MINERAL CYCLES

Although the biosphere is mainly composed of hydrogen, carbon, nitrogen and oxygen, other elements are essential constituents of living matter. Notable among them are phosphorus and sulfur

by Edward S. Deevey, Jr.

The periodic table lists more than 100 chemical elements. Yet ecologists have defined the biosphere as the locus of interaction of only four of them: hydrogen, carbon, nitrogen and oxygen. In the periodic table these four are numbered 1, 6, 7 and 8. This definition, although it deals handsomely with much of the chemistry of life, turns out to be a little too restrictive. But when we enlarge it to include phosphorus and sulfur, as we do here, we have gone no farther up the table than element No. 16. From this it should be apparent that no element lighter than sulfur can be ignored, either by ecologists or by anyone else. The fact is that most human problems—all environmental ones, anyway—arise from the exceptional reactivity of six of the 16 lightest elements.

Because our definition of the biosphere is based more on reactivity than on atomic number, it is a minimum definition. It is not intended to exclude heavier elements that react with the primary six. As a matter of empirical fact it is known that no element lighter than iron and cobalt, elements No. 26 and No. 27, is unimportant to the biosphere. Beyond copper, No. 29, there are a few conspicuously reactive elements such as the heavy halogens bromine and iodine. Most of the heavies are metals, such as gold, mercury and lead (Nos. 79, 80 and

82), however, and their main effect on the lightweight biosphere is to depress it. Toward the end of the periodic table are some famously overweight metals whose tendency to lighten themselves has disastrous effects on any light substances that get in the way.

In order to understand how it is that many elements interact with the essential six, one must briefly reflect on the biosphere as a whole. Because the biosphere is so reactive, its influence on the hydrosphere, the lithosphere and the atmosphere is inversely proportional to its mass. This mass is very small. An average square centimeter of the earth's surface supports a tiny amount of biosphere: 580 milligrams, less than the weight of two aspirin tablets. A roughly equivalent mass is found in the same area of hydrosphere a single centimeter deep, or in a paper-thin slice of lithosphere. Still, from a worm's-eye view the biosphere has real substance, particularly on land, where it amounts to 200 oven-dry tons on an average hectare.
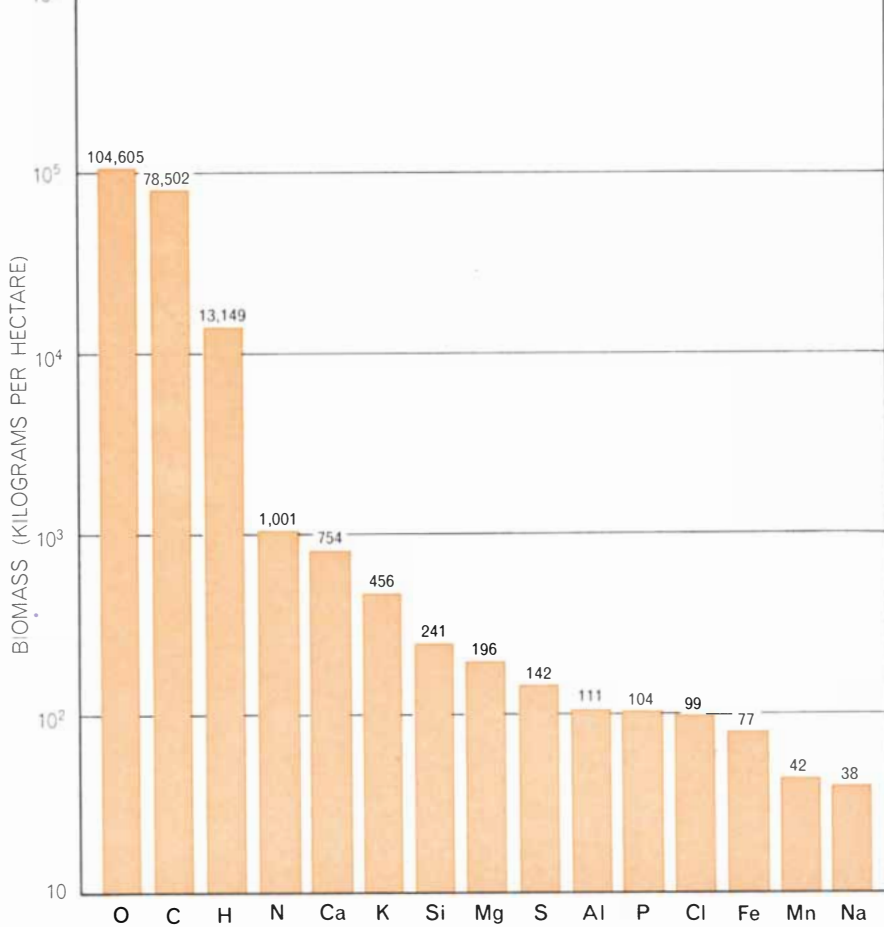
A glance at a partial list of the elements that compose the biosphere shows why hydrogen, oxygen, carbon and nitrogen dominate conceptions of biosphere chemistry. Together these elements constitute all but a tiny fraction of the average terrestrial vegetation, which in turn constitutes more than 99 percent of the world's standing crop. The quantities are shown in the chart on the next page, based on a splendid compilation by L. E. Rodin and N. I. Basilevich. What I have done is to weight their chemical analyses in proportion to the kinds of land area they represent. The weighting factors, for desert, forest, tundra and so on, are the same ones I used to calculate the earth's production of carbon in an earlier article ["The Human Population," by Edward S. Deevey, Jr.; SCIENTIFIC AMERICAN, September, 1960]. Inciden-

tally, on the basis of this new calculation terrestrial carbon production comes out at 65×10^9 tons of carbon per year, about 15 percent more than the figure I computed before.

What chemical compounds do these elements form? The standard way to determine the chemical composition of an organic substance is to burn it and collect the products. The list of components that results from this destructive procedure expresses some obvious facts, such as the familiar one that the biosphere is mainly carbon dioxide and water. Nitrogen, a major constituent of protein, seems surprisingly scarce (about five parts per 1,000 by weight) until we remember that the biosphere is chiefly wood, that is, not protein but the carbohydrate cellulose.

The destructive procedure would also leave a smudge, about 12 parts per 1,000 of the total, loosely called ash. Its dominant elements calcium, potassium, silicon and magnesium have important biochemical functions. One atom of magnesium, for instance, lies at the center of every molecule of chlorophyll, and silicon, the stuff of sand, is obviously useful for building hard structures. Iron and manganese also play central roles in the biosphere, a fact that could not be guessed from their position in our chart. In biochemistry as in geochemistry the importance of these elements is in governing oxidation-reduction reactions, but the masses involved are small. As for the major cations—ions of such elements as calcium, potassium, magnesium and sodium—new insights have just begun to flood in with their discovery in rainwater.

There are many other metallic elements that appear in trace amounts. Not all of them are listed in the chart because some could be accidental con-

COMPOSITION OF THE BIOSPHERE is dominated by oxygen, carbon and hydrogen, as is indicated by the bars in this logarithmic chart. The units are kilograms per hectare of land surface. Key to the symbols for the chemical elements is at the bottom of the page.

