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Controls of Atmospheric O₂ and CO₂: Past, Present, and Future

Geochemical models of the earth's surface environment, focusing on O₂ and CO₂ cycles, suggest that a dynamic steady-state system exists, maintained over time by effective feedback mechanisms

During the past 600 million years (Phanerozoic time), the earth has supported a complex population of organisms. Their numbers and diversity may have waxed and waned, but the ocean and the atmosphere remained within the ranges of compositions necessary for the survival and evolutionary change of life (e.g. Margulis and Lovelock 1974). Because all the carbon dioxide of the atmosphere is used by photosynthesizing organisms and enters and leaves surface ocean waters every few years, and because it is all used in weathering processes on the land every few thousands of years, efficient feedback mechanisms must have operated to hold atmospheric CO₂

within relatively narrow limits during all the environmental changes of Phanerozoic time. If at any interval during that vast time span CO₂ had dropped to less than one third of its present value, almost all photosynthesis would have stopped. The fossil record tells us that such an event has not occurred.

The argument for maintenance of atmospheric CO₂ within a narrow concentration range, despite its circulation in and out of the atmosphere millions of times, can be extended to other components of the earth's surface system. Chemical elements such as calcium, magnesium, sodium, potassium, silicon, sulfur, and carbon have circulated many, many times from land to sea and back again, from land or sea to the atmosphere, or from the sea into the sediments of the ocean floor, to be returned to the land by uplift of the sediments or retreat of the sea. The conclusion that the long-term circulation of materials of the earth's surface environment can be regarded as a dynamic system, protected from severe perturbations by effective feedback mechanisms and without major secular trends, seems reasonable.

In this article we will examine first the distribution of sedimentary rock masses as a function of their ages to draw conclusions concerning the cycling rates of the components of the earth's surface system (the *exogenic* cycle). Then the Phanerozoic system will be modeled in terms of reservoirs and fluxes of major components of the earth's metabolic systems, and we will illustrate some of the feedback mechanisms that seem to have operated to resist or restore perturbations of the system. Most attention will be given to CO₂ and O₂, although it can

be shown that similar feedback mechanisms operate for other chemicals.

The life cycle of sedimentary rocks

Sedimentary rocks are born by deposition from wind and water; they die when they are eroded or transformed chemically into other kinds of rocks. Rock masses can be assigned birth rates and death rates, and they can be subdivided into age groups. The colored portion of Figure 1 shows the observed mass-age distribution of the sedimentary rock population for Phanerozoic time (Gregor 1970). Mass and age data for older sedimentary rocks are insufficient to show the distribution earlier than 700 million years ago, although a complete representation would extend back to at least 3.5 billion years. Even for Phanerozoic time, the smallest age groups that can be separated are 50-million-year intervals. However, it is readily apparent from Figure 1 that the mass diminishes in an apparently exponential fashion from the present back to about 350 million years ago; after an increase, it then again decreases exponentially back to 700 million years.

This relation has been noted by several investigators (c.f. Gregor 1970; Li 1972; Garrels and Mackenzie 1969, 1971a,b) and is subject to different interpretations. Here we present ours, which is consistent with the data and with a dynamic Phanerozoic "average" circulating exogenic system. Figure 1 also shows a calculated sedimentary rock distribution according to our model, superimposed on the observed distribution. We have extended the model back to 2 billion years, but that part of the model be-

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yond 700 million years is entirely speculative in terms of the times of the maxima and minima shown.

The model (essentially that of Li 1972 or Garrels and Mackenzie 1971a,b) assumes a constant rate of sediment birth, a constant *total* death rate, and, of course, a constant total mass. Despite the overall constancy, the model accommodates variations in specific rates, and in fact we can discern two subcycles having distinctly different death rates. The model shows that young sediments are more susceptible to destruction than older ones, and that their mass decays exponentially at a relatively high rate. If this rate had been maintained since the beginning of sediment deposition, it would have left almost no record of very old rocks. However, about 350–400 million years ago, something happened to slow the rate of destruction of the sedimentary rocks then in existence, thus accounting for the presence today of the maximum in mass of sedimentary rock of that age. Perhaps this event was the folding and distortion of the sediments. As a result of such folding, areas of outcrop relative to mass would have been diminished, the probability of destruction of mass declined, and the half-life of these older sediments increased. After that event a new sub-cycle began, during which the deposition of sediments has been proportional to the mass of the existing sediments, with a constant death rate of 22% per million years, or a half-life of about 150 million years. In the model the death rate of all sediments older than those of the current sub-cycle is assumed to be the same at any instant of time and is adjusted to maintain the constancy of the total sedimentary rock population.

A test of the model, which was initially developed to account for the age distribution of sedimentary *masses*, has recently become available. Blatt and Jones (1975) determined the relative areas of exposure to erosion of sedimentary rocks as a function of their ages. Figure 2 compares their relative areas, as a function of 100-million-year age groups, with the predicted erosional rate of the same age groups from our model. The correspondence between percentage of area exposed and percentage contribution to present-day deposition is obvious and well within the probable error of mass and area estimations.

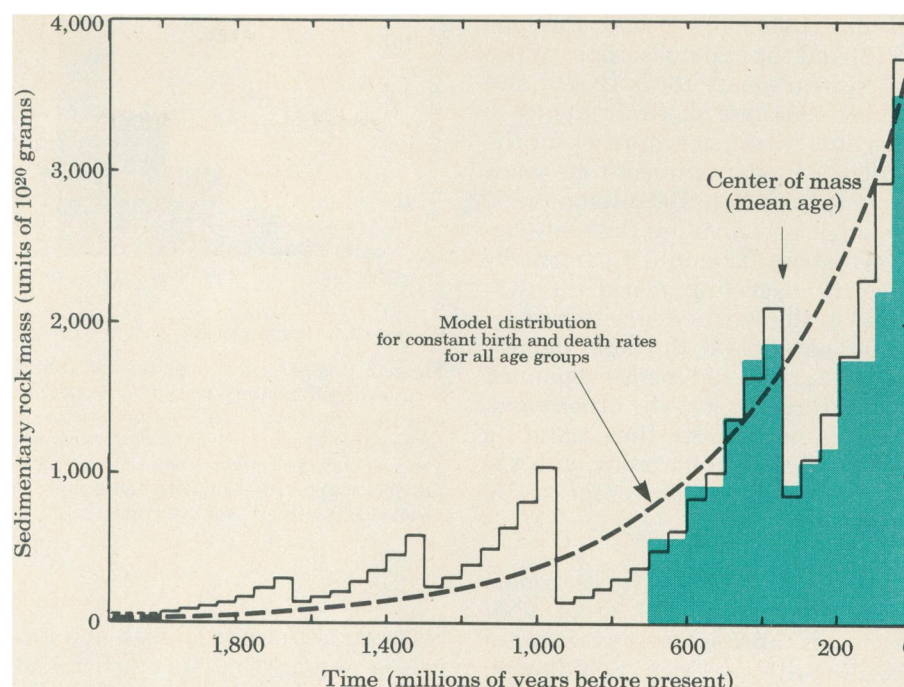


Figure 1. The age distribution of earth's sedimentary rock mass is shown both as estimated from direct measurement (*color*) and as calculated from the model (*black outline*). As the graph shows, the model is consistent with the data and with the concept of a dynamic average circulating exogenic system throughout Phanerozoic time. Values are for age groups at 50-million-year intervals. The model is based on the following conditions: (1) Constant birth

