);
4. the role of solar radiation in driving such gaseous metabolism (Ingenhousz 1779);
5. the unification of theories of plant nutrition (de Saussure 1804);
6. the wholly inorganic nutrition of green plants (de Saussure 1804; Sprengel 1839; Liebig 1840);
7. the role of microbes in organic decomposition (Schwann 1837; Cagniard-Latour 1838);
8. the global significance of the biogeochemical cycles of carbon and nitrogen powered by solar energy (Dumas 1841; Dumas & Boussingault 1844);
9. the recognition that the primitive atmosphere was anaerobic, and that the gradual evolution of plants, accompanied by the locking up of their residues as fossilized carbon, was responsible for an atmosphere rich in oxygen (Spencer 1844; Koene 1856);
10. the major role of microbial decomposers in biogeochemical cycles (Cohn 1872);
11. the recognition of the qualitative equality of the biosphere with the lithosphere, hydrosphere and atmosphere (Suess 1875; Vernadsky 1924, 1926);
12. the involvement of specific micro-organisms in the cycles of elements such as nitrogen, sulfur, and iron (Winogradsky 1887—1894; and others);
13. the fitness of the environment for living organisms (Henderson 1913);
14. the plausible origin of life through prebiotic synthesis of organic molecules in a primitive reducing environment, and their consumption initially by heterotraphic organisms (Oparin 1924; Haldane 1929; Miller 1953);

15. the large-scale regulation of biogeochemical cycles in general by the biota (Vernadsky 1924, 1926; Redfield 1934, 1958); and
16. the view of humanity as a major geological agent (Vernadsky 1945; Hanya & Akiyama 1987).

It should be emphasized in conjunction with this list of conceptual advances that solar energy plays a dominant role in driving not only the carbon and nitrogen cycles mentioned in item (8) above but also many other processes important in biogeochemistry:

- the hydrologic cycle, the ocean currents, and the winds;
- the synthesis of prebiotic organic molecules (if such were not provided by comets);
- the weathering cycle, as a result of organic acids (including carbonic acid) produced by living organisms and especially by microbial decomposition; and
- various redox cycles dependent on the oxygen formed by photosynthesis and on reduced substances produced as a result of organic decomposition.

Concluding remarks

Biogeochemistry represents a very gradual coalescence and eventual synthesis of three diverse disciplines into a recognized branch of science. In it the most fundamental aspects of knowledge of the planet Earth are being studied by scientists at the same time, and in the same way, that they seek a better understanding of extremely important practical problems. Most notable among such problems are those caused by human manipulation of biogeochemical cycles on nature's own scale. The challenge that faces humanity is nothing less than the maintenance of the balance of nature represented by those cycles, which will require a greatly improved understanding of planetary biogeochemistry.

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