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## A New Look at the Long-term Carbon Cycle

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### ABSTRACT

The long-term carbon cycle is the cycle that operates over millions of years and that involves the slow exchange of carbon between rocks and the surficial system consisting of the ocean, atmosphere, biota, and soils. It is distinguished from the short-term carbon cycle, in which carbon is rapidly exchanged only within the surficial system. A new type of diagram illustrates the cause-effect relations involved in the long-term carbon cycle and how these processes affect the levels of atmospheric O<sub>2</sub> and CO<sub>2</sub>. The diagram also includes the cycle of phosphorus as it affects the burial of organic matter in sediments. The diagram is distinctly different from, and is here compared to, the more traditional representation of geochemical cycles in terms of box models. By following paths leading from causes to effects, one can trace complex loops that demonstrate positive and negative feedback, and this allows discovery of new subcycles that deserve further study. This type of diagram should be applicable in general to other geological and geochemical processes.

### INTRODUCTION

The term "carbon cycle" means many things to many people. For those concerned with the present growth of CO<sub>2</sub> in the atmosphere, due to deforestation and the burning of fossil fuels, the carbon cycle consists of those sources and sinks that exchange carbon with the atmosphere on a human time scale. This includes the biosphere, oceans, and soils, and I refer to it here as the short-term carbon cycle. This cycle is also the dominant control on atmospheric CO<sub>2</sub> over longer periods, including the glacial-interglacial stages of the Quaternary. However, as one goes back further in geologic time, one must take into account the exchange of carbon between rocks and the combined biosphere-hydrosphere-atmosphere-soil system. This gives rise to the concept of the long-term carbon cycle, and it is this cycle that is the dominant influence on the levels of atmospheric oxygen and carbon dioxide over millions of years (Holland, 1978). (Humans have accelerated this cycle by the burning of organic carbon in

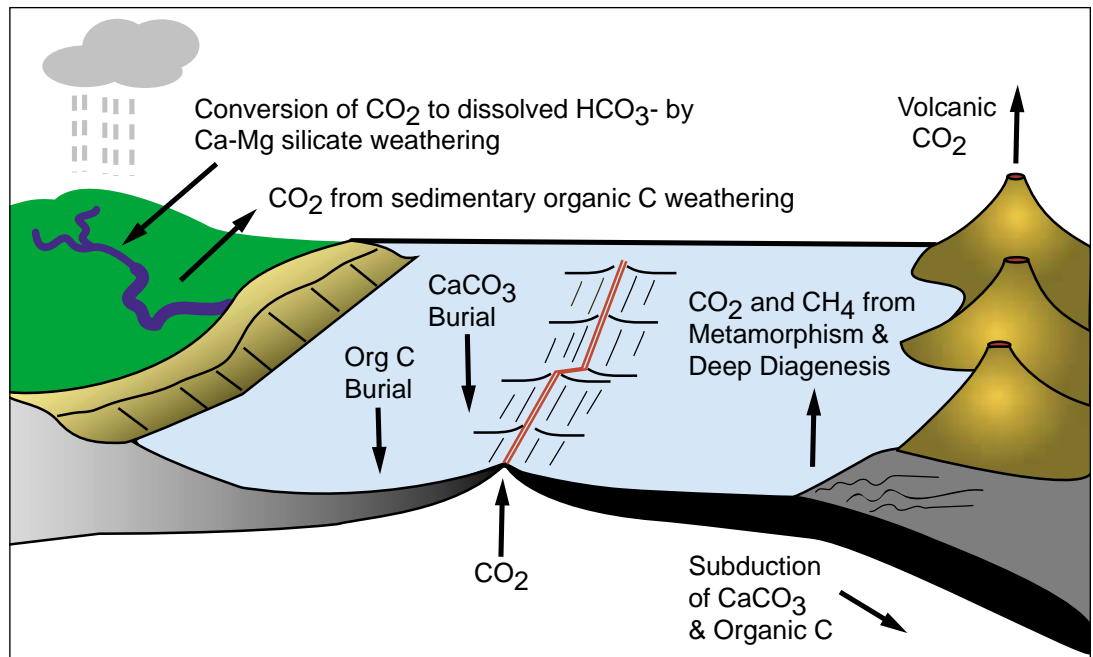


Figure 1. An idealized and simplified representation of the surficial aspects of the long-term carbon cycle. Note the exchange of carbon between rocks, on the one hand, and the oceans and atmosphere, on the other; this is the distinguishing characteristic of the long-term cycle.