rate of sediments of $3,750 \times 10^{20}$ grams per 50×10^6 years; (2) constant total death rate of sediments by erosion or metamorphism; (3) constant total mass of sediments of $32,000 \times 10^{20}$ grams; (4) half-life of most recent cycle equal to 150×10^6 years; (5) half-life of older cycles adjusted to maintain constant mass, but the same for all older cycle rocks at any time; (6) average life expectancy of rocks of 350×10^6 years.

The present-day age distribution of the population of sedimentary rocks is thus consistent with the assumption of a nearly constant total rate of deposition and destruction throughout Phanerozoic time. It must be emphasized that the sampling has been limited to large age groups, and any fluctuations with response times of less than 50 million years or so would not be seen. Even so, the sedimentary rock population distribution is in accord with the concept of average steady-state cycling of sedimentary mass during Phanerozoic time. As a corollary, to a first approximation, steady-state cycling of mass can be shown to be in accord with a model in which the composition of materials reaching the ocean via streams, glaciers, wind, and groundwater flow has been nearly constant over Phanerozoic time, suggesting that there has been little *evolutionary* change in seawater composition during the Phanerozoic (Garrels and Mackenzie 1974; Mackenzie 1975). Furthermore, although the average rate of erosion deduced from the model is about 75×10^{14} g/yr, about one third of the

present rate (Garrels and Mackenzie 1971a,b), this is about the rate expected for Phanerozoic time, if man's influence has greatly accelerated erosional rates (Judson 1968) and if continental area today is about 20% greater than the average for Phanerozoic time (Sloss and Speed 1974).

A model for the Phanerozoic system

In a "perfect" dynamic steady-state system, each of the chemical components would circulate in the exogenic cycle at a constant rate, and a network of reservoirs and fluxes could be constructed that would describe the behavior of any given component at any given time. Several kinds of information reveal that the flux rates and reservoir sizes of major components of Phanerozoic exogenic cycles tended to fluctuate markedly. Some examples of the types of information available are presented below.

Organic content and carbon isotopes. The age variation in organic content of Phanerozoic sedimentary rocks

(Ronov 1958; Trask and Patnode 1942) and the carbon isotopic values (δC) of carbonate rocks (Keith and Weber 1964) are shown in Figure 3. The data, which are averages for the various Periods, represent time spans ranging from 30 to 100 million years. Organic carbon values fluctuate between about 0.2 and 0.8 percent by weight, suggesting marked differences in the rate of deposition of organic materials if the total depositional rate of sediments remained nearly constant. On the other hand, there is no definite time trend—a finding that is in harmony with the concept of a dynamic average steady state.

Period values for δC in carbonate rocks show changes of about $\pm 1\%$ from an unweighted average of $+0.6\%$, with no trend. Schidlowski and his colleagues (1975) have demonstrated that the average Phanerozoic δC value applies to Precambrian sedimentary rocks as well. Variations of δC in carbonate rocks are usually interpreted as the result of variations in the ratio of carbon deposited as organic carbon to that deposited inorganically as carbonate minerals. The average value of about $+0.6\%$ corresponds to a ratio of total carbon in organics to total carbon in carbonate rocks of about 1:4. A fluctuation of 1% from the mean indicates a range in depositional ratio of 1:3.5 to 1:6 (Broecker 1970a)—a relatively minor fluctuation considering the length of Phanerozoic time.

Interestingly, the fluctuations of organic content and δC values as shown in Figure 3 are opposite to the expected pattern. Although most models predict that these two parameters should vary sympathetically (see Junge et al. 1975), organic content is found to rise when δC is low. Whatever the explanation of the data, they are consistent with a negative feedback model, in which any perturbation of the system that produces a change in the ratio of organic to inorganic carbon deposited is compensated, and the system remains nearly constant through time.

Sulfur isotopes. Variations in the sulfur isotopic values (δS) of evaporite deposits, which measure within about 1% the sulfur isotopic composition of the seawater from which they precipitated, are large and irregular (Fig. 4). The variations are so large, and the

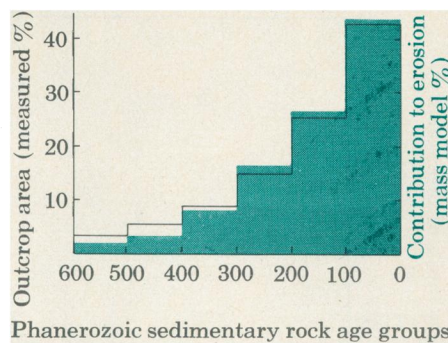


Figure 2. Comparison of the measured area of outcrop of sedimentary rocks (black outline) and their predicted contribution to erosion (color) over the past 600 million years reveals a correspondence between the two factors that provides support for the model. Age groups are given at 100-million-year intervals.

restoration times from high and low values so long, that it is difficult to decide whether or not there is a dynamic mean that tends to be restored by feedback mechanisms. Low values of δS can be correlated well with times of "excess" gypsum deposition, as shown in Figure 4. According to Garrels and Perry (1974), the range of δS from $+30\%$ to $+10\%$ corresponds to a variation of $\pm 30\%$ in the average total amount of sulfate stored in sedimentary rocks and in the ocean. Consequently the evidence from sulfur isotopes tells the same general story that is deduced from secular variation of carbon isotopes and carbon content of rocks: there has been large-scale transfer of sulfate into and out of its reservoir in sedimentary rocks, but mechanisms exist to restore the changes.

Reservoirs and fluxes. We have constructed a system of fluxes and reservoirs of some of the major components of the exogenic cycle involving atmospheric CO_2 and O_2 (Fig. 5; Tables 1 and 2). (The reservoirs and fluxes have been taken almost entirely from the work of Garrels and Mackenzie and co-workers; see references.) A similar model has been constructed by Schidlowski et al. (1975); agreement between the two models is quite good and is particularly heartening because they were constructed independently. The chief difference is that Schidlowski and his colleagues used present-day erosional rates to obtain their mean fluxes, whereas we use values about one-third as large, drawing on the model of sedimentary rock mass-age relations (Fig. 1) to obtain erosional rates.

