Articles

Atmospheric Carbon Dioxide Levels Over Phanerozoic Time

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A new model has been constructed for calculating the level of atmospheric CO_2 during the past 570 million years. A series of successive steady states for CO_2 is used in order to calculate CO_2 level from a feedback function for the weathering of silicate minerals. Processes considered are: sedimentary burial of organic matter and carbonates; continental weathering of silicates, carbonates, and organic matter; and volcanic and metamorphic degassing of CO_2. Sediment burial rates are calculated with the use of an isotope mass-balance model and carbon isotopic data on ancient seawater. Weathering rates are calculated from estimates of past changes in continental land area, mean elevation, and river runoff combined with estimates of the effects of the evolution of vascular land plants. Past degassing rates are estimated from changes in the rate of generation of sea floor and the shift of carbonate deposition from platforms to the deep sea. The model results indicate that CO_2 levels were high during the Mesozoic and early Paleozoic and low during the Permo-Carboniferous and late Cenozoic. These results correspond to independently deduced Phanerozoic paleoclimates and support the notion that the atmospheric CO_2 greenhouse mechanism is a major control on climate over very long time scales.

CARBON DIOXIDE IN THE ATMOSPHERE IS A GREENHOUSE gas. In other words, because of its radiation absorbing properties, changes in CO_2 concentration over time can bring about changes in global climate. As is well known, increases in CO_2 during the past century due mainly to human activities have given rise to the environmental problem of global warming and its many and varied consequences. Also, changes in CO_2 levels, due mainly to natural perturbations of the ocean-atmosphere-biosphere system, have been documented for the past 150,000 years by the analysis of bubbles of air trapped in glacial ice (*1*). Thus, the atmospheric CO_2 level does change with time, but what about at longer time scales? Studies of the geochemical carbon cycle (*2*) have shown that the transfer of carbon from rocks to and from the surficial environment over millions of years is far greater than that present at any one time. Thus, it is quite reasonable to speculate that natural long-term processes involving carbon stored in rocks have also brought about changes in atmospheric CO_2 (but at rates that are far too slow to explain the changes observed on human time scales). The purpose of this article is to suggest that gradual CO_2 variations have occurred during the past 570 million years (Phanerozoic time) and that they have been large.

The approach adopted is to model the geochemical carbon cycle and its effect on atmospheric CO_2. The geochemical carbon cycle (*2*) refers to the transfer of carbon between rocks and the ocean-atmosphere system on a multimillion-year time scale and is illustrated in Fig. 1. The ocean and atmosphere are lumped together in Fig. 1 because of their very small carbon contents and short residence times compared to that of the rock reservoirs. The major processes of the cycle are: (i) uptake of CO_2 from the atmosphere during the weathering of silicate and carbonate rocks and transformation of it to dissolved HCO_3^- in ground water and river water; (ii) precipitation of the HCO_3^- in the oceans, after transfer there by rivers, as $CaCO_3$ and other carbonate minerals; (iii) the thermal decomposition of carbonate minerals upon burial to great depths by way of magmatic and metamorphic activity, resulting in transfer of CO_2 back to the atmosphere plus oceans; (iv) the burial of organic matter, representing the remains of dead organisms, in sediments followed much later by the weathering of this material after uplift onto the continents; and (v) the thermal breakdown at depth via diagenesis, metamorphism, and magmatism of organic matter followed by air oxidation of reduced carbon-containing gases upon evasion to the atmosphere.

The major processes of the geochemical carbon cycle can be summarized most simply by the following reactions:

$$CO_2 + CaSiO_3 \underset{\text{metamorphism, magmatism}}{\overset{\text{weathering}}{\rightleftarrows}} CaCO_3 + SiO_2$$

$$CO_2 + MgSiO_3 \underset{\text{metamorphism, magmatism}}{\overset{\text{weathering}}{\rightleftarrows}} MgCO_3 + SiO_2$$

$$CO_2 + H_2O \underset{\text{weathering, metamorphism, plus air oxidation}}{\overset{\text{organic burial}}{\rightleftarrows}} CH_2O + O_2$$

The first two reactions represent the combination of steps (i), (ii), and (iii) above and are normally referred to as the Urey reactions (*3*). (The formulas given for minerals are generalized to represent all calcium and magnesium silicates and carbonates and do not refer to any specific mineral.) The third reaction is of the same form as that normally written for the processes of photosynthesis and respiration but refers instead to their geological equivalents. In other words, going from left to right the reaction refers to net photosynthesis or the difference between global photosynthesis and respiration as represented by the burial of organic matter in sediments. Likewise, the reaction going from right to left represents the oxidation of rocks and volcanic gases, analogous to long-term respiration.