sedimentary rocks that otherwise would oxidize only very slowly by weathering.) A cause-effect-type diagram, previously used in modeling physiology (Grodins, 1963; Riggs, 1970), climate (Saltzman and Moritz, 1980; Saltzman and Maasch, 1991), and ocean nutrients and oxygen (Lenton, 1998) can be used also to illustrate the various kinds of feedbacks that control CO<sub>2</sub> and O<sub>2</sub> in the long-term (multimillion-year) carbon cycle.

### LONG-TERM CARBON CYCLE

Summaries of the processes that affect carbon transfer as part of the long-term carbon cycle (Fig. 1), and how they affect atmospheric CO<sub>2</sub> and O<sub>2</sub> can be found in a variety of sources (e.g., Garrels and Perry, 1974; Walker, 1977; Holland, 1978, 1984; Berner, 1989, 1998). The processes affecting CO<sub>2</sub> can be divided into two subcycles. The first, the silicate-carbonate subcycle, involves the uptake of atmospheric CO<sub>2</sub> (processed mostly by photosynthesis and respiration to form soil CO<sub>2</sub> and organic acids) during the weathering of Ca and Mg silicate minerals. A representative generalized reaction for Ca is:



The dissolved Ca<sup>++</sup> and HCO<sub>3</sub><sup>-</sup> are carried by rivers to the sea, where they are precipitated (almost always by means of a biological process) as CaCO<sub>3</sub> in sediments:

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**In Memoriam**

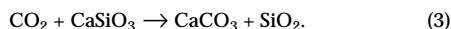
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Donald J. Colquhoun Columbia, South Carolina June 4, 1999	Charles D. Hollister Woods Hole, Massachusetts August 23, 1999	Lois S. Kent Champaign, Illinois September 21, 1999
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**A New Look continued from p. 1**

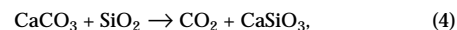


(Mg is removed from the oceans by dolomite formation or by exchange for Ca with ridge basalts, the Ca being subsequently precipitated as CaCO<sub>3</sub>). The net overall reaction (Ebelmen, 1845; Urey, 1952) is:



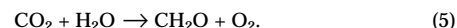
In this way CO<sub>2</sub> is removed from the atmosphere and buried as limestone. The weathering of Ca and Mg carbonates, by comparison, does not result in net loss of CO<sub>2</sub> to the rock record because the weathering reaction for carbonates is simply the reverse of reaction 2 or its dolomite

[MgCa(CO<sub>3</sub>)<sub>2</sub>] analogue. To replace the CO<sub>2</sub> lost to the rock record, degassing occurs as a result of the thermal breakdown of carbonates at depth by volcanism, metamorphism, or deep diagenesis. This process completes the silicate-carbonate subcycle and can be represented for Ca simply by:



which is the reverse of reaction 3.

The other carbon subcycle is that for organic matter. This subcycle affects both CO<sub>2</sub> and O<sub>2</sub>. The burial of organic matter in sediments represents a net excess of photosynthesis over respiration and can be represented by the reaction normally applied to photosynthesis:



## The Need for Integrated Solutions

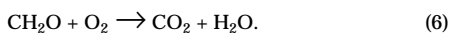
Many of the problems we face today — climate change, global warming, ozone depletion, species endangerment and habitat loss, earthquake prediction, coastal population centers, resource distribution and extraction—cannot be easily solved solely from the perspective of one discipline. Scientists, like physicians, are becoming more specialized; yesterday's naturalists are today's biologists, zoologists, botanists, geologists, geophysicists, meteorologists, and myriad other specialties.