Other authors, for example Berkner and Marshall (1965), Holland (1973), and Walker (1974), have analyzed portions of the exogenic cycle involving O_2 and CO_2 .

The model is supposed to represent the mean of Phanerozoic conditions and is shown as a balanced steady-state system. The reservoirs chosen are those considered to participate in major control of atmospheric oxygen and carbon dioxide. We should emphasize that, to include all the important aspects of operation of the exogenic cycle, we would need many more reservoirs and fluxes than are shown in Figure 5. Currently we are wrestling with a model that has about twice as many reservoirs, and we hope someday to be able to simulate the real world with a model sufficiently complex that the results obtained from it will have some valid predictive value. On the other hand, the system shown is sufficient to illustrate the basic behavior of a more inclusive model, and the results obtained from this restricted system can be used to define its inadequacies and to point to the important relations that must be investigated to improve it.

We must use numbers in our model, because an entirely qualitative discussion is impossible. Also, we must discuss the diagram as if there were no questions concerning the accuracy of the numbers or the validity of the processes hypothesized. Otherwise we would require many more pages of justification, qualification, and explanation.

For the sake of discussion, we have given the various reservoirs in the system the numbers 1–7. Fluxes are designated by the letter "F" with subscript numbers representing the two reservoirs involved in the transfer. The direction of flow is indicated by the order of the subscript numbers. For example, F_{23} represents the carbon fixed by photosynthesis which circulates from the CO_2 reservoir (2) to the oceanic biomass (3). At the top center of the diagram is the rapidly operating photosynthetic cycle involving the atmosphere and ocean. Photosynthesis on the land has been omitted, and we have treated it as a closed cycle for which photosynthesis is equaled by oxidation and decay. This is equivalent to saying that significant "leakage" from the photosynthetic cycle—organic material

deposited and preserved in sedimentary rocks—is material derived from marine photosynthesis, an assumption in agreement with observation.

The rate of marine photosynthesis is about $2,500 \times 10^{12}$ moles of CO_2 fixed per year (F_{23}) with production of $2,500 \times 10^{12}$ moles of O_2 (F_{21}). Almost all the organic matter formed is reoxidized in the surface ocean, utilizing almost all the O_2 produced (F_{13}). However, about 3.5×10^{12} moles of organic material sinks to the ocean floor each year (F_{34}), causing a *net* production of 3.5×10^{12} moles of oxygen in the atmosphere. Of the material that sinks to the ocean floor (F_{34}), about 30% is oxidized to CO_2 (F_{42}) by bacterial reduction of sulfate to iron sulfide (pyrite) (F_{46}), and returns to the ocean and atmosphere. The remaining 70% is preserved in the sediments (F_{45}).

Of the 3.5×10^{12} moles of oxygen added to the atmosphere each year by photosynthesis, 30% is used in oxidizing reduced substances in rocks exposed to erosion (F_{16}). Here we have called all this reduced material pyrite. A more complete model would have a separate reservoir for other reduced iron compounds, but the amount of oxygen they use is small in comparison to that used in the oxidation of pyrite. The size of the reduced substances reservoir (Res. 6) is given in moles of oxygen demand—the moles of oxygen required to oxidize the entire reservoir to sulfate and ferric oxide. The remaining 70% of the net production of oxygen in the atmosphere by photosynthesis is assigned to the oxidation of organic materials in rocks that have been exposed to erosion at the land surface (F_{15}). It is worth noting, despite our disclaimer on explanation and justification, that present-day estimates of the amount of old organic carbon oxidized (F_{15}) are in good agreement with estimates of new organic carbon buried (F_{45}). The CO_2 resulting from oxidation of old organics returns to the atmosphere (F_{52}). Thus the dynamic balance of atmospheric oxygen during Phanerozoic time rests on the condition that *new organics reaching the seafloor each year equal pyrite and old organic material oxidized during weathering and erosion*.

The CaCO_3 reservoir and its fluxes can be regarded as the atmospheric

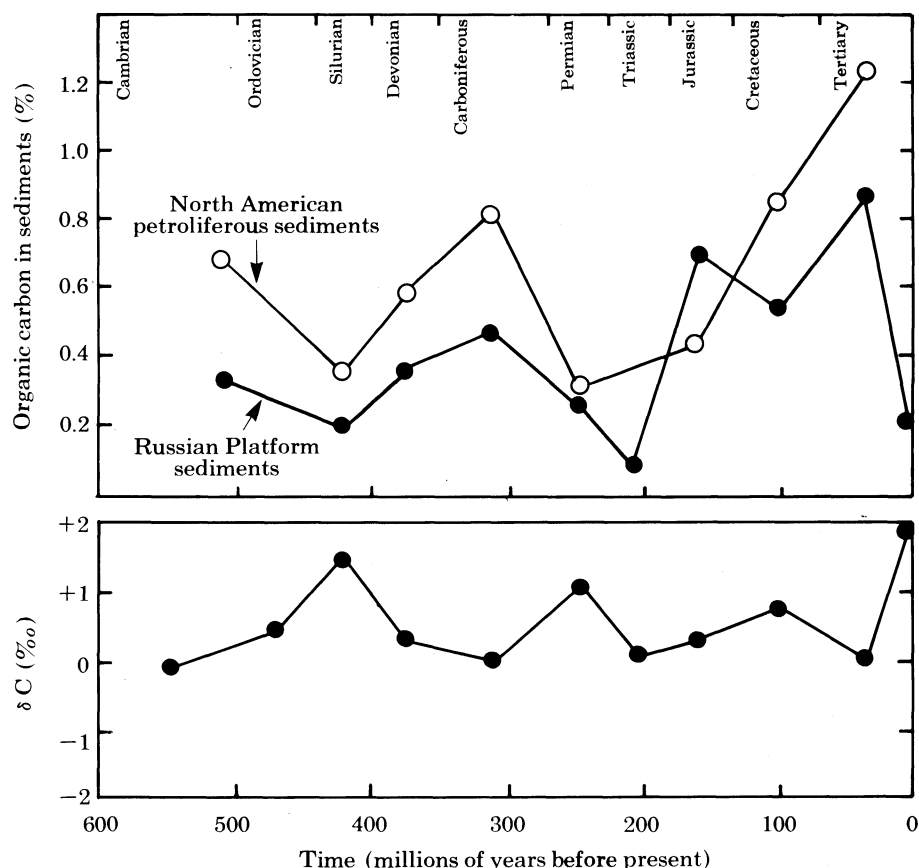


Figure 3. The organic carbon content of sediments and the carbon isotopic composition of carbonate rocks are plotted as a function of geologic age. Values are Period averages. Al-

though the values fluctuate, perturbations that produce a change in the ratio of organic to inorganic carbon are compensated, and the system remains nearly constant through time.