The weathering of carbonate minerals, which is an essential

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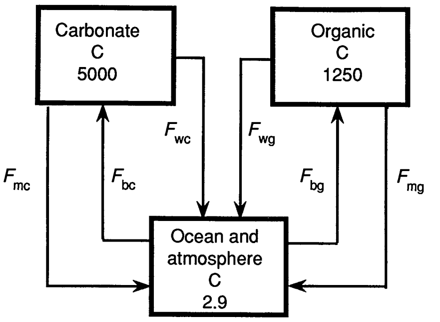

Fig. 1. Schematic representation of the geochemical carbon cycle. Masses of carbon (in 10^{18} moles) are based on the data of (*6*). Symbols for fluxes are defined in Table 1.

component of the geochemical carbon cycle (Fig. 1), is not represented in the above reactions. This is because the atmospheric CO_2 that is taken up by this reaction is soon returned to the atmosphere during precipitation of HCO_3^- in the ocean as carbonate minerals (*2*). On a multimillion-year time scale there is a negligible effect on atmospheric CO_2. By contrast, because of the long lag between the transformation of calcium and magnesium silicates to carbonates and the thermal decarbonation of these carbonates, a large imbalance in CO_2 fluxes can occur. In other words, it is the Urey reactions (and to a lesser extent the organic matter reactions) that dominate the system.

The Model

Modeling of the geochemical carbon cycle, in whole or in part, has been done by many workers (*4*). The model presented here is basically a greatly expanded steady-state version of the carbon mass balance model of Garrels and Lerman (*5*). It is much simpler mathematically than those that the BLAG group constructed earlier (*6, 7*), but more complex geologically and biologically. Mathematical simplification comes about by lumping all carbonate minerals together, following only the cycle of carbon and not that of other elements, combining the oceans and atmosphere into one reservoir, and calculating CO_2 level in the atmosphere as a succession of steady states. The steady-state assumption has been shown to be justified by other studies (*6, 8, 9*). The procedure is to assume that during each 1-million-year period (the time step of the numerical model) inputs of CO_2 to the ocean-atmosphere system are balanced by outputs. This assumption is reasonable because of the very rapid turnover of carbon in the ocean-atmosphere system—a result of its very small capacity for carbon storage compared to that of rocks.

Geological and biological complexity are added to the Garrels and Lerman model by introducing dimensionless parameters to represent the effects of geological and biological evolution over time. Because of the assumption of a steady-state atmosphere-plus-ocean reservoir, the actual calculation of CO_2 level is done differently than that used in the earlier models (*6, 7*). The method is to calculate the value of the feedback function for weathering $f_B(CO_2)$ by a combination of mass balance expressions for both total carbon and carbon-13 and expressions for weathering and metamorphic and volcanic degassing. Atmospheric CO_2 is then calculated from $f_B(CO_2)$. The appropriate expressions are:

$$F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg} \tag{1}$$

$$\delta_c(F_{wc} + F_{mc}) + \delta_g(F_{wg} + F_{mg}) = \delta_o F_{bc} + (\delta_o - \alpha_c)F_{bg} \tag{2}$$

$$F_{wc} = f_B(CO_2) f_A(t) f_D(t) f_E(t)\, k_{wc} C \tag{3}$$

$$F_{mc} = f_G(t) f_C(t)\, k_{mc} C \tag{4}$$

$$F_{wg} = f_A(t) f_D(t) f_R(t)\, k_{wg} G \tag{5}$$

$$F_{mg} = f_G(t)\, k_{mg} G \tag{6}$$

$$F_{ws} = F_{bc} - F_{wc} = f_B(CO_2) f_A(t) f_D(t) f_R(t) f_E(t) F_{ws}(0) \tag{7}$$

where all terms are defined in Table 1.