Earth now exists somewhere along a spectrum of an experiment started more than 4.55 billion years ago. We know neither the input parameters nor the experimental design. Geologists trained as the observers of clues produced from Earth's processes are in a unique position: as interpreters of these natural systems, we are adept at solving complex problems using knowledge from many different scientific disciplines.

GSA's leadership recognized the unique role that geoscientists play in interpreting earth systems but realized that the trend in earth science education, as in medicine, was toward increasing specialization. Therefore, they placed a specific goal within our strategic plan to emphasize the value of and need for integration. Goal 2 of the GSA strategic plan is: *To catalyze cooperative interactions among earth, life, planetary, and social scientists who investigate natural systems over varying scales of time and space.* This goal is further divided into objectives that specifically define GSA's role in creating opportunities for cooperative interaction.

This year's Annual Meeting in Denver provided an opportunity for our members to interact on key issues. With the theme

This reaction explains how organic matter burial results in the production of atmospheric O<sub>2</sub>. To complete the organic subcycle, O<sub>2</sub> is consumed and CO<sub>2</sub> produced by the oxidation of organic matter in old sediments exposed to weathering on land:



This reaction also represents the overall process of the thermal breakdown of organic matter, followed by the degassing to the surface of reduced carbon-containing gases (exemplified by CH<sub>4</sub> in Fig. 1) and their rapid oxidation to CO<sub>2</sub> by atmospheric O<sub>2</sub>.

In sum, reactions 3–6 constitute the long-term carbon cycle and are one way of representing it. Figure 1 is another means

"Ordinary mortals communicate rather freely, while intellectuals have succeeded in erecting barriers between them that they don't know how to dissolve."

—Marie Curie

"Crossing Divides," the meeting emphasized multidisciplinary and integrative science.

Seven Pardee Keynote Symposia (named for the late Joseph Thomas Pardee) formed the core of the technical presentations and covered a wide range of topics from climate, global tectonics, and impact events, to the role geoscience plays in environmental and legal decisions.

Societal impact and focus were woven throughout the technical sessions, providing ethical, historical, legal, and philosophical points of view. Many other sessions addressed the impact of geoscience on

society. Public policy was a critical element in sessions addressing coastal geological risk, the need for greater predictive capability, and creationism versus evolution in the classroom.

As we enter the new millennium, geoscience will continue to play a central role in interpreting natural systems for society. GSA will continue to enhance its role, providing venues for debate and dialogue for natural-system scientists.



At Dinosaur Ridge near Morrison, Colorado.

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### A Definition of Geology

Eldridge Moores

A decade ago after extensive debate, the GSA Council adopted the following definition:

*Geology is used in the broad sense—the study of Earth and other planets and planetary objects using any and all available techniques; it includes geochemistry and geophysics.*

Geology incorporates the study of rocks and their history, the internal structure and processes of the planet and their connection with the surficial rock and land form record, as well as the development and history of life. Geology is the study of complex systems that involves the oceans, atmosphere, biosphere, and the solid Earth. The planetary science revolution has extended geology's scope to include other planetary bodies in addition to Earth.

In keeping with this broad definition of geology, GSA's divisions focus, among other things, on resources, geophysics, planetary geology, global geologic processes, active geologic processes, and the societal impact of geology. Similarly, associated societies represent fields such as mineralogy, geochemistry, paleontology and paleobiology, engineering geology, geoscience education and information, and economic geology.

This diversity of interests encompassed under the GSA umbrella underscores the Society's involvement in and commitment to the integrative nature of geology.

of representation, which can be simplified in the form of a box model diagram (see below). However, there is another way of looking at the long-term carbon cycle that does not simply show sinks, sources, and fluxes, as do cartoons like Figure 1 or box model diagrams. Instead of focusing on fluxes and reservoirs, one can look at causes and effects.