CO_2 buffering system. Carbonate rocks are dissolved by reaction with water and CO_2 (F_{27}), and the products are carried to the ocean by streams (F_{74}); there CaCO_3 is precipitated, returning CO_2 to the atmosphere (F_{42}). The weathering of rocks containing calcium silicates (not represented here) also uses CO_2 from the atmosphere. The calcium entering the ocean via this route precipitates from the ocean as CaCO_3 , and a return of CO_2 to the atmosphere by the conversion of CaCO_3 to CaSiO_3 at depth in the earth is required to keep the system in balance.

The fluxes into the ocean from the weathering of CaCO_3 are much larger than those for CaSiO_3 , however, and the ability of the system to act as a buffer for atmospheric CO_2 derives from the maintenance of an approximate equilibrium between CO_2 in the atmosphere and an ocean saturated with CaCO_3 . Dissolved CO_2 in the oceans (including CO_2 and HCO_3^-) is 60 times more abundant than atmospheric CO_2 , and additions of CO_2 to the atmosphere tend, over a few

thousand years, to redistribute in approximately the same ratio. If CO_2 is drawn from the atmosphere by processes involving photosynthesis and organic carbon burial (the network in the center of Fig. 5), the ocean tends to give up its CO_2 to restore the atmosphere.

In our model the assumption is made that the oceans are continuously in equilibrium with calcium carbonate and atmospheric CO_2 : the only *net* fluxes of CO_2 between the ocean and the CaCO_3 reservoir are those required to maintain this equilibrium.

Feedbacks. The operation of the Phanerozoic system and its feedbacks can be illustrated by first following the qualitative effects of a perturbation of the steady-state system. For example, man has increased erosional rates by deforestation, overgrazing, and other activities. Increased erosion exposes more pyrite and old organic carbon to oxidation, increasing the fluxes F_{16} , F_{52} , F_{15} , and F_{42} and resulting in a net drain on atmospheric oxygen and an increase in atmo-

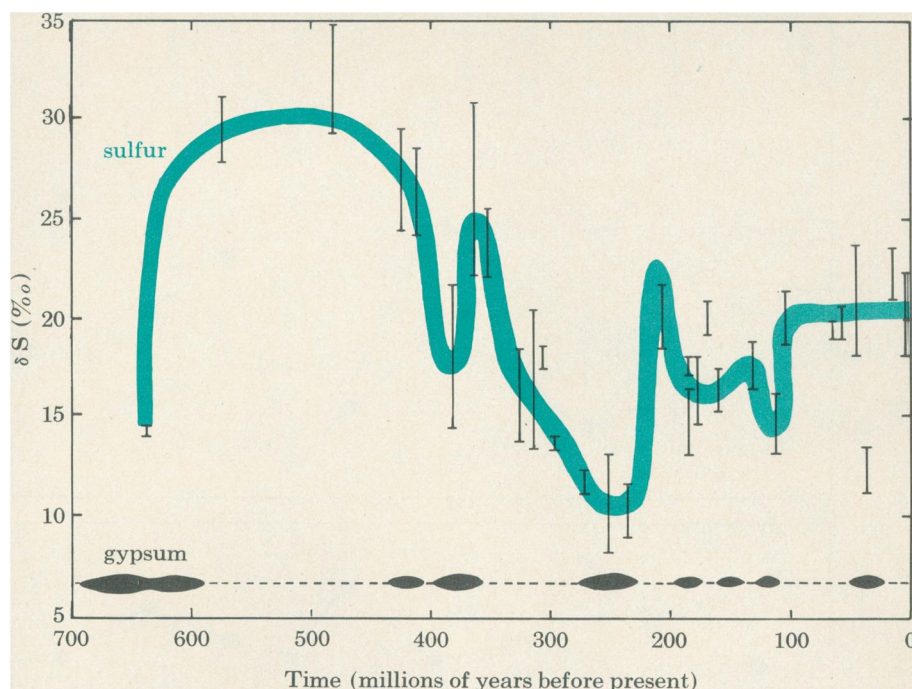


Figure 4. The sulfur isotopic composition of evaporites is shown as a function of geologic age. Colored curve represents the generalized trend of deposition over time; bars bracket the

range of values. Despite large fluctuations, the system as a whole shows no major secular trend.

spheric CO_2 . Because the rate of photosynthesis in the steady-state system is assumed to be controlled by nutrients such as phosphorus and nitrogen rather than CO_2 , presumably there would be little change in either photosynthetic rate or oceanic biomass as a result of increased atmospheric CO_2 , and the CO_2 , over a period of thousands of years, would redistribute itself between atmosphere and ocean. As oxygen slowly declined, the fraction of the biomass reaching the seafloor would increase, and the net production of oxygen from photosynthesis would increase—a negative feedback to the perturbation. Increased organic material reaching the seafloor (F_{34}) would increase the amount of sulfate reduced (F_{46}) and increase the flux of reduced materials to Reservoir 6. This negative feedback mechanism would counteract the decrease in size of the reduced reservoir as a result of the accelerated rate of erosion.

Similarly, the increased storage of organic material in the organic reservoir (F_{45}) would tend to offset the decrease in size of that reservoir caused by accelerated erosion. Solely on the basis of those qualitative chains of responses we can conclude that atmospheric oxygen, if the initial increased rate of erosion were main-

tained, might well come to a new lower steady-state value, CO_2 to a somewhat higher value, and the reduced materials and organic reservoirs would be diminished. The time scale for changing to the new steady state would be quite long, because the changes in the fluxes are of the order of perhaps 1×10^{13} moles/year, whereas most reservoirs involved are of the order of 10^{20} moles. In 100,000 years, for example, the reservoirs (except CO_2) would change by only a percent or so.

Numerical modeling

For a system of fluxes and reservoirs of even the modest complexity of the one shown in Figure 5, quantitative predictions of the results of perturbations require functional relations between reservoirs and fluxes. We have attempted to set up such functions, and the ones we have chosen are given in Table 3. We are the first to admit that these relations are not at all well defined; but we suggest that it is of greatest importance, if the responses of the earth's metabolism to perturbations are to be understood, to do experiments and make observations that will define them. Also, we emphasize that our whole treatment of the problem is geared to long-term responses, of the order of millions of

years or more, and that prediction of short-term responses requires subdivision of the reservoirs and fluxes into much smaller sub-reservoirs with their accompanying fluxes.