charts on the opposite page can serve as a substitute, we can cast a Holmesian eye over the list. Our thinking will be more productive if we compare the composition of the biosphere with the composition of the lithosphere, the hydrosphere and the atmosphere. For this comparison all four of the "spheres" in the chart are converted from parts by weight to atoms per 100 atoms. (The masses of the four spheres being very different, these percentages will give no idea of the earth's mean or total composition.)
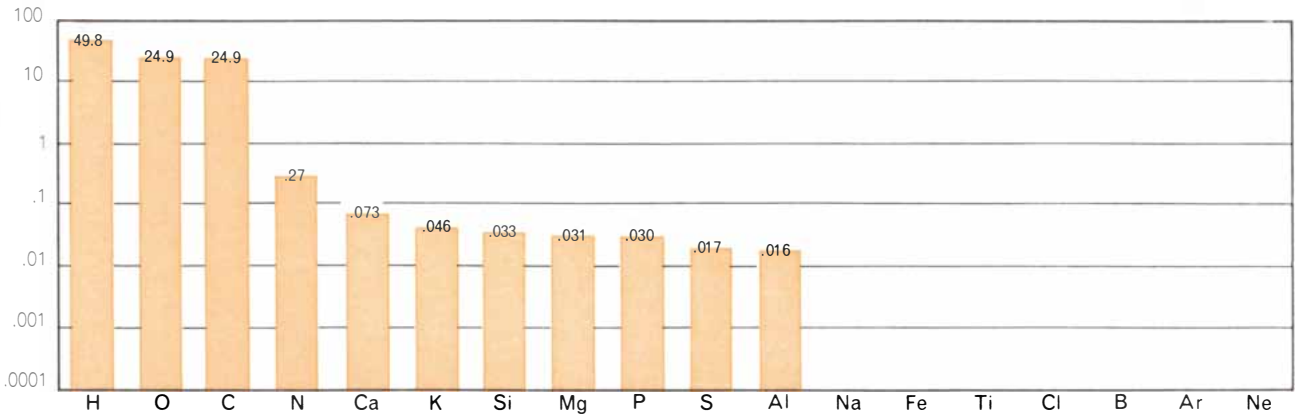
At first glance the four spheres do not seem to belong in the same universe. Not surprisingly, the lithosphere turns out to be a slightly metallic aluminum silicate. ("Here is no water but only rock/Rock and no water and the sandy road," as T. S. Eliot put it in "The Waste Land.") The biosphere, in sharp contrast, is both wet and carbonaceous. A single class of compounds, formaldehyde (CH_2O) and its polymers, including cellulose, could make up more than 98 percent of the total (by weight). Still, even when it is dried in an oven at 110 degrees Celsius, life is mainly hydrogen and oxygen, in close approximation to the proportions known as water. In other words, the biosphere is notably carboxylated: it is both more hydrated and chemically more reduced (hydrogenated) than is the lithosphere from which, in some sense, it came. Among the 10 most abundant elements of the lithosphere there is no obvious source for life's carbon. Hydrogen is also fairly far down the list for rock (and would be farther down if I had not copied some old figures from Frank W. Clarke's *The Data of Geochemistry,* which overweight the acidic rocks of continents).

Even the elementary Dr. Watson might conclude that life's hydrogen comes from some inorganic hydrate—water, for instance—and indeed the hydrosphere provides an ample and ready supply. This will not work for carbon, though, and in trying to account for carboxylation we can make a deduction that is truly elementary in the Holmesian, or nonobvious, sense. We begin
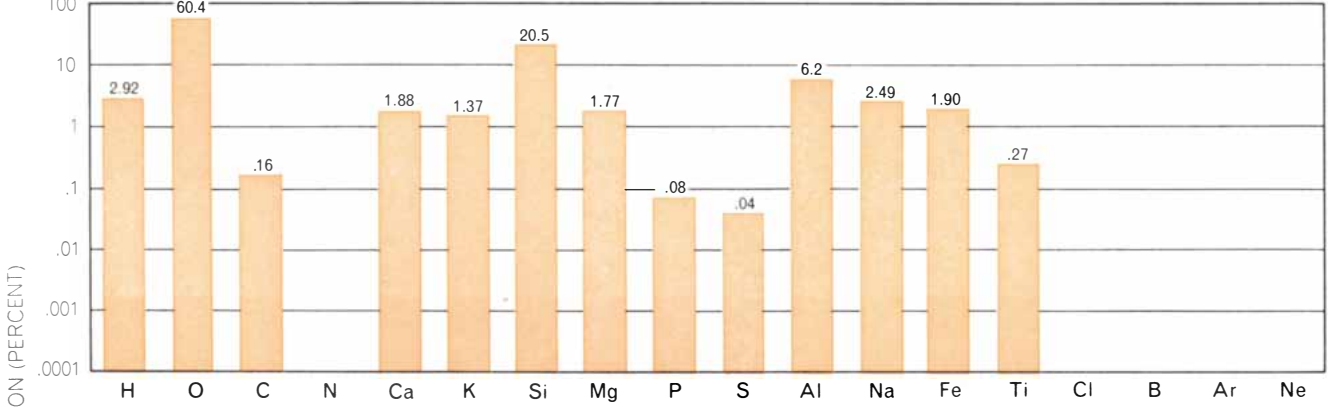
taminants. There remain two, sulfur and phosphorus, each amounting to more than 10 percent of the nitrogen, that do not look like contaminants. To ignore these elements as "traces" or even to think of them as "ash" or "inorganic" elements is to misconstrue the chemical architecture of the biosphere.

A listing of elements and compounds does not reveal that architecture. There is a big difference between a finished house and a pile of building materials. Nevertheless, a list is a useful point of departure. If it is made with care, it can protect ecologists from the kind of mistake that architects sometimes make, such as forgetting the plumbing.

When a list contains as much information as a shopping list—when it shows amounts as well as kinds of materials—some conclusions can be drawn from the relative proportions. (As a former bureaucrat I have learned that a "laundry list" contains even more ambiguous information than a "shopping list"; good bureaucrats keep both.) If a housewife's shopping list showed a pound of coffee, four pork chops and 100 pounds of

sugar, for example, we would know that madame is either hoarding or running a private business. If she also wants a ton of flour, she is evidently baking, not distilling. The inclusion of two dozen light bulbs would suggest that she works mainly at night, but the listing of 10 dozen light bulbs would point to a faulty generator.

As it happens, this kind of semiquantitative ratiocination was applied to ash, and to biogeochemistry, by the master of nonobvious deduction, Sherlock Holmes. Unfortunately no copy of his analytical results (the monograph on cigar ash, cited in Chapter 4 of "A Study in Scarlet") has yet come to light. If the

Al	ALUMINUM	Cl	CHLORINE	Mn	MANGANESE	P	PHOSPHORUS
Ar	ARGON	Fe	IRON	N	NITROGEN	S	SULFUR
B	BORON	H	HYDROGEN	Na	SODIUM	Si	SILICON
C	CARBON	K	POTASSIUM	Ne	NEON	Ti	TITANIUM
Ca	CALCIUM	Mg	MAGNESIUM	O	OXYGEN		

RELATIVE AMOUNTS OF ELEMENTS in the biosphere, the lithosphere, the hydrosphere and the atmosphere are presented in the charts on the opposite page. Here, however, amounts are given not as kilograms per hectare but as atoms per 100 atoms. Here again scale is logarithmic to show less abundant elements, which otherwise could not be compared.
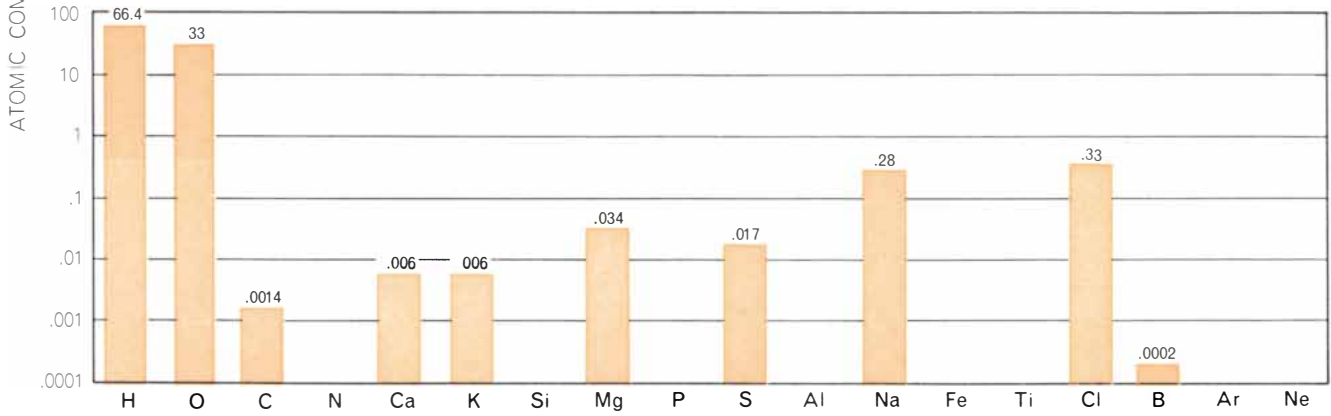
BIOSPHERE