### CAUSE-EFFECT FEEDBACK DIAGRAM FOR THE LONG-TERM CARBON CYCLE

Figure 2 is another way of looking at the long-term carbon cycle as it affects the levels of atmospheric CO<sub>2</sub> and O<sub>2</sub>. (See caption for a detailed discussion of concepts and terminology.) Some processes involving phosphorus (P) are included

because of the importance of P as a limiting nutrient in the photosynthetic fixation of carbon. An example of an inverse effect is the increased oxidation of organic carbon to CO<sub>2</sub> by weathering leading to a decrease in atmospheric O<sub>2</sub>. An example of a direct response is increased burial of organic carbon in sediments leading to an increase in atmospheric O<sub>2</sub> (via reaction 5 above). *This type of diagram should not be confused with similar-appearing geochemical box models.* (For comparison, traditional box model diagrams for the short-term and long-term carbon cycles are discussed further below.)

Following arrows around a cycle, Figure 2 allows one to deduce whether the

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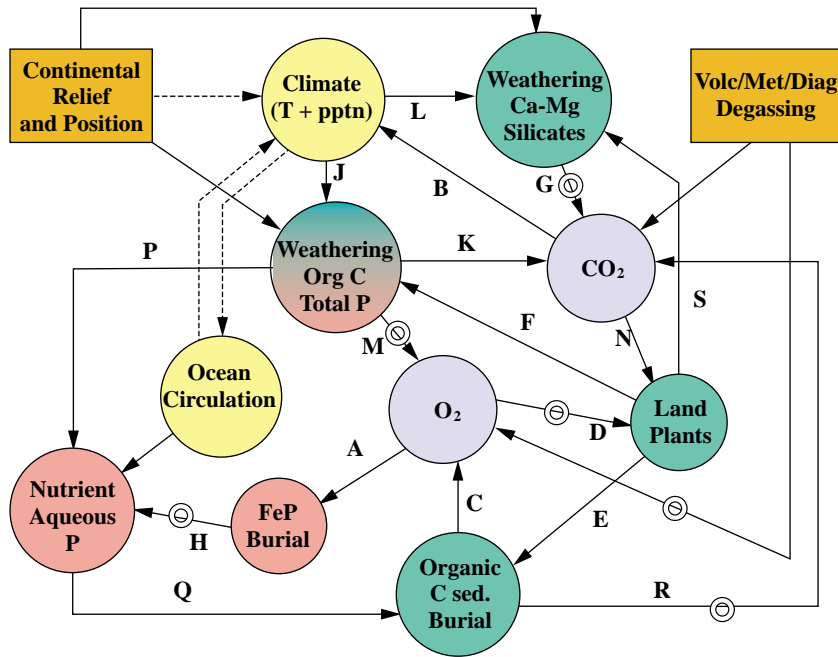


Figure 2. Cause-effect feedback diagram for the long-term carbon cycle. Arrows originate at causes and end at effects. The arrows do not simply represent fluxes from one reservoir to another. Arrows with small concentric circles represent inverse responses; e.g., as Ca-Mg silicate weathering increases, CO<sub>2</sub> decreases. Arrows without concentric circles represent direct responses; e.g., as organic C burial goes up, O<sub>2</sub> goes up. Letters adjacent to arrows designate paths followed by feedback loops. The blue regions marked O<sub>2</sub> and CO<sub>2</sub> refer to atmospheric gases. Surficial processes involving carbon are in green, phosphorus in pink, and those not directly involving either C or P in yellow (T is temperature; pptn is precipitation). Tectonic processes (volcanic, metamorphic, diagenetic degassing; continental relief and position) are in orange boxes. Dashed lines between climate and tectonics or ocean circulation refer to complex combinations of physical processes not discussed in this paper. Nutrient aqueous P is phosphorus dissolved in natural waters that is available for uptake via photosynthesis, both continental and marine; FeP represents phosphate adsorbed on hydrous ferric oxides. Organic C and P burial includes that on the continents and in marine sediments. For diagrammatic clarity, arrows from organic carbon burial to organic weathering or degassing (i.e., recycling of carbon) are not shown (see text). There is no arrow going directly from O<sub>2</sub> to the weathering of organic carbon because of evidence that changes in atmospheric O<sub>2</sub> probably do not affect organic carbon weathering rate (see text).