The functional relationships listed in Table 3 are derived chiefly from observations of the behavior of the materials of the various reservoirs under present-day conditions, plus what we regard as reasonable deductions, plus a few guesses. A brief discussion of the flux-reservoir relations, in the order listed in Table 3, may help to show the criteria we have used.

The first relation given—correlating fraction of organic material reaching the ocean floor with the mass of oxygen in the atmosphere—is probably the most important relation of all. It has been derived in an indirect way. According to Schidlowski et al. (1975) and in agreement with our own data, the percentage of organic material in sedimentary rocks shows no trend with time, even if the time range examined is 3.5 billion years. The remarkable conclusion, assuming roughly constant rates of sedimentary rock deposition, is that the functional relation between amount of organics preserved per year and mass of oxygen in the atmosphere must be one that is nearly independent of oxygen mass.

In the absence of free oxygen, with fermentative decay being the principal decay mechanism, the fraction of photosynthesized material that became buried in the oceans must have been substantial. Under present conditions, the fraction of photosynthesized organics that become buried in sediments is only about 0.1%. Thus we are presented with the situation illustrated in Figure 6. As atmospheric oxygen increases, the rate of marine photosynthesis increases and the oceanic biomass increases proportionately, but the flux of organic material to the seafloor remains essentially constant. A doubling of the biomass, at constant oxygen, would double the flux of organics to the seafloor because the fraction oxidized would remain the same. This is the basis for the reservoir-flux relation given as No. 1 in Table 3.

Flux relations Nos. 2 and 3 are based on the observation that no pyrite and no second-cycle eroded organic materials are deposited in new sedi-

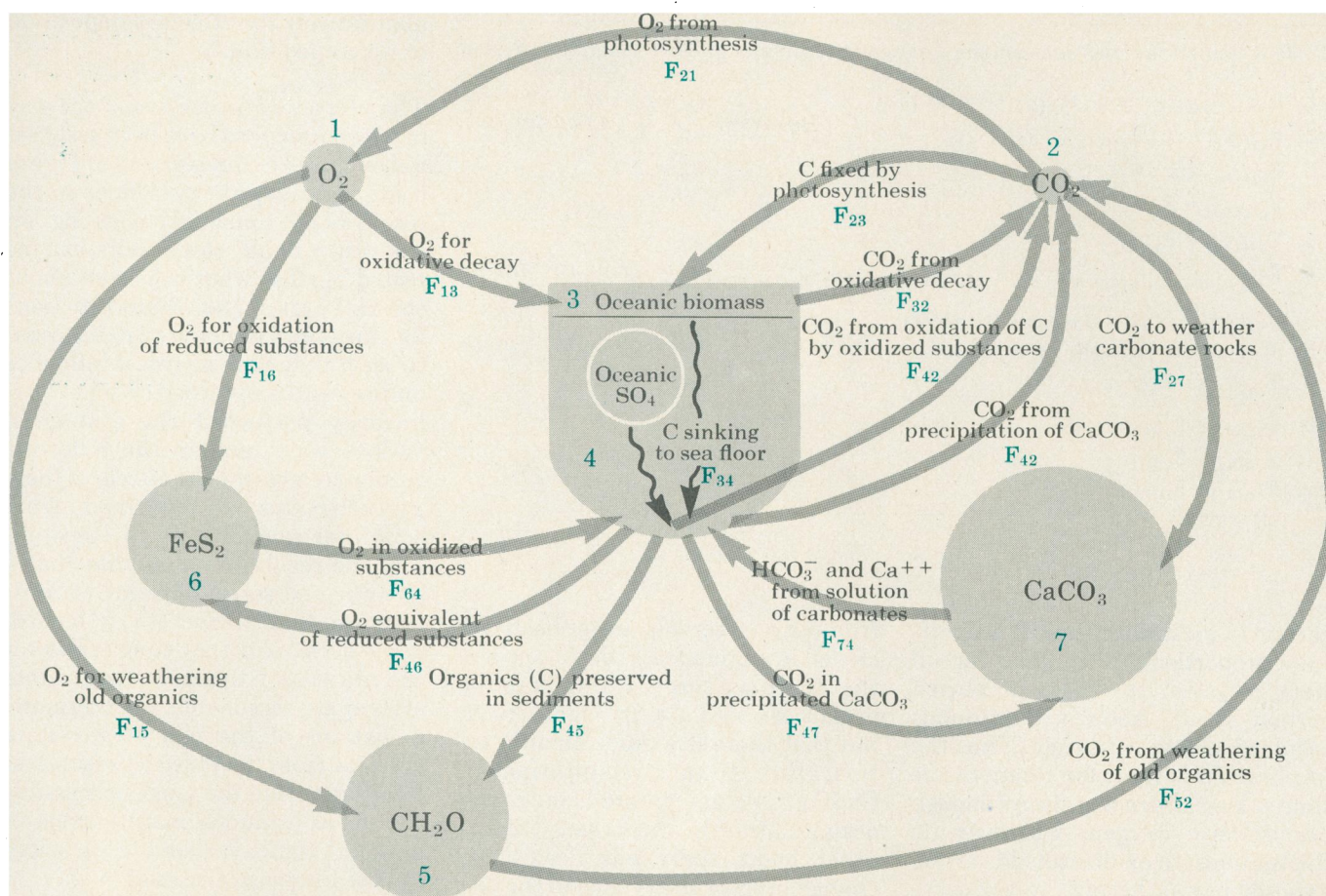


Figure 5. The diagram represents the relationships among the reservoirs and fluxes for the major components of the exogenic cycle involving CO_2 and O_2 . See Tables 1 and 2 for magnitudes of reservoir masses and values of fluxes.

ments. Also, the minimum oxygen pressure required for oxidation of pyrite or organic materials is extremely low. Furthermore, detrital or second-cycle pyrite has not been found in significant quantities in sedimentary rocks of marine origin younger than about 2×10^9 years. Even in rocks older than 2×10^9 years most pyrite seems to be the result of reduction of sulfate, undoubtedly by bacteria. Consequently the oxygen demand of the reduced reservoir was made proportional to the size of the reservoir, that is, proportional to the rate of erosion of pyrite-bearing rocks.