ATOMIC COMPOSITION (PERCENT)

H	O	C	N	Ca	K	Si	Mg	P	S	Al	Na	Fe	Ti	Cl	B	Ar	Ne

Values: H 49.8, O 24.9, C 24.9, N .27, Ca .073, K .046, Si .033, Mg .031, P .030, S .017, Al .016

LITHOSPHERE

Values: H 2.92, O 60.4, C .16, Ca 1.88, K 1.37, Si 20.5, Mg 1.77, P .08, S .04, Al 6.2, Na 2.49, Fe 1.90, Ti .27

HYDROSPHERE

Values: H 66.4, O 33, C .0014, Ca .006, K 006, Mg .034, S .017, Na .28, Cl .33, B .0002

ATMOSPHERE

Values: O 21, C .03, N 78.3, Ar .93, Ne .0018

© 1970 SCIENTIFIC AMERICAN, INC
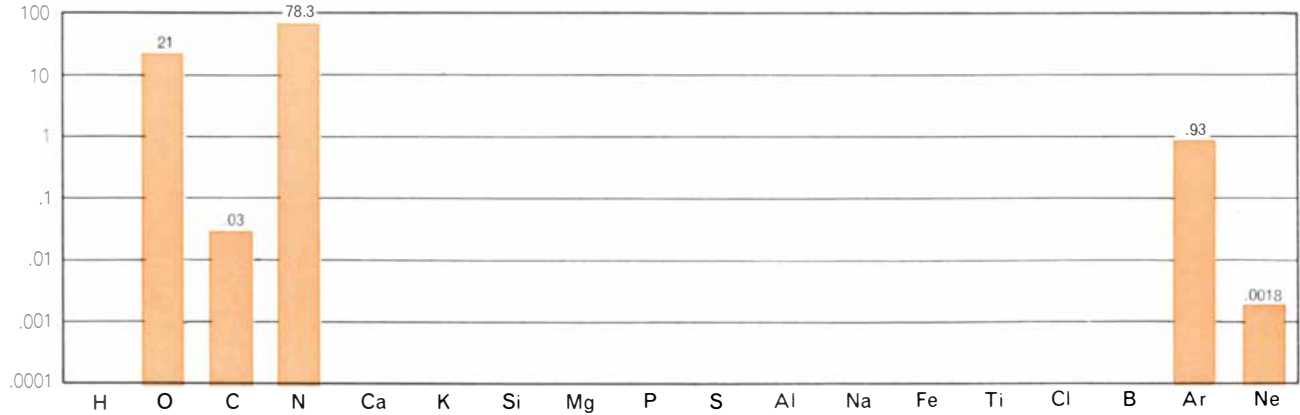
again by noting that life is mainly aqueous, and also that it concentrates carbon in proportions far greater than those in any accessible source. Is it possible that these facts are related? If they are, what do we know about water that throws any light on this relation and on the behavior of carbon? (At this point a lesser detective might reach for the carbonated water and pause for a reply.)

Instead of guessing, Holmes would proceed with his review of the evidence. Water, of course, is continuously recycled near the earth's surface, by runoff, evaporation and condensation. That is, it flows in rivers from the lithosphere to the hydrosphere, and it returns to rewash the land by way of the atmosphere. Any water-soluble elements are certain to track this cycle at least partway, from land to sea, although they may find the sea to be a sink, as boron does. If they

are to get out, they can reach the land as part of an uplifted sea bottom, but that is a chancy mechanism. Recycling is both faster and surer if the element is volatile as well as soluble, so that one of its compounds can move landward through the atmosphere as water does.

In the biosphere there are at least three elements besides those of water—carbon, nitrogen and sulfur—that fall in this doubly mobile class. Among their airborne compounds are carbon dioxide (CO_2), methane (CH_4), free nitrogen (N_2), ammonia (NH_3), hydrogen sulfide (H_2S) and sulfur dioxide (SO_2). It is interesting that when carbon, nitrogen and sulfur are recycled, their valence changes. It may not be an accident that all three are more reduced in the biosphere than they are in the external world. Be that as it may, they all seem

to belong to the biosphere, which is otherwise mainly water. Hence all three must be recycled together, *along with the water* (said Holmes with an air of quiet triumph), if the earth is to sustain its most unusual hydrate. ("And what is that?" I asked. "Why, *carbohydrate,* of course," said Holmes.)

I call this deduction nonobvious, because in an obvious variant it has become so familiar as to inhibit thought. The outlines of the carbon cycle, in organisms at any rate, have been evident since Joseph Priestley's day. The critical step, "obviously," is the photosynthetic reduction of carbon dioxide. That reaction is a hydrogenation, yielding formaldehyde. Its source of hydrogen is the dehydrogenation of water, with the liberation of oxygen. The chemical energy thus captured, by a process unique to green plants, becomes available, inside
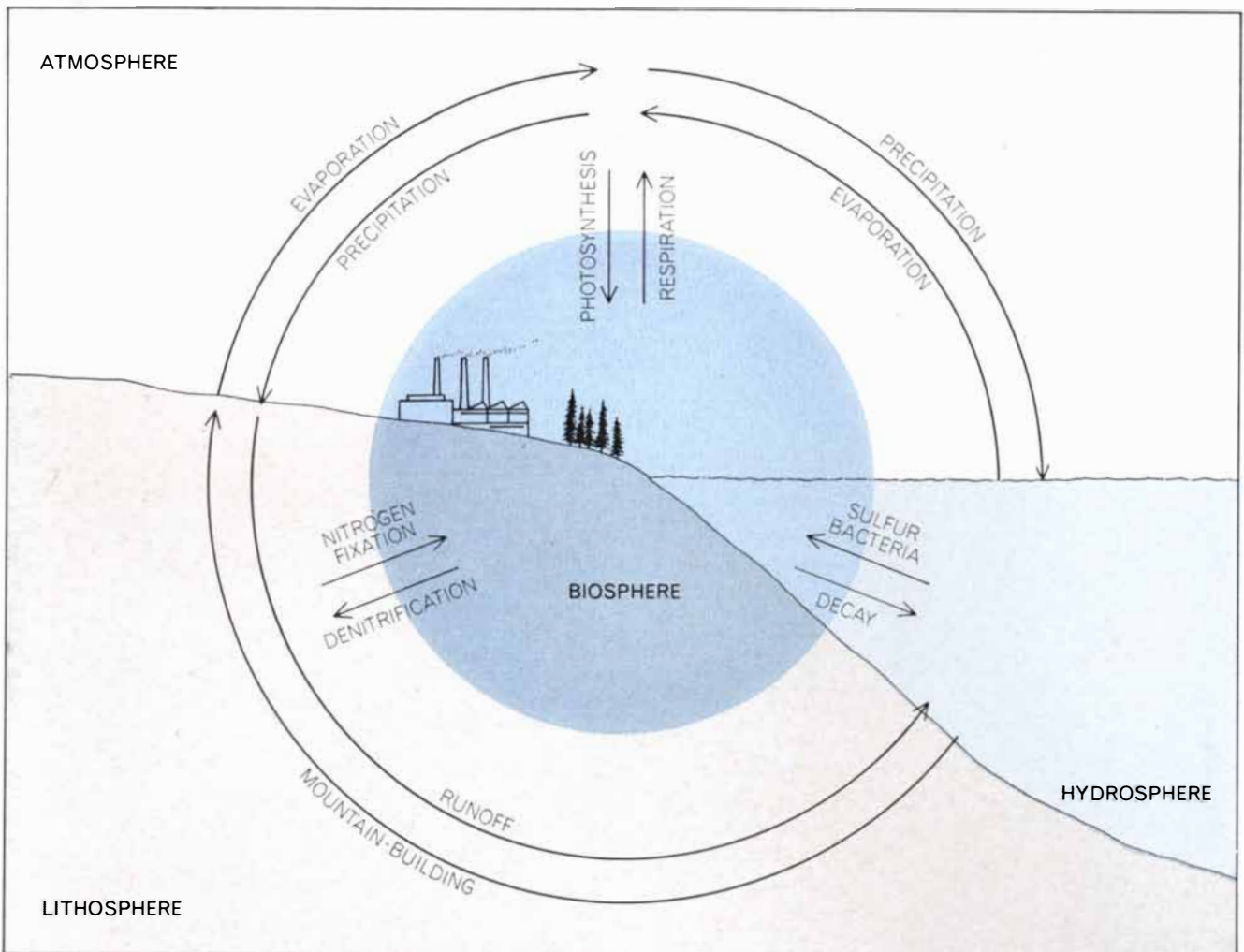
CARBOXYLATION CYCLE supplies the biosphere with carbon, oxygen, hydrogen, nitrogen and sulfur by carrying them from the lithosphere, the hydrosphere and the atmosphere. Curved arrows at upper right and left represent any or all of these five elements that travel from the atmosphere to the lithosphere or to the hydrosphere by precipitation, or back to the atmosphere by evaporation. Curved arrows at bottom indicate direct routes between the lithosphere and the hydrosphere such as runoff, mountain-building and the hydration of minerals. Biosphere (*color*) captures these elements by providing alternative routes. Top pair of straight arrows show exchange between the biosphere and the atmosphere, carbon, for example, being exchanged by photosynthesis and respiration. Pair of straight arrows at right show exchange between the biosphere and the hydrosphere, that of sulfur being mediated by bacteria. Pair of arrows at left indicate soil-biosphere exchanges including nitrogen fixation and denitrification by microorganisms.