A New Look *continued from p. 3*

cycle ends up leading to positive or negative feedback. Negative feedback results when an increase or decrease of a variable results, at the end of a cycle, in a dampening of this increase or decrease. Positive feedback results in amplification of an initial increase or decrease. Discerning negative from positive feedback is the major advantage of using diagrams like this. If during a cycle, the sum of small concentric circles is an odd number, the cycle leads to negative feedback. If the sum of small circles is even, including zero, the feedback is positive. As an example, follow the path marked by arrows B, L, and G. Because only one small circle is encountered, this cycle should result in negative feedback. Increased atmospheric CO<sub>2</sub> should lead to a warmer and wetter Earth, via the atmospheric greenhouse effect, which should lead in turn to enhanced weathering of Ca-Mg silicates and uptake of CO<sub>2</sub>. This negative feedback loop has been emphasized in several studies as an important control on atmospheric CO<sub>2</sub> over geologic time (see discussion in Berner and Caldeira, 1997).

The loop N-S-G (just one small concentric circle) represents the fertilization of plant growth by CO<sub>2</sub>, which in turn accelerates weathering of Ca-Mg silicates and uptake of CO<sub>2</sub>. This process has been proposed as a means of providing additional negative feedback for stabilizing atmospheric carbon dioxide over geologic time (Volk, 1987). The quantitative significance of this feedback remains to be seen.

Other negative feedback loops that have been emphasized as controls on atmospheric oxygen are also shown on the diagram. Consider the loop A-H-Q. An

increase in the level of atmospheric O<sub>2</sub> should lead to a more oxygen-rich ocean and greater burial of hydrous ferric oxides in sediments. Dissolved phosphate adsorbs strongly to ferric oxides under aerobic conditions, so that greater burial of ferric oxides should entail greater burial of adsorbed phosphate (designated as FeP in Fig. 2). For a constant flux of P to the sea, removal of P from seawater as FeP should lead to less nutrient phosphorus available for organic production. If it is assumed that the limiting nutrient for organic production in the ocean is phosphate (Holland, 1978), less P availability for organic uptake should lead to a lower rate of organic matter sedimentation and burial and, thus, a lower production of O<sub>2</sub>. Overall what started as an increase in O<sub>2</sub> results ultimately in a decrease—i.e., a negative feedback. This loop has been forcefully advocated by Holland (1994) and Van Cappellen and Ingall (1996) as a major control of atmospheric O<sub>2</sub>.

Another negative feedback loop involving phosphorus has been advanced by Kump (1988). Following path D-E-C we get negative feedback as follows: increased O<sub>2</sub> leads to a greater frequency of fires, which reduces the standing crop of land plants. Fewer land plants leads to less sedimentary burial of terrestrial organic carbon and, consequently, less global burial of total organic matter. This then results in less oxygen production. (Phosphorus not buried with terrestrial organic matter is carried to the sea where it is deposited with marine organic matter that has a lower C/P ratio than terrestrial organic matter, leading globally to less C burial per unit of P burial.)

Another negative feedback loop involving phosphorus is shown by the complex path D-F-P-Q-C, which has one concentric small circle, a path advanced by Lenton (1998) as a major control on O<sub>2</sub>. Higher O<sub>2</sub> should lead to greater frequency of forest fires and a lower standing crop of land plants. Fewer land plants should lead, in turn, to less weathering of phosphate minerals because of the accelerating effect of plants on weathering in general (e.g., Lovelock and Watson, 1982; Berner, 1998). Less weathering of phosphate means less liberation of P to solution, and ultimately to less phosphate in seawater. Less oceanic dissolved P, if it is a limiting nutrient, should lead to less burial of organic matter, and finally a lower production of O<sub>2</sub>—a negative feedback.

Several feedback loops have heretofore been neglected but should lead to positive feedback. Consider the simple loop D-F-M, which contains two small concentric circles signifying positive feedback. Greater atmospheric O<sub>2</sub> should lead to fewer land plants, which should lead to less weathering of organic matter, which should lead to less O<sub>2</sub> uptake and, therefore, an increase in O<sub>2</sub>. Another positive loop is B-J-K. Higher CO<sub>2</sub> should bring about warmer temperatures and greater precipitation, leading to enhanced weathering of organic matter and production of CO<sub>2</sub>.