The relation of the mass of free oxygen in the atmosphere to the rate of oxidation of old organic materials exposed to erosion is assumed to be the same as that for pyrite. The basic argument for making the rate of oxidation dependent only on the size of the organic reservoir—that is to say, on the rate of exposure of old carbon to the atmosphere—is the lack of a trend in the percentage of organic

Table 1. Sizes of reservoirs of major components of the exogenic cycle involving CO_2 and O_2 (units of 10^{18} moles)

C in living biomass (Res. 3)	0.0006
CO_2 in atmosphere (Res. 2)	0.055
C in ocean as CO_2 and HCO_3^- (Res. 4)	3.234
Ca in ocean (Res. 4)	14
O_2 in atmosphere (Res. 1)	38
O_2 in SO_4 in ocean (Res. 4)	84
O_2 total demand for substances (primarily FeS_2) in reduced reservoir (Res. 6)	400
C in sedimentary organics (Res. 5)	1,000
CaCO_3 (Res. 7)	4,000

Table 2. Sizes of fluxes of major components of the exogenic cycle involving CO_2 and O_2 (units of 10^{12} moles/year)

O_2 from photosynthesis (F_{21})	2,500
C fixed by photosynthesis (F_{23})	2,500
O_2 for oxidative decay (F_{13})	2,496.5
CO_2 from oxidative decay (F_{32})	2,496.5
O_2 for oxidation of reduced substances (F_{16})	1
O_2 for weathering of old organics (F_{15})	2.5
O_2 in oxidized substances (F_{64})	1
O_2 equivalent of reduced substances (F_{46})	1
C sinking to sea floor (F_{34})	3.5
C preserved in sediments (F_{45})	2.5
CO_2 from oxidation of C by oxidized substances (F_{42})	1
CO_2 from weathering of old organics (F_{52})	2.5

Table 3. Functional relations among fluxes and reservoirs of the Phanerozoic system

1. $\log_{10} F_{34}(C) - \log_{10} F_{23}(C) = -k_1 M_1(O_2)$	$k_1 = 7.5102 \times 10^{-20}/\text{yr}$
2. $F_{16}(O_2) = k_{16} M_6(\text{oxygen demand})$	$k_{16} = 2.5 \times 10^{-9}/\text{yr}$
3. $F_{15}(O_2) = k_{15} M_5(C)$	$k_{15} = 2.5 \times 10^{-9}/\text{yr}$
4. $F_{64}(O_2) = F_{16}(O_2)$	
5. $F_{52}(O_2) = F_{15}(O_2)$	
6. $F_{46}(\text{reduced substances}) = k_{46} F_{34}(C) M_4(O_2 \text{ in } SO_4^-)$	$k_{46} = 3.40 \times 10^{-21}/\text{mole}$
7. $F_{45}(C) = F_{34}(C) - F_{46}(\text{reduced substances})$	
8. $M_2(CO_2) = k_2 M_4(Ca) M_4^2(HCO_3^-)$	$k_2 = 3.78 \times 10^{-40}/\text{mole}^2$
9. $M_4(CO_2) = k_3 M_2(CO_2)$	$k_3 = 0.254$
10. $F_{21}(O_2) = F_{23}(C)$	
11. $F_{13}(O_2) = F_{32}(CO_2)$	
12. $F_{13}(O_2) = F_{21}(O_2) - F_{34}(C)$	

carbon in rocks with time. If a significant proportion of old organic carbon were recycled, the mass of buried carbon should show a continuous secular increase with time. Thus the implication is that, for Phanerozoic time at least, there was always enough atmospheric oxygen, whatever its fluctuations, to oxidize all old carbon exposed to weathering.

The restorative flux for the reduced reservoir (No. 6), formation of pyrite in sediments, is assumed to be proportional to the sulfate concentration of seawater and to the flux of organic material reaching the seafloor. Consequently we have set up this flux as a function of the product of the mass of seawater sulfate and the organic flux to the seafloor. The residual organic material is added to the organic reservoir (No. 7).

It is assumed that the ocean is always in equilibrium with calcium carbonate (No. 8). Today the surface waters are oversaturated and the deep waters are undersaturated, but various independent estimates of present-day rates of addition of calcium to the ocean and its removal are equivalent. Thus our basic tenet is that higher atmospheric CO_2 would result in more dissolved calcium carbonate, and that equilibrium for the reaction

$$CO_2 + H_2O + CaCO_3 = Ca^{++} + 2HCO_3^-$$

would be approached within a few thousands of years after a CO_2 increase or decrease.

Neither a reservoir for calcium sulfate nor fluxes into and out of the ocean

from this reservoir have been included in our model. Today it appears that there is a flux of $CaSO_4$ into the oceans of about 1×10^{12} moles S/yr, but that there is a much smaller return flux from precipitation of $CaSO_4$. Calcium sulfate is currently accumulating in the ocean. On the other hand, there has been little change in δS of the oceans in the last 100 million years (Fig. 4). Because changes in δS are controlled by changes in the ratio of sulfur entering the ocean from $CaSO_4$ and FeS_2 and the ratio of sulfur leaving the oceans as these two species, we can only conclude for the moment that deposition and nondeposition must alternate in such a way as to have maintained a nearly constant reservoir of gypsum for the last 100 million years, even though the size of the reservoir fluctuated markedly prior to that time. Our treatment of the effect of gypsum is to run the system without considering it, and then to estimate

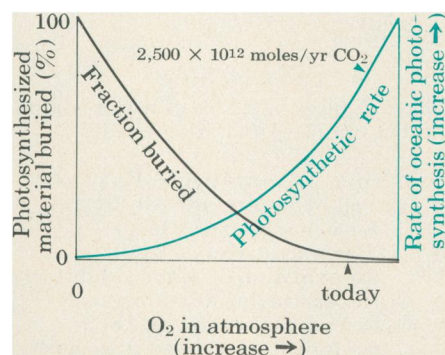


Figure 6. The rate of marine photosynthesis and the fraction of photosynthesized material buried beneath the oceans are shown as functions of the partial pressure of O_2 in the atmosphere.

qualitatively the effects of deposition or nondeposition.

The preceding discussion of the way in which functions have been assigned to the fluxes and reservoirs of Figure 5 may not inspire confidence in the results of our numerical modeling. On the other hand, the results can be tested against what is known about the real system; alternate functions for fluxes and reservoirs can be tested to see if they have a critical influence on the results obtained. We have arbitrarily perturbed the system in various ways, and in the following section we present the effects of these perturbations as obtained from computer calculations. In our opinion, the results demonstrate that a complicated series of negative feedbacks *do* tend to operate in the exogenic cycle, and that time scales for the restoration to a new steady-state system are reasonable. Furthermore, deviations of the new steady-state systems from the chosen "mean system" are within the range permissible for the continuous maintenance of abundant and varied life on earth during Phanerozoic time.

Perturbations of the steady-state system

Increasing the rate of erosion. One of man's effects on the exogenic cycle has been to increase the average rate of erosion since the beginning of Phanerozoic time by a factor of about three. It is difficult to say just when man's influence reached this level. Important anthropogenic effects may date back several thousands of years in the Mediterranean countries and in Africa, where overgrazing, in particular, has been blamed for loss of vegetation, change in albedo of the areas affected, and other important erosional and climatic changes.