the cell, for all other vital reactions (does it not?). After its utilization, which includes consumption by animals, the re-oxidized carbon dioxide can rejoin any geochemical cycles it likes.

All other vital reactions? Well, not quite all. The chemical reduction of nitrogen is one hydrogenation essential to green plants that they cannot perform for themselves. As one result, even elementary textbooks admit, the carbon and nitrogen cycles are necessarily interdependent. Without microorganisms that take nitrogen from the air and hydrogenate it (they can use carbon dioxide as a carbon source), all the nitrogen in the biosphere would soon appear in the atmosphere in stable, oxidized form. (The textbooks concede this point somewhat grudgingly, because much of the biological nitrogen cycle operates below the oxidation state of free nitrogen by the reversible reduction of nitrate and nitrite to amino acids and ammonia.)

If, as it turns out, sulfur too is recycled by way of the hydrologic cycle but independently of green plants, it becomes necessary to look beyond carbon and water for the clue to carboxylation. In other words, some biologists are not unlike architects who forget about the plumbing. In their preoccupation with carbon dioxide reduction as the starting point for cell biochemistry they tend to forget two other hydrogenations, those of sulfur and nitrogen, that are just as important.

A check is needed here, to be sure that these two elements are really intrinsic to the biosphere. In the case of sulfur the fig ures show it to be very scarce, and if it is a contaminant, the whole argument might be superflous. Sulfur, however, is no contaminant; no protein can be made without it. In fact, sulfur is the "stiffening" in protein. A protein cannot perform its function unless it is folded and shaped in a particular way. This three-dimensional structure is maintained by bonds between sulfur atoms that link one segment of a protein molecule to another. Without these sulfur bonds a protein would coil randomly, like a carelessly dropped rope.

The reason for the apparent scarcity of sulfur is the low protein content of woody tissue; any animal body contains much more. Cod-meal protein, for example, with 2.26 percent of the sulfurous amino acid methionine, has the empirical formula $H_{555}C_{265}O_{174}N_{83}S$. Although other proteins differ in the proportions, the substance of the biosphere must always contain these fiv e elements.
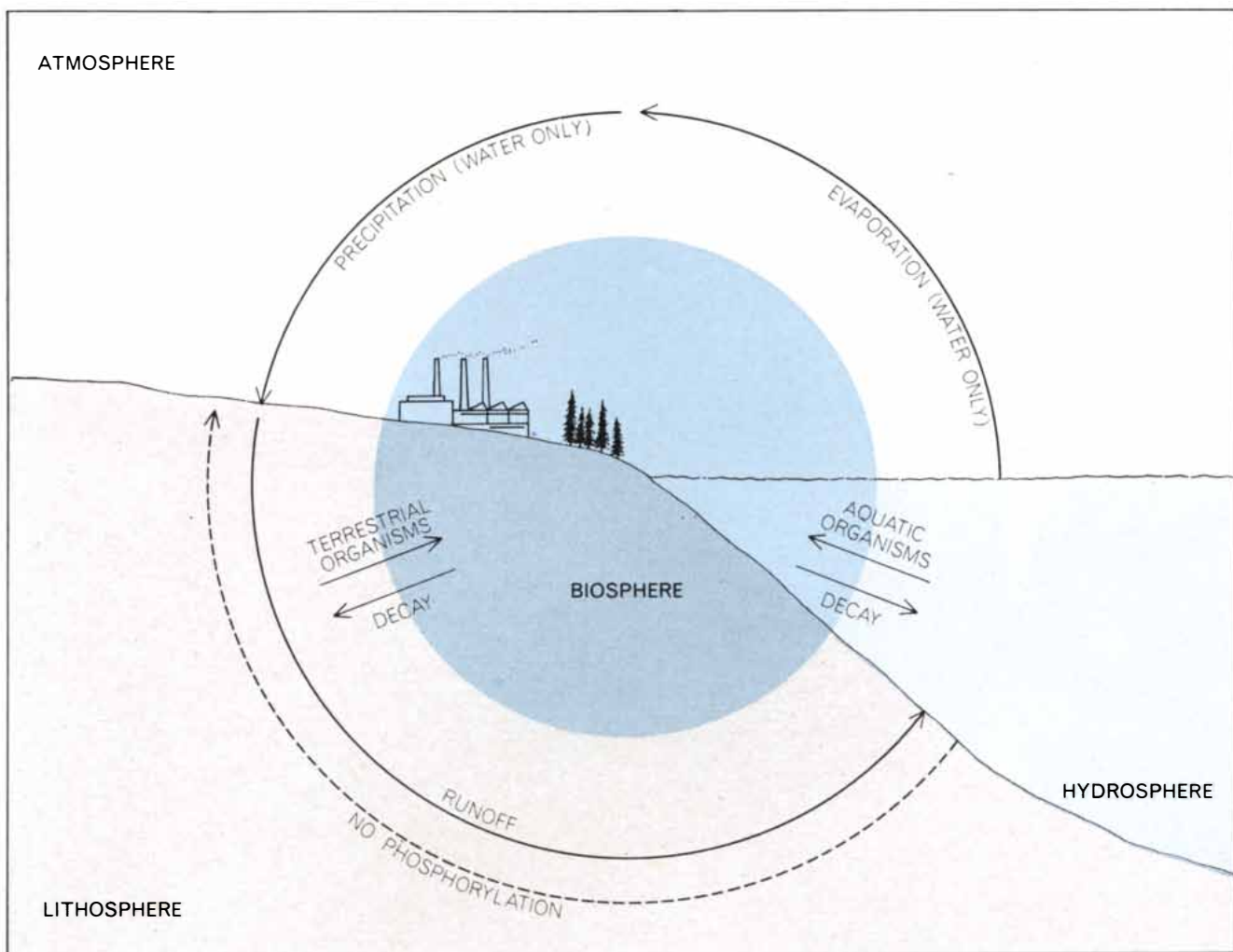
SOLUBLE-ELEMENT CYCLE is followed by minerals such as phosphorus that dissolve in water but are not volatile, that is, they are not carried into the air by evaporation (*curved arrow at right*). The curved arrow at bottom shows that phosphorus is washed from the lithosphere into the hydrosphere by runoff from rainfall (*curved arrow at top left*). The broken curved arrow at bottom indicates that phosphorus in the hydrosphere does not normally return to the lithosphere and that therefore the ocean would become a phosphorus sink. The upper straight arrows at right and left, however, show that the organisms of the biosphere impede this development by absorbing some phosphorus. The straight arrows pointing from the biosphere to the lithosphere and to the hydrosphere indicate the decay of organic matter. On land the soluble-element cycle is continued when decay returns phosphorus to the lithosphere. Without an atmospheric link from ocean to land, however, the cycle is actually a one-way flow with interruptions.