The procedure of calculation was as follows. Values of the dimensionless parameters $f_A(t)$, $f_D(t)$, $f_R(t)$, $f_E(t)$, $f_G(t)$, and $f_C(t)$ and values for k_{wc}, k_{mc}, k_{wg}, k_{mg}, and δ_o were taken from the literature or estimated (see Table 2 and Figs. 2 and 3). Initial values for C, G, $f_B(CO_2)$, δ_c, and δ_g at 570 million years ago (Ma) were assumed, and the program was run. At each 1-million-year time step appropriate values of F_{wc}, F_{mc}, F_{wg}, and F_{mg} were calculated and substituted into Eqs. 1 and 2, and the two equations were then solved for F_{bc} and F_{bg}. From values of F_{bc} and F_{wc}, Eq. 7 was solved for $f_B(CO_2)$ and, thus, for CO_2 level (see below). The process was

Table 1. Definition of terms used in equations.

Parameter	Definition
F_{wc}; F_{wg}	= rate of release of carbon to the ocean-atmosphere system by the weathering of carbonates (c) and organic matter (g)
F_{mc}; F_{mg}	= rate of carbon release to the ocean-atmosphere by the metamorphic and volcanic breakdown of carbonates (c) and organic matter (g)
F_{bc}; F_{bg}	= burial rate of carbon as carbonates (c) and as organic matter (g) in sediments
F_{ws}	= rate of uptake of CO_2 for the weathering of Ca and Mg silicates followed by precipitation of the Ca and Mg as carbonates (Urey reactions)
$F_{ws}(0)$	= value of F_{ws} at present
$f_B(CO_2)$	= dimensionless feedback function expressing the dependence of weathering on atmospheric CO_2
RCO_2	= ratio of atmospheric $CO_2(t)$ to atmospheric $CO_2(0)$
$f_A(t)$	= ratio of land area (*t*)/land area (0)
$f_D(t)$	= ratio of river runoff (*t*) to river runoff (0) (per unit area) due to changes in paleogeography. [Dependence of runoff on atmospheric CO_2 is included in $f_B(CO_2)$; see (*6*)]
$f_R(t)$	= ratio of mean land elevation (*t*) to mean land elevation (0)
$f_E(t)$	= dimensionless parameter expressing the dependence of weathering rate on soil biological activity due to land plants [$f_E(t) = 1$ at present]
$f_G(t)$	= degassing rate (*t*) divided by degassing rate (0) due to tectonics; assumed to be equal to the rate of new sea-floor generation (sea-floor spreading rate)
$f_C(t)$	= dimensionless parameter expressing the dependence of degassing rate on the relative proportions of carbonates on shallow platforms and in the deep sea [$f_C(t) = 1$ at present]
δ	= $\delta^{13}C$ value (‰); δ_C for carbonates, δ_g for organic matter, and δ_o for the oceans
α_c	= isotope fractionation factor between organic matter and carbonates
k_{wc}; k_{wg}	= rate constants for weathering of carbonates and organic matter, respectively
k_{mc}; k_{mg}	= rate constants for metamorphic and volcanic breakdown of carbonates and organic matter, respectively
C; G	= masses of carbon as carbonates and as organic matter
t	= time
(0)	= present (average for past 1 million years)