In modeling this situation, we increased the global rate of erosion threefold, thus changing the oxygen demand of pyrite and organic carbon exposed to erosion each year by a factor of three. In the model, this corresponds to increasing the oxygen demand by the reduced reservoir and by the organic carbon reservoir, and retaining the assumption that all reduced substances and old organic materials exposed to erosion are oxidized completely. Table 4 shows the output from the computer. The notable changes are that atmospheric

Table 4. Changes in reservoirs and fluxes resulting from tripling the rate of erosion

Time (millions of years)	O ₂ reservoir (units of 10 ¹⁸ moles)	CO ₂ reservoir (units of 10 ¹⁸ moles)	Pyrite reservoir (units of 10 ¹⁸ moles O ₂ equivalent)	Oceanic sulfate reservoir (units of 10 ¹⁸ moles O ₂ in SO ₄)	Organic carbon reservoir (units of 10 ¹⁸ moles C)	Carbon flux to seafloor (units of 10 ¹² moles/yr)
0	38.0	0.055	400	84.0	1,000	3.5
1	33.3	0.074	399	85.3	997	7.9
2	31.7	0.099	398	85.7	996	9.9
3	31.7	0.115	398	85.8	995	10.4
4	31.7	0.121	398	85.6	995	10.4
5	31.7	0.125	398	85.6	995	10.4
6	31.7	0.128	398	85.5	995	10.4
7	31.7	0.131	398	85.5	995	10.4
8	31.7	0.134	399	85.2	995	10.4
9	31.7	0.137	399	85.4	995	10.4
10	31.7	0.140	399	85.3	995	10.4

Table 5. Changes in reservoirs and fluxes resulting from doubling the rate of photosynthesis and maintaining the increased rate

Time (millions of years)	O ₂ reservoir (units of 10 ¹⁸ moles)	CO ₂ reservoir (units of 10 ¹⁸ moles)	Pyrite reservoir (units of 10 ¹⁸ moles O ₂ equivalent)	Oceanic sulfate reservoir (units of 10 ¹⁸ moles O ₂ in SO ₄)	Organic carbon reservoir (units of 10 ¹⁸ moles C)	Carbon flux to seafloor (units of 10 ¹² moles/yr)
0	38.0	0.055	400	84.0	1,000	3.5
1	40.2	0.019	401	83.4	1,001	4.8
2	41.1	0.0080	401	83.1	1,002	4.1
3	41.5	0.0042	401	83.0	1,002	3.8
4	41.7	0.0030	401	83.0	1,003	3.7
5	41.9	0.0022	401	82.9	1,003	3.6
6	41.9	0.0020	401	82.9	1,003	3.6
7	42.0	0.0017	401	82.9	1,003	3.5

oxygen reaches a new steady state within about 2 million years at a level about 15% below the present level, whereas atmospheric CO₂ rises to about 2.5 times the present value (~800 ppm). The other reservoirs are not affected greatly. However, the flux of organic carbon to the seafloor is tripled.

The overall response to the system can be summarized as follows: (1) Increase in oxygen consumption by increased erosional rate lowers atmospheric oxygen. (2) Decreased atmospheric oxygen results in a complementary increase in the amount of organic material reaching the ocean floor. (3) The increase in organics reaching the ocean floor increases the return flux of reduced materials to the reduced reservoir (increase in pyrite synthesis) and increases the rate of accumulation of organic materials, to accommodate the increased rate of organic consumption because of the accelerated erosional rate. (4) Atmospheric CO₂ also increases threefold, resulting in increased dissolved CaCO₃ in the oceans. (5) The

photosynthetic rate is slightly reduced from $2,500 \times 10^{12}$ moles CO₂/yr to $2,460 \times 10^{12}$ moles CO₂/yr.

Although the rate of deposition of organic materials is increased, the percentage of organic materials in new sediments would remain the same, because of the concomitant increase in other eroded materials. Also, despite some increased storage of CaCO₃ in the oceans because of increased atmospheric CO₂, the circulation rate of CaCO₃ through the oceans would increase, so that there would be only a slight change in the ratio of organic material buried to inorganic carbonate deposited, and hence little effect on the $\delta^{13}\text{C}$ values for organic materials or for carbonates deposited. Furthermore, any isotope effect would be restricted to the few millions of years necessary to reach the new steady state. The increased burial rate of organic material presumably would be supported by an increased nutrient supply from the land to the oceans.

The effects of accelerated erosion,

even though they must be considered over a time scale of several million years, might possibly be greater than those of the burning of fossil fuels, in terms of oxygen depletion and CO₂ increase (Broecker 1970b). Man's greatest long-term contribution to the exogenic cycle may be his drastic effects on erosion rates.

The results of the modeling suggest that an increase in the rate of erosion tends to make the whole machine run faster. Changes in atmospheric oxygen and CO₂ would occur, but a new steady state would develop before the disturbance of previous levels became drastic.

Doubling the rate of photosynthesis. In this second scenario, the perturbation is an instantaneous doubling of the rate of photosynthesis to a constant value. How such a perturbation could be accomplished in the real world is hard to imagine—perhaps it might be a result of man's adding nutrients to the oceans, perhaps a result of increase in the rate at which nutrients well up from deep

Table 6. Doomsday scenario: Changes in reservoirs resulting from cessation of photosynthesis

Time (millions of years)	O ₂ reservoir (units of 10 ¹⁸ moles)	CO ₂ reservoir (units of 10 ¹⁸ moles)	Pyrite reservoir (units of 10 ¹⁸ moles O ₂ equivalent)	Oceanic sulfate reservoir (units of 10 ¹⁸ moles O ₂ in SO ₄)	Organic carbon reservoir (units of 10 ¹⁸ moles C)
0	38.0	0.055	400	84	1,000
1	34.5	0.056	399	85	998
2	31.0	0.21	398	86	995
3	27.6	0.42	397	87	993
4	24.1	0.70	396	88	990
5	20.6	1.03	395	89	988
6	17.2	1.41	394	90	985
7	13.8	1.84	393	91	983
8	10.3	2.30	392	92	980
9	7.0	2.80	391	93	978
10	3.6	3.32	390	94	975
11	0.28	3.88	389	95	973
12	Near zero	3.88	389	95	973

oceans. The results of this perturbation are shown in Table 5. According to the model, atmospheric oxygen would climb to a new steady state at a 10% higher value. The feedbacks are as follows: Increase in the rate of photosynthesis would increase the size of the biomass and consequently the flux of organic carbon to the seafloor. More organic carbon would be preserved initially, causing net addition of oxygen to the atmosphere. With a rise in oxygen, the flux of organics to the seafloor would diminish again. The pyrite reservoir would increase slightly, because of the initial increase of organic carbon reaching the seafloor, resulting in an increase in the rate of reduction of oceanic sulfate. Oceanic sulfate would be correspondingly depleted.