It has been known for many years that sulfur is recycled from the sea back to the land by way of the atmosphere. Calculations confirming this fact by Erik Eriksson of the International Meteorological Institution show that the world's rocks contain too little sulfur, by a factor of about three, to account for the sulfate delivered annually by the world's rivers. About three-quarters of the total budget (in 1940) is therefore inferred to have come from the atmosphere. Of this amount about a third, or a quarter of the total, can have come from industrial sources—better known these days as "sulfur dioxide pollution." The other two-thirds, or half the total budget as of 1940, must take some more natural route from the hydrosphere.

When Eriksson wrote, in 1959, the question was still open, whether the cycled sulfur reaches the land as an aerosol from sea spray or as hydrogen sulfide (H_2S). If the principal volatile compound is a sulfide, it must be made by sulfate-reducing bacteria, because no other "room temperature" source of sulfide is known. M. LeRoy Jensen and Noboyuki Nakai, then working at Yale University, settled this question in favor of the bacteria, by showing that atmospheric sulfur, although it falls in rain as sulfate, contains less of the heavy isotope sulfur 34 than seawater sulfate does. What the natural isotopic label shows is that the sulfate in rain entered the atmosphere not as sea spray but as sulfide, there to be oxidized to sulfur dioxide. After dissolution in rainwater, sulfate (and sulfuric acid) are formed.

The principle of the Jensen-Nakai demonstration is worth noticing, because it applies to the cycling of carbon as well as of sulfur, and barring some technical difficulties it could also apply to nitrogen. The route followed through oxidation-reduction reactions by ordinary sulfur (sulfur 32) is analogous to the route followed by ordinary carbon (carbon 12) in photosynthesis. These lighter, more mobile isotopes appear preferentially in reduced compounds such as hydrogen sulfide, methane and formaldehyde. At equilibrium in a closed system the oxidation products (carbon dioxide or sulfate) have correspondingly more of the heavier isotopes carbon 13 and sulfur 34 without change in the total mass. If, however, a reduced and isotopically light product escapes, as hydrogen sulfide does from the hydrosphere, equilibrium is not attained, and if the gaseous product is trapped and reoxidized in a separate system, the oxide (sulfur dioxide in this case) remains light.

Exactly where within the hydrosphere
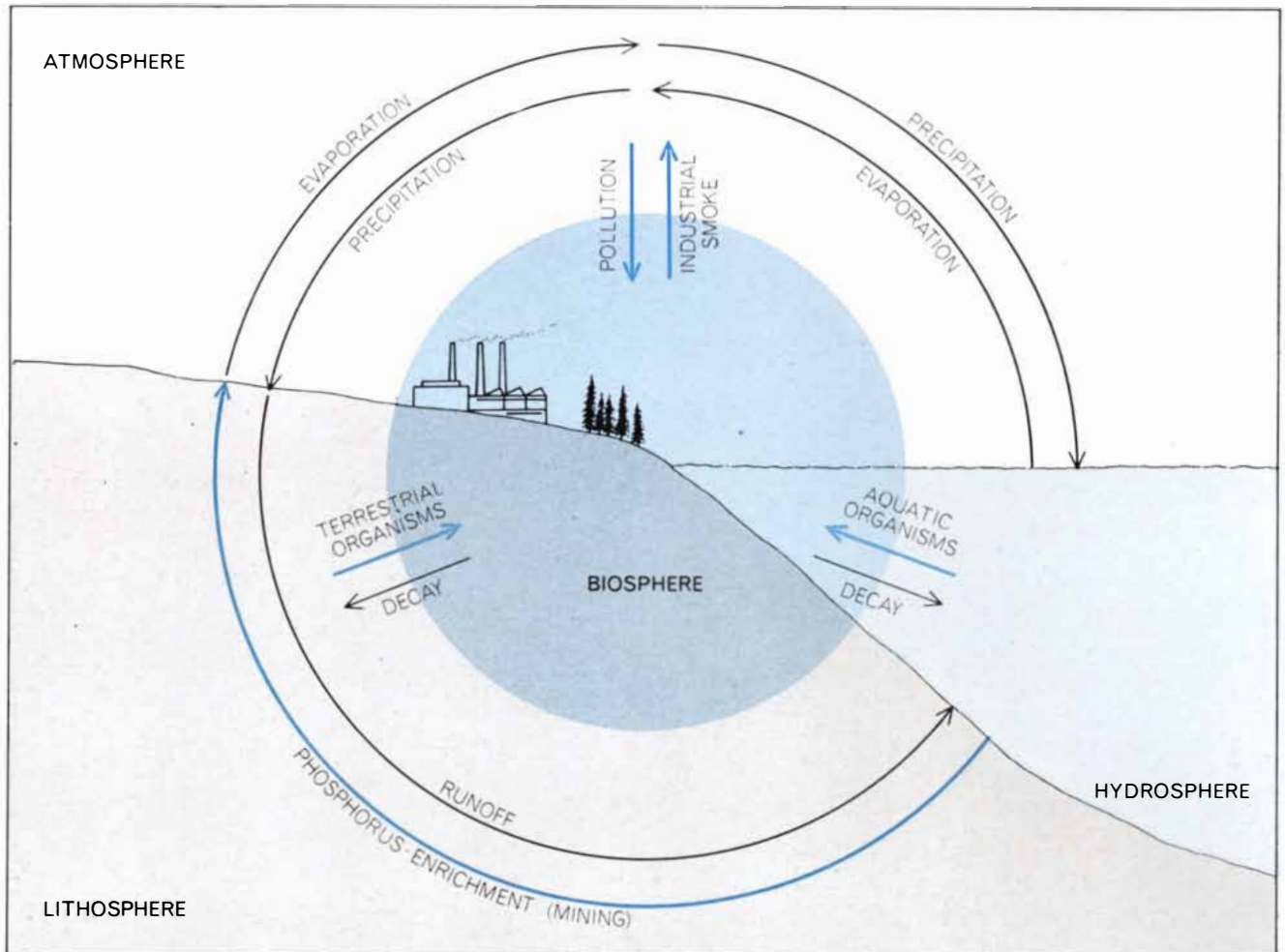
EUTROPHICATION OF THE BIOSPHERE is the intensive cycling of phosphorus, nitrogen and sulfur. Colored curved arrow at bottom represents beginning of the process: the human use of phosphorus as fertilizer, which returns phosphorus to the lithosphere, thereby reversing the phosphorus cycle. Colored straight arrows at left and right indicate that phosphorus added to the lithosphere (and to phosphorus already present) is then taken up by phytoplankton and other organisms as well as by crops. Other straight arrows at right and left show that phosphorus and other elements return to the lithosphere and hydrosphere by decay. Once phosphorus is plentiful, scarcity of nitrogen and sulfur may limit eutrophication. Arrows at top represent carbon dioxide, nitrate and sulfate from industrial activity rising into atmosphere and falling in rain. They may promote eutrophication of dry land since vegetation may reabsorb them from air and soil. Curved arrows indicate routes followed by elements that are both soluble and volatile.