Finally, there is the complex cycle B-J-P-Q-R. This is an additional possible negative feedback mechanism for stabilizing atmospheric CO<sub>2</sub>. Higher atmospheric CO<sub>2</sub> should lead to: a warmer and wetter climate, greater weathering of phosphate minerals, more P delivered to the sea, more organic matter burial, and, thus,

enhanced removal of CO<sub>2</sub>. This possible stabilizing mechanism and the two destabilizing feedbacks discussed above deserve further study.

Examination of Figure 2 reveals that there is no positive arrow directly from atmospheric oxygen to weathering of organic matter. It is often assumed that a higher level of atmospheric oxygen would lead to greater oxidation of organic matter during weathering. However, because organic matter weathers so fast, the rate-limiting step in oxidation is likely to be the exposure of organic matter in sedimentary rocks to air by erosion, and not the actual oxidation process (Holland, 1978, 1994). (Lack of direct dependence of organic-matter oxidation on O<sub>2</sub> does not preclude possible indirect dependence involving land plants—see path D-F, for example.) The idea of direct dependence of organic matter weathering on O<sub>2</sub> is not supported by laboratory determinations of the rate of aqueous coal oxidation as a function of O<sub>2</sub> level (Chang and Berner, 1999). (Coal was studied as a sulfur-free representative of sedimentary organic matter.) Results indicate that there is a low-order dependence of oxidation rate on O<sub>2</sub> level, possibly approaching zeroth-order kinetics on long time scales, and the oxidation rate itself is rapid compared to rates of erosion.

The tectonic processes included within orange squares in Figure 2—continental relief and position and volcanic, metamorphic, and diagenetic degassing—have been considered here as boundary effects (forcing functions), not involved in feedback loops. The actual situation is more complicated (see Fig. 1). Organic matter and the Ca-Mg carbonates resulting from Ca-Mg silicate weathering are eventually buried to depths where they are thermally decomposed, leading to metamorphic (plus diagenetic) and volcanic degassing of CO<sub>2</sub> and degassing of reduced carbon-containing gases (generalized in Fig. 1 as CH<sub>4</sub>) that react with atmospheric O<sub>2</sub>. Thus, there should be more arrows in Figure 2. However, because of the time lag for burial and thermal decomposition, these longer-term processes have been omitted from the diagram for clarity, as has the effect of exposing previously deposited organic matter much later to oxidative weathering (arrow from organic burial to organic weathering). However, if sea-level change is rapid, this process may constitute rapid recycling of carbon (Berner, 1989) and can lead to negative feedback and the stabilization of O<sub>2</sub>.

Although it affects mainly the short-term carbon cycle, ocean circulation is also shown in Figure 2 because of its effect on the phosphorus cycle and eventually on the carbon cycle. Greater overturn of the ocean should lead, in general, to a greater supply of P to surface waters (“nutrient aqueous P”) where it can be

used to fix carbon during photosynthesis, resulting ultimately in increased organic-carbon burial. Ocean circulation is affected by climate and vice versa, which leads to a link to the whole panoply of processes connected with climate and the necessity of using a much enlarged cause-effect diagram involving continental ice sheets, ocean temperature, solar forcing, etc., as well as some of the processes shown in Figure 2 (see Saltzman and Moritz [1980] or Saltzman and Maasch [1991] for an example of such an expanded diagram). To retain clarity, these relations are omit-

ted from Figure 2 and represented by dashed arrows.