However, because of the increase in size of the organic reservoir, CO₂ would be drawn from the atmosphere-ocean system. With loss of CO₂ from the system, the amount of calcium, bicarbonate, and dissolved carbon dioxide in the ocean would diminish, and oceanic pH would rise to about 9. The lowering of atmospheric CO₂ would be so great that it would drop below the level (about 0.15×10^{18} moles) necessary to maintain photosynthesis. In other words, the model shows that an increased rate of photosynthesis could cause CO₂ to become a "limiting nutrient," and a doubled rate of photosynthesis could be maintained only if there were a source of CO₂ not considered by us. It seems likely that this perturbation is an "impossible" one. The simulation is useful simply for

showing that CO₂ supply probably can be an important feedback for controlling the photosynthetic rate, even though it has been shown to be a limiting nutrient today only in a few small freshwater bodies.

Doomsday. We thought it might be interesting to run a Doomsday scenario in which photosynthesis is instantaneously halted. Jacques Cousteau, in a letter from the Cousteau Society (1975), has constructed such a scenario. We quote a few sentences to suggest the kinds of changes and the time scales he envisions: "With life departed, the ocean would become, in effect, one enormous cesspool. Billions of decaying bodies, large and small, would create such an insupportable stench that man would be forced to leave the coastal regions. . . . Then would be visited the final plague, anoxia. . . . And so man would finally die, slowly gasping out his life on some barren hill. He would have survived the oceans for perhaps 30 years."

Table 6 summarizes the results from the model depicting cessation of photosynthesis on the earth. The first event, disappearance of the oceanic biomass within less than a year, takes place so quickly that we cannot show it in the table. Residence time for the biomass is only a few months, so it would be consumed rapidly by oxidative decay. However, its decay would increase atmospheric CO₂ by less than 0.1% and deplete atmospheric O₂ by about 0.001%. Thus we would predict a sterile ocean after a very short time, although there might

be local "cesspool effects" from concentrations of dead organisms near shore.

After that, following Table 6, oxygen would be continuously depleted over a period of 10 million years or so. When it finally disappears, the model becomes inoperative. The time scale shown is probably a minimum, because the rate at which oxygen is consumed by the weathering of pyrite and old organic carbon might well diminish as oxygen pressure became lower. There would be significant changes in the pyrite and oceanic sulfate reservoirs as a result of oxygen consumption by the pyrite reservoir, increasing oceanic sulfate. Without a flux of organic material to the seafloor, oceanic sulfate from pyrite oxidation would accumulate, having no mechanism for reduction, although conceivably it could be removed in CaSO₄ deposits. The organic carbon reservoir also would be diminished.

An important point is that, at the time oxygen disappears, the ocean contains even more sulfate than at steady state in an oxygenated world. Reduction of sulfate in the oceans and in the CaSO₄ reservoir would have to wait for the transport of old organic carbon into the sea. After free oxygen disappears, old organic carbon could act as a reductant for sulfate. We have not modeled the system, but it would surely take a very long time, perhaps hundreds of millions of years, to remove all the sulfate from the exogenic system.

We agree with Cousteau on the effects

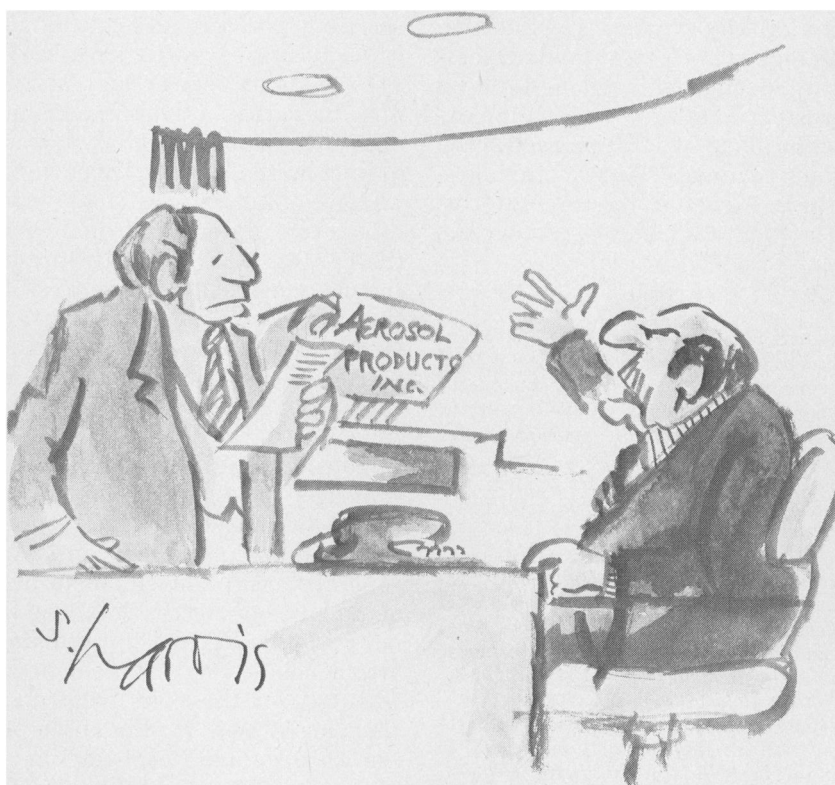
of removing oxygen from the atmosphere, but our time scale gives the human race much more room for contemplation of the end. As modeled, CO₂ pressure would rise by a factor of 70, to about 10⁻² atmospheres. Oceanic pH would drop to about 7. Undoubtedly the result is fortuitous, but many estimates for the early anoxic earth put CO₂ pressure at about this value. We suspect that feedbacks might come into operation to lessen the rise of CO₂—such as conversion of Mg-silicates to Mg-containing carbonates—like the mineral dolomite.

We have tried to show that even if we use a simple and somewhat incomplete model for the exogenic system, negative feedbacks to perturbations operate to restore the system to new steady states that are not drastically displaced from the original state. The response times for the perturbations we have examined are of the order of millions of years. The only perturbation modeled by us, including several not discussed here, that does not result in a new steady state is that depicting the elimination of life. This is in agreement with Lovelock and Margulis's "Gaia" hypothesis (1974), in that the biosphere plays an active adaptive role in maintaining the earth in a state of equilibrium; in particular, the earth's atmosphere is maintained and regulated by life and its interaction with the total exogenic system.

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"Oh, for Pete's sake, let's just get some ozone and send it back up there!"