	(KILOGRAMS PER HECTARE)	(KILOGRAMS PER HECTARE)	(KILOGRAMS PER HECTARE)
CALCIUM (Ca^{++})	2.8 →	3.0 →	+0.2
MAGNESIUM (Mg^{++})	1.1 →	1.8 →	+0.7
SODIUM (Na^+)	2.1 →	4.2 →	+2.1
POTASSIUM (K^+)	1.8 →	1.1 →	−0.7
CHLORIDE (Cl^-)	2.8 →	4.1 →	+1.3
SULFATE (SO_4^{--})	30.0 →	29.4 →	−0.6
AMMONIUM (NH_4^+)	2.1 →	0.3 →	−1.8
NITRATE (NO_3^-)	6.7 →	4.8 →	−1.9
SILICON DIOXIDE (SiO_2)	1.9 →	20.9 →	+19.0
ALUMINUM (Al^{+++})	−−	1.4	+
BICARBONATE (HCO_3^-)	0	0.7 →	+0.7
TOTAL	51.4 →	71.7 →	+20.3

EUTROPHICATION OF DRY LAND is indicated by the imbalance between the quantity of certain ions falling from the atmosphere on the forest at Watershed No. 6 at Hubbard Brook in New Hampshire and the output of these ions in the brook itself. Input (*smaller arrows at left*) of some elements such as calcium, magnesium and sodium is smaller than the output (*larger arrows at right*). The input of potassium, ammonium, sulfate and nitrate, however, is larger (*larger arrows at left*) than output of these substances (*smaller arrows*). The excess of input indicates that the forest is utilizing these four substances as it grows.

a

DRY MATTER — 199,725

ASH — 2,468

NITROGEN — 1,001

BIOMASS (KILOGRAMS PER HECTARE)

b

DRY MATTER — 13,381 / 11,233 / 2,148

ASH — 489 / 410 / 79

NITROGEN — 162 / 124 / 38

BIOMASS (KILOGRAMS PER HECTARE PER YEAR)

OTHER EVIDENCE FOR EUTROPHICATION is provided by studies of the earth's standing crop on dry land. In *a* biomass, or weighable dry matter that includes ash and nitrogen, totals about 200,000 kilograms per hectare. In *b* the first set of bars shows that the dry matter increases in an average year by 13,381 kilograms per hectare (*color*). About 11,000 kilograms is lost in the form of litter fall (*gray*) such as fallen leaves and branches, giving a "mean increment" of 2,148 kilograms per hectare (*open bar*). The second set of bars shows that ash increases by 489 kilograms per hectare (*color*) but is reduced by litter fall (*gray*) to 79 kilograms (*open bar*). The third set of bars shows that nitrogen increases by 162 kilograms (*color*), a gain that is reduced by litter fall (*gray*) to 38 kilograms per hectare.
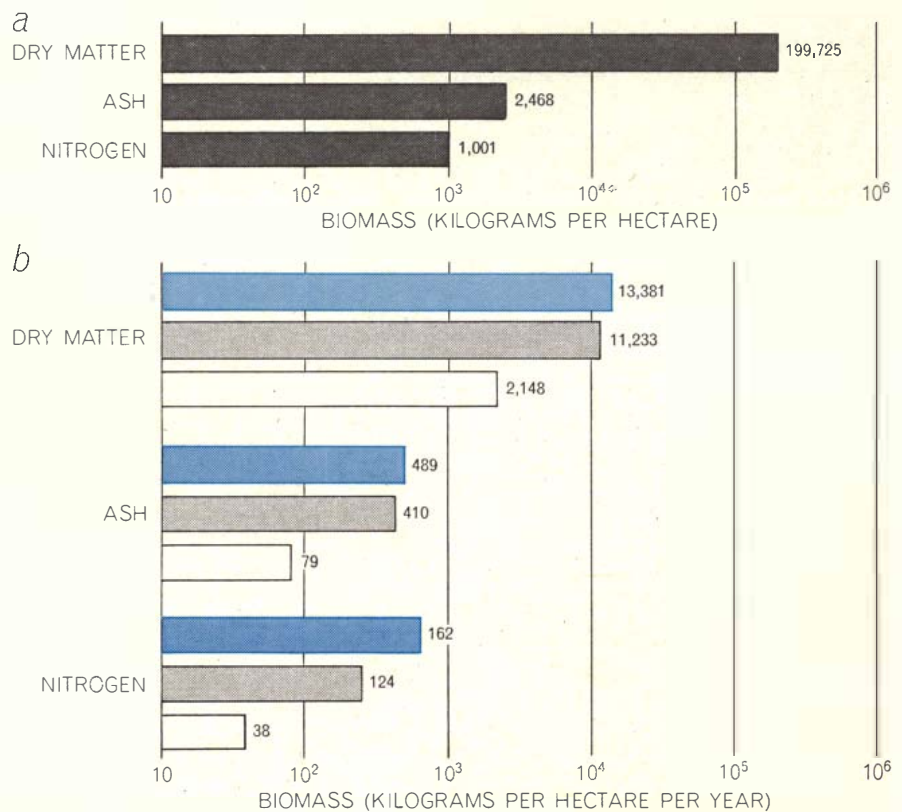
most sulfate-reducers reside is still unclear. The known ones are obligate anaerobes, and their habitat is mud. Swamps, marshes and the floor of eutrophic lakes must all be important, and they may be quantitatively more important than the blue mud of estuaries and continental shelves. The sulfur metabolism of such large systems is not easy to study, even with isotopic tools. Minze Stuiver, now at the University of Washington, injected radioactively labeled sulfate ions into one eutrophic lake, Linsley Pond in Connecticut. Sulfate reduction proved to be intense, as had been expected. This lake, however, has quite a bit of ferrous iron in its deeper waters, and more in the mud itself. In the presence of the ferrous iron all the labeled sulfide was firmly held in the mud as ferrous sulfide, and no hydrogen sulfide escaped. At least for the duration of the radioactive label, with its half-life of 89 days, this mass of mud was not a source of atmospheric sulfur but a sink.

It follows from all of this that the cycling of sulfur in nature is no less relevant to carboxylation than the cycling of carbon and nitrogen. Without downgrading photosynthesis, we can say that carbon fixation is only one of at least three critical steps in the global synthesis of protein. All three are hydrogenations, achieved with the aid of enzymes, which are themselves proteins, and therefore occur only in the biosphere. Of the three reductions, however, only the reduction of carbon calls for green plants and sunlight. The other two, the reduction of nitrogen and of sulfur, are accomplished anaerobically, by microbes. Thus the locus of the nitrogen and sulfur reductions is, broadly speaking, oxygen-deficient soil and mud. Both loci are separated spatially from that airy, sunlit world where green plants (addicted, like human societies, to the external disposal of wastes) are thoughtlessly liberating oxygen.

With three critical steps for five elements, moving through four "spheres" of abstract space, one feels the need for a picture—a "systems model"—just to keep track of the relations. The two-dimensional analogue on page 152 is simple but adequate. Although it fails to specify fluxes, or any chemical quantities, it provides a mental framework for the movement of five elements: hydrogen, oxygen, carbon, nitrogen and sulfur, either alone or in combinations such as water, nitrate, the dioxides of carbon and sulfur, and carbohydrate. The synthetic output is the biosphere, with the

empirical composition of protein. The central or regulatory position of the biosphere in this model follows from the fact that for all five elements it is both a source and a temporary sink. For any element that might be tempted to cycle around the edges of the model, the biosphere provides several high-energy alternatives. The most interesting of these are the reductions of carbon, nitrogen and sulfur, each concentrated at a different interface, two being out of immediate contact with air. Water, although it is able in principle to cycle independently, is the source of the hydrogen that energizes the biosphere, and cannot long avoid the biospheric loop as long as the biosphere functions.