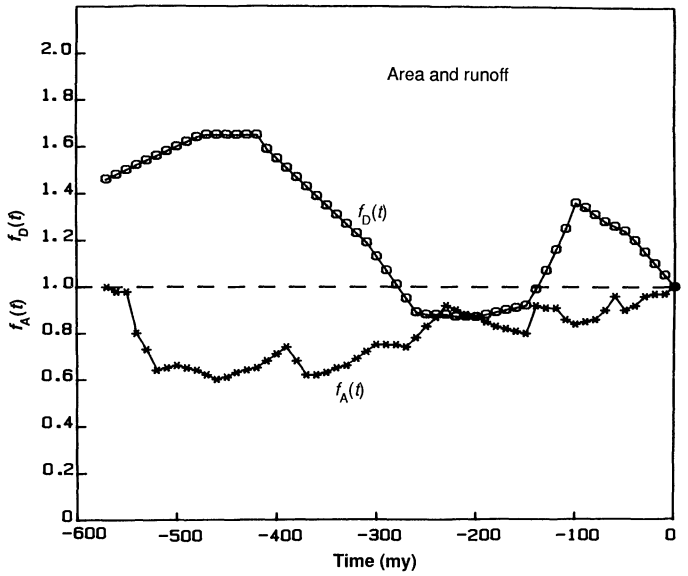

Fig. 2. Plots versus time of $f_A(t)$, land area at time t divided by land area today, and $f_D(t)$ (continental runoff at time t divided by continental runoff today). Values of $f_A(t)$ are based on the paleogeographic reconstructions of Barron and others (*22*) and Ronov (*23*). Values of $f_D(t)$ are based on the work of Tardy *et al.* (*24*), who calculated runoff changes per unit area by keeping track of changes in precipitation minus evaporation on the continents that resulted from past continental drift beneath fixed (present-day) latitudinal climatic zones. No account of changes in orography or monosoonality was made; my, million years.

then iterated until a constant value of $f_B(CO_2)$ was obtained (rapid convergence required minimal iteration). New values of C, G, δ_c, and δ_g were then calculated with the use of four additional mass balance expressions:

$$dC/dt = F_{bc} - (F_{wc} + F_{mc}) \tag{8}$$

$$dG/dt = F_{bg} - (F_{wg} + F_{mg}) \tag{9}$$

$$d(\delta_c C)/dt = \delta_o F_{bc} - \delta_c(F_{wc} + F_{mc}) \tag{10}$$

$$d(\delta_g G)/dt = (\delta_o - \alpha_c)F_{bg} - \delta_g(F_{wg} + F_{mg}) \tag{11}$$

and the procedure was repeated at the next 1-million-year time step and so on. Initial values were then adjusted so that present-day values for the various fluxes were retrieved (see Table 2). Use of shorter time steps was found to be unnecessary in that the calculation procedure converged rapidly.

As one can see, the terms $f_E(t)$ and $f_B(CO_2)$ are omitted from the expression for the weathering of organic matter. This was done because organic matter is attacked by O_2, not CO_2, and the biological production of CO_2 or soil acids should have little effect on organic matter oxidation. The parameter $f_R(t)$ is omitted from the weathering expression for carbonates because their weathering has been shown to be relatively unaffected by changes in elevation or relief (*10*).

Table 2. Values of key parameters used in the model for CO_2; my, million years.

Parameter	Total range or value	Source
$f_A(t)$	See Fig. 2	(*22, 23*)
$f_D(t)$	See Fig. 2	(*24*)
$f_R(t)$	1.00 to 0.79	$= 1 + \log_{10} f_A(t)$
$f_C(t)$	1.00 to 0.50	For 570 to 150 Ma: $f_C(t) = C$ For 150 to 0 Ma: $f_C(t) = C + (1 - C) \exp [-0.03 (150 - t)]$ $C = 0.50, 0.75, 1.00$ [see (*25, 26*)]
$f_E(t)$	1.00 to 0.15	For 570 to 350 Ma: $f_E(t) = 0.15, 0.30, 0.50, 1.00$ (*16*) For 300 to 130 Ma: $f_E(t) = 0.50, 0.63, 0.75, 1.00$ (*17*) For 80 to 0 Ma: $f_E(t) = 1.00$ For 350 to 300 Ma [rise of vascular land plants (*12*)] and 130 to 80 my [rise of angiosperms (*13*)], $f_E(t)$ calculated by linear interpolation
$f_G(t)$	See Fig. 3 (i) 1.00 to 1.36 (ii)	(i) Degassing equals sea floor generation rate from inversion of sea level data (*27*); (ii) One-half the variation from sea level inversion due to other effects on sea level (*28*)
$\delta_c(570)$	1.5 per mil;	(*18*)
$\delta_g(570)$	−23.5 per mil	(*18*)
δ_o	−0.80 to 6.20 per mil	(*29*) (smoothed curve fit)
α_c	21.8 to 30.0 per mil	For 570 to 140 Ma: $\alpha_c = 25$ per mil; for 140 to 0 Ma (*30*)
k_{wc}	0.00267 my^{-1}	Total $k_{wc} + k_{mc}$ from (*18*); k_{wc}/k_{mc} from (*6*)
k_{mc}	0.00133 my^{-1}	Total $k_{wc} + k_{mc}$ from (*18*); k_{wc}/k_{mc} from (*6*)
k_{wg}	0.0030 my^{-1}	Total $k_{wg} + k_{mg}$ from (*18*)
k_{mg}	0.0010 my^{-1}	Total $k_{wg} + k_{mg}$ from (*18*)
C(0)	5000×10^{18} mol	(*6*)
G(0)	1250×10^{18} mol	(*6*)