A summary of the effects of increased elevation and relief, due to mountain uplift, on climate (dashed arrows in Fig. 2) is presented by Ruddiman (1997); for the effect on climate of changes in land size, and position relative to latitudinal climate zones (i.e., continental drift), see Otto-Bliesner (1995). In general, it is believed that large-scale mountain uplift results in

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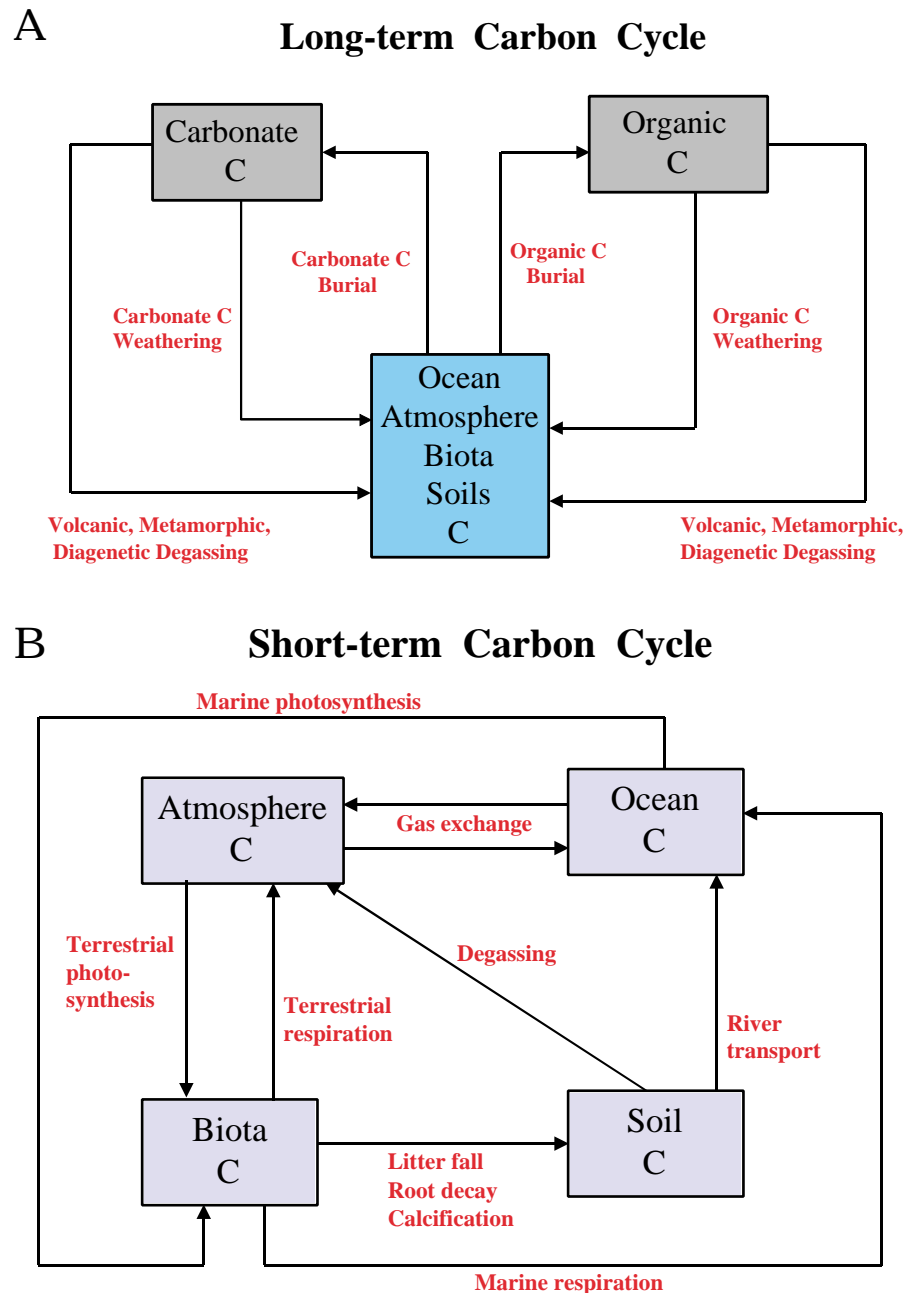


Figure 3. Box model diagrams for the carbon cycle. Boxes represent reservoirs, and arrows represent mass fluxes between reservoirs. A: The long-term carbon cycle. The sum of all input fluxes to the surficial reservoir must be very close to the sum of all output fluxes because storage of appreciable carbon in the surficial reservoir over millions of years is impossible (see Berner and Caldeira, 1997). B: The short-term carbon cycle. Human effects are not shown; deforestation would be an acceleration of terrestrial respiration, but fossil fuel burning is an acceleration of sedimentary organic matter weathering, a flux from the long-term carbon cycle (see A).