It is easy to be bemused by so fascinating a model. Its function, however, is to clarify thought. If further thought disrupts the model, nothing is lost but a few lines on paper. More or less instantly, by reference to the table of biospheric composition, we can see that the model is incomplete. Phosphorus has been left out, along with calcium, potassium, silicon and magnesium, four elements that are commoner in the biosphere than sulfur is. Will any or all of these cycle tamely through the model, or will they disrupt it beyond repair?
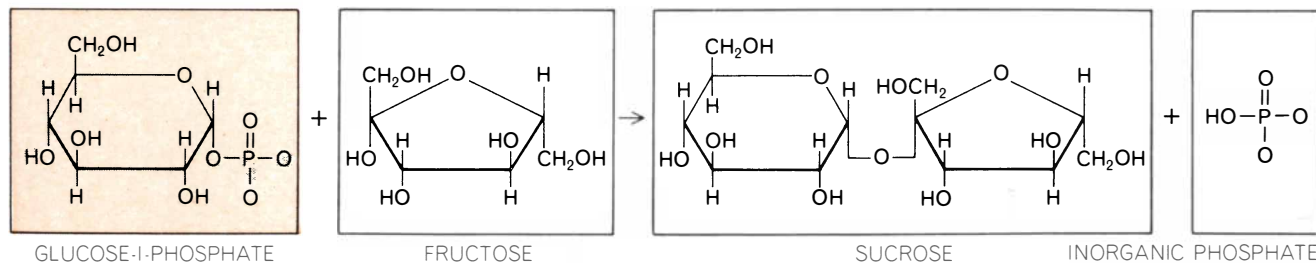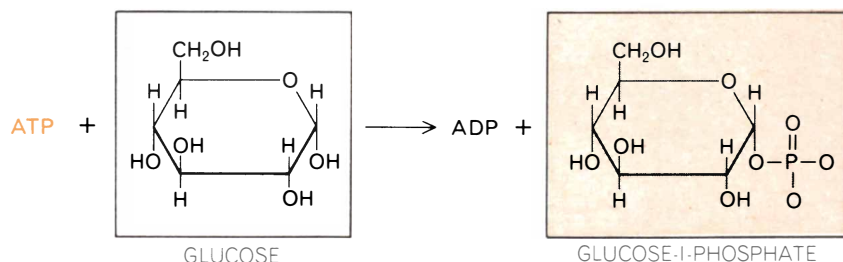
For phosphorus, but not yet for the others, the answer is clear: With one significant modification, the model can accommodate phosphorus. First, let us be sure, as we made sure for sulfur, that phosphorus is necessary to the biosphere. It is not a constituent of protein, but no protein can be made without it. The "high-energy phosphate bond," reversibly moving between adenosine diphosphate (ADP) and adenosine triphosphate (ATP), is the universal fuel for all biochemical work within the cell. The photosynthetic fixation of carbon would be a fruitless tour de force if it were not followed by the phosphorylation of the sugar produced. Thus although neither ADP nor ATP contains much phosphorus, one phosphorus atom per molecule of adenosine is absolutely essential. No life (including microbial life) is possible without it.
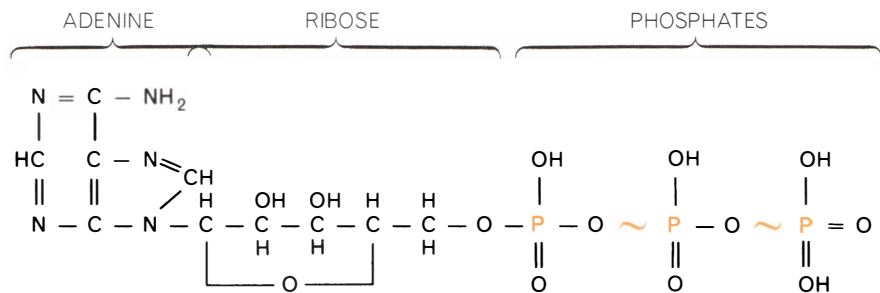
UNIVERSAL FUEL of living matter is adenosine triphosphate (ATP). High-energy phosphate bonds of ATP ($\sim$) each store 12,000 calories and release 7,500 calories when broken.
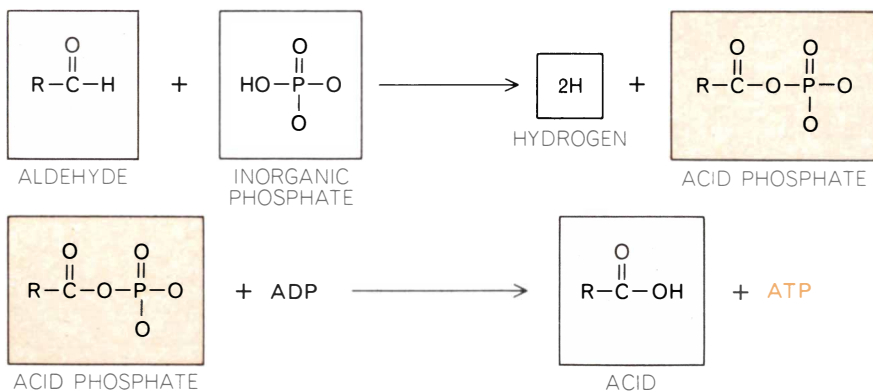

PRODUCTION OF ATP, shown in generalized form, consists of two stages. The first stage begins as aldehyde reacts with an inorganic phosphate to produce hydrogen and acid phosphate. In second stage (*bottom*) acid phosphate (*shading*) reacts with ADP (adenosine diphosphate) to make an organic acid and ATP (*color*). R stands for radicals, or side groups.

Our provisional model of the biosphere has been constructed on two explicit assumptions: (1) the biosphere necessarily contains the five elements of protein and (2) all five are both soluble and volatile. If we now add phosphorus as a sixth necessary element, we can safely assume its solubility in water, and the crucial question concerns its volatility. Except as sea spray in coastal

SYNTHESIS OF SUCROSE is an example of a reaction for which ATP (*color*) supplies energy. The reaction begins at upper left as the ATP molecule combines with glucose molecule, releasing 7,500 calories. The reaction produces ADP and glucose-1-phosphate. In a second stage of the reaction (*bottom*) glucose-1-phosphate combines with fructose, yielding sucrose and inorganic phosphate.

156
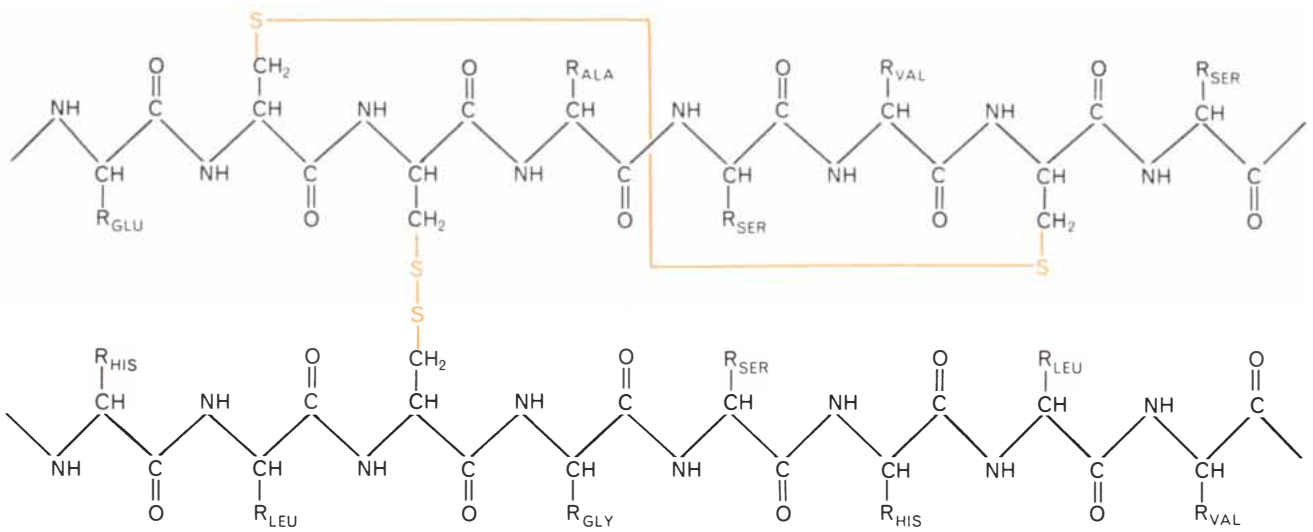
BASIC FUNCTION OF SULFUR in living matter appears to be to provide a linkage between the polypeptide chains in a protein molecule. These linkages help the protein maintain its three-dimensional shape so that it can perform its function. In this segment of a bovine insulin molecule disulfide bonds (*color*) are formed between sulfur atoms, which are present in the amino acid cystine. Cystine is a subunit of both polypeptide chains. Because the molecule is displayed in two dimensions it is flattened. Therefore the bond between the top and bottom cystine groups on the upper chain appears broken. In the normal three-dimensional state, however, this chain is twisted and folded because of the disulfide bond in a way indicated by the colored line that joins the two sulfur atoms. (The other bond is one of two that links the chains.) The shape of the insulin molecule maintained by these bonds enables it to control the metabolism of sugar. The other amino acids in this molecular segment, whose side chains are indicated by the letter *R*, are glutamic acid (GLU), alanine (ALA), serine (SER), valine (VAL), histidine (HIS), leucine (LEU) and glycine (GLY).

zones, or as dust in the vicinity of exposed phosphate rock, phosphorus is unknown in the atmosphere; none of its ordinary compounds has any appreciable vapor pressure. It therefore tracks the hydrologic cycle only partway, from the lithosphere to the hydrosphere, and in a world uncomplicated by a biosphere the ocean would be its only sink. In terms of my model this amounts to uncoupling the atmospheric reservoir (except for water), omitting the half-arrow showing the return of phosphorus from the hydrosphere to the lithosphere and leaving the biosphere's phosphorus as a feedback loop, diverting some of the one-way flow from rock to ocean. Geometrically at least, the model is general enough to accommodate these changes, some version of which will be needed if any permanent sinks are discovered in the system.