Once values of the weathering feedback function, $f_B(CO_2)$, were obtained the value of RCO_2, the ratio of mass of CO_2 in the atmosphere at time t to that at present, was calculated for each time period. For this purpose expressions were used that expand on the earlier BLAG formulation for $f_B(CO_2)$ (*6*). In the BLAG model weathering feedback appears only in terms of changes in global mean surface temperature that are attributed to changes in atmospheric CO_2 levels according to the greenhouse effect. There is no direct response of weathering to atmospheric CO_2 levels, and changes in temperature are felt as changes in river runoff and in temperature-controlled rates of CO_2 uptake (HCO_3^- production) by weathering. In the present model allowance for the direct fertilization by CO_2 of land plant productivity is included, and this change results both in greater rock weathering and a stronger negative feedback. The BLAG feedback term, which can be represented in simplified form as $f_B(CO_2) = RCO_2^{0.22}$, is multiplied by an additional CO_2 fertilization term on the basis of a similar approach by Volk (*9*). In other words:

$$f_B(CO_2) = [2RCO_2/(1 + RCO_2)]^{0.4} RCO_2^{0.22} \tag{12}$$

The first term on the right within brackets represents a Michaelis-Menten type formulation, and is used to express the concept that global productivity at high atmospheric CO_2 levels is ultimately limited by factors other than the CO_2 level. The 0.4 power signifies that on a global scale many natural (nonagricultural) plant ecosystems probably respond more weakly to CO_2 because of nutrient, water, or light limitation (*11*), and that weathering rate does not linearly track productivity (*9*). It is equivalent to assuming that only 35% of land vegetation responds to CO_2 fertilization as it affects weathering rate. Because the global response of plant productivity to CO_2 is not well established (*11*), let alone its effect on rock weathering, Eq. 12 should be considered only as a crude first-order approximation. However, regardless of exact formulation, it is necessary to introduce stronger feedback than is available in the BLAG model because over Phanerozoic time the BLAG formulation results in excessive CO_2 variation (for example, $RCO_2 > 100$ during the Cretaceous).

This new fertilization-BLAG feedback formulation is only applicable to the land biota at present. Because vascular land plants did

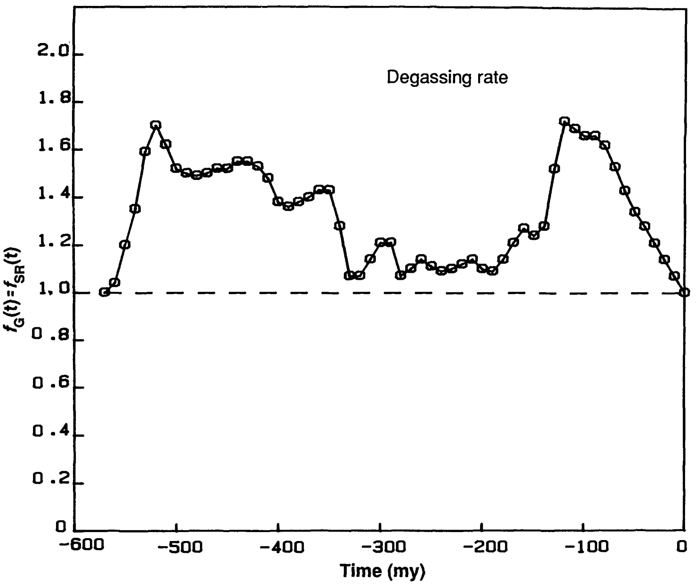

Fig. 3. Plot of $f_G(t)$, the rate of tectonically controlled volcanic and metamorphic degassing of CO_2 at time t divided by the same rate today. The parameter $f_G(t)$ is set equal to $f_{SR}(t)$, the rate