A New Look *continued from p. 5*

global cooling, which has led some workers to suggest that such cooling led in the past to increased, not decreased, weathering of silicates. However, this constitutes positive feedback, because the removal of CO<sub>2</sub> during weathering results in further global cooling due to the atmospheric greenhouse effect. If this positive feedback were continued for a million years or more, unreasonable drops in CO<sub>2</sub> and runaway icehouse conditions would result—see Berner and Caldeira (1997).

#### BOX MODEL DIAGRAMS

The traditional geochemical box models shown in Figure 3 are very useful for constructing models that quantify fluxes and changes in sizes of various repositories. However, by themselves they shed no light on the various processes affecting the fluxes nor can they be used to decipher negative or positive feedback. In this way they are complemented by cause-effect diagrams like Figure 2.

Note that the reservoirs normally considered in studies of the short-term carbon cycle (ocean, atmosphere, biota, soils) are combined in the long-term cycle. This is reasonable because of the very small masses of carbon in these surficial reservoirs (total of  $50 \times 10^{18}$  g C, most in the ocean) as compared to the carbon in carbonate rocks ( $60\,000 \times 10^{18}$  g C) and in shales and coals ( $15\,000 \times 10^{18}$  g C). Because of their small size and lack of long-term storage capacity over millions of years, the sum of all input fluxes to the combined surficial reservoir in the long-term carbon cycle must be very close to the sum of all output fluxes (Berner and Caldeira, 1997).

Perturbation of the carbon cycles (Fig. 3) by humans comes from burning coal, oil, and natural gas, by cement production, and by deforestation. Fossil-fuel burning involves the acceleration of the oxidative weathering of sedimentary organic matter, which is a component of the long-term cycle (Fig. 3A). Cement production, which involves decarbonation of limestone and is analogous to metamorphic degassing, also brings about an acceleration of the long-term C cycle. Only deforestation, which is analogous to excess terrestrial respiration, involves a

perturbation of the short-term cycle. Thus, both long- and short-term carbon cycles are involved in the whole problem of anthropogenically altered carbon fluxes, the present-day increase of CO<sub>2</sub> in the atmosphere, and consequent global warming due to the atmospheric greenhouse effect.

#### CONCLUSIONS

The diagrams shown here summarize present knowledge of processes involved in the carbon cycles that affect atmospheric CO<sub>2</sub> and O<sub>2</sub> over multimillion year time scales. Cycles of other elements, like sulfur and iron, exert an important, but secondary, effect on the level of atmospheric oxygen. (A summary of the geochemical cycles of carbon and sulfur as they affect O<sub>2</sub> and how modeling of them is done can be found in papers by Berner and Petsch [1998] and Berner [1999].) Processes affecting methane, such as clathrate formation and decomposition, or the methane greenhouse effect, require new diagrams. (The methane shown emitting to the atmosphere in Fig. 1 is assumed to be oxidized rapidly to CO<sub>2</sub>.) To investigate the carbon cycle further, the time constants for the various cause-effect relations must be enumerated, as has been attempted recently for processes affecting O<sub>2</sub> by Lenton (1998). It is possible that with the proper time constants, a combination of negative and positive feedback could result in oscillations in concentrations of O<sub>2</sub> or CO<sub>2</sub>. Although the diagram shown in Figure 2, representing a new way of thinking about the carbon cycle, will be revised, it provides a simple shorthand representation of our knowledge of the long-term carbon cycle and a mechanism for illustrating and discovering negative and positive feedback loops. Application of this diagram to other geochemical or geological cycles could provide new insights into earth processes.

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#### About People

GSA Fellow Ian Carmichael, University of California, Berkeley, has been elected a Fellow of the Royal Society (London).

Fellow Margaret Leinen, University of Rhode Island, has been named the National Science Foundation's assistant director for geosciences, as of January 2000.

Fellow Richard Marston has assumed the Sun Chair of Earth System Science in the School of Geology at Oklahoma State University.