For any soluble but nonvolatile element a closed natural cycle is possible only through the biosphere. The model hints at the reason why many elements—vanadium, cobalt, nickel and molybdenum among them—are best known in aquatic organisms and cycle mainly within the hydrosphere. Now, however, the model, nonquantitative though it is, suggests something else. If the biosphere demands such an element as phosphorus (and the cases of iron and manganese should be similar), two alternative inferences are permissible, depending on

the magnitudes of reservoirs and fluxes. If the lithosphere contains an ample supply of phosphorus, or if the flux to the hydrospheric sink is large, the biosphere can take off what it needs and waste the rest. It is commonly believed such elements as sodium and calcium are thus wasted by terrestrial vegetation, although ecologists are beginning to doubt it. On the other hand, if the quantity is scanty or the flux small, the element will be in critically short supply. And if short supply is chronic, the output of the entire system could be expected to be adjusted to the rate of exploitation of one critical element, much as the performance of a bureaucracy is closely geared to the supply of paper clips.

In undisturbed nature the chronic shortage of phosphorus is notorious; that is what most people mean by "soil infertility." In the lithosphere phosphorus is scarcer than carbon, and in the hydrosphere, because phosphorus falls in the parts-per-billion range, it fails to show up at all in the chart of constituents on page 151. Apart from its natural scarcity, phosphorus is freely soluble only in acid solution or under reducing conditions. On the surface of an alkaline and oxidized earth it tends to be immobilized as calcium phosphate or ferric phosphate. In lake waters, where the output of carbohydrate is thriftily attuned to phosphorus concentrations of the order of 50 micro-

grams per liter, doubling the phosphorus input commonly doubles the standing crop of plankton and pondweeds.

Under these conditions the situation in a lake changes drastically. If phosphorus is plentiful, nitrate may become the critically short nutrient for a crop that needs about 15 atoms of nitrogen for one of phosphorus. Blue-green algae may then take over the plankton because by reducing atmospheric nitrogen they escape the dependence that other algae have on nitrate. Meanwhile, judging from much recent experience, the phosphorus input will probably have doubled again—but the subject under discussion is no longer undisturbed nature. What started as "cottage eutrophication," by seepage from a few septic tanks, has been escalated into a noisome mess by "treated" sewage and polyphosphate detergents. To conserve biogeochemical parity the atmosphere has begun to deliver into lakes nitrate and sulfate from the combustion of fossil fuels.

It would be wrong to read too much into a systems model. "Conserving biogeochemical parity" is just a figure of speech, technically hyperbole, and ironical at that. After all, the pollution of the air by nitrate and sulfate is quite independent—technologically, spatially and politically—of the pollution of water by phosphorus. If the accelerated phosphorus cycle in lakes takes advantage of these added inputs, we dare not say that

157

nitrate and sulfate have been drawn into the biosphere from the atmosphere, as U.S. power was drawn to a Canadian circuit breaker in the Northeast blackout of 1965. What the model tells us is that matters can look that way from the standpoint of the biosphere. If the lake segment of the phosphorus cycle is accelerated to the point where nitrogen and sulfur are as critical as phosphorus used to be, and if there is a new source of nitrate and sulfate in the atmosphere, the atmosphere is adequately coupled to all other subsystems to ensure the success of the newly accelerated loop. The loop, known as eutrophication, is thus amplified from a lacustrine nuisance to a systems problem, and around such lakes as Lake Erie it threatens to become a cancer in the global ecosystem.

The trouble started, of course, when the world's one-way phosphorus cycle was first reversed and then accelerated by human activity. Since bird guano was discovered on desert islands, later to be supplemented in fertilizers by phosphate rock, marine phosphate has been restored to the lithosphere in ever increasing amounts. As a device for growing people in ever increasing numbers the practice cannot be faulted, but if people are to continue to flourish in the biosphere, they will have to pay more attention to scarce resources. Phosphorus is much too valuable to be thoughtlessly shared with blue-green algae.

The term eutrophication, which means enrichment, usually inadvertent, is not ordinarily applied to forests and deserts. I dare to extend it to the terrestrial biosphere because two new lines of evidence have suddenly appeared to suggest that the known pollution of air by nitrate and sulfate also encourages the bloom on dry land. The first line of evidence comes from Hubbard Brook, N.H., where F. Herbert Bormann of the Yale School of Forestry and Gene E. Likens of Cornell University have had six forested watersheds under close study since 1963. What interests us here is the difference, per hectare of ecosystem, between the input of ions in rainfall (plus dry fallout, if any) and the output as measured at a dam at the foot of each drainage basin.

Among the common ions entering and leaving Watershed No. 6 at Hubbard Brook, chloride and three positive ions—calcium, magnesium and sodium—show an excess of output over input, presumably derived from the local rocks and soil. These four ions conform, if only barely, to the idea that the biosphere wastes excess salts on their way to the sea. In contrast, potassium and ammonium (NH_4) and the two major negative ions, sulfate and nitrate, are avidly held by this segment of the biosphere, as is indicated by the fact that their input exceeds their output. In the case of potassium all but 700 grams per hectare is captured. Collectively the "nonvolatile" minerals, including silica, that fall from the clear New Hampshire sky amounted to some 13 kilograms per hectare in a typical year. With sulfate, nitrate and ammonium added, the total reached 51.4 kilograms per hectare.

The second line of evidence indicates that the biosphere as a whole is becoming larger. Ecologists expect to find growth in secondary forests, but climax vegetation should be in a steady state, with annual gains balancing losses. According to figures I have recompiled from Rodin and Basilevich, the mean world vegetation is not yet at climax. After the known quantity of dead leaves, branches and other litter is subtracted from the net production of new tissue, the difference is always positive, at an average 2,148 kilograms of new biomass per hectare of land per year. With ash making up 1.2 percent of this biomass, about 26 kilograms of ash is annually withdrawn from an average hectare to sustain the increment of carbohydrate. The input of airborne elements at Hubbard Brook could provide this ash twice over, with no contribution from the local lithosphere.

This comparison is impressionistic, and it may be misleading. Apart from industrial sulfate, which (as sulfuric acid) is perhaps as likely to corrode the biosphere as to nourish it, the world's vegetation may be in no danger of instant eutrophication. (If the biosphere is really becoming larger, the input of industrial carbon dioxide may constitute another major nutrient.) The modes of recycling discovered at Hubbard Brook are nonetheless astonishing. Added to what we know or can safely infer about other volatile elements, such studies underscore the necessity of a global view of biochemistry. What can be said with assurance is that there is a unique and nearly ubiquitous compound, with the empirical formula $H_{2960}O_{1480}C_{1480}N_{16}-P_{1.8}S$, called living matter. Its synthesis, on an oxidized and uncarboxylated earth, is the most intricate feat of chemical engineering ever performed—and the most delicate operation that people have ever tampered with.

GUANO-COVERED ISLAND off the coast of Peru is a source of phosphate and nitrate for fertilizer. Guano has been deposited during many millenniums by generations of birds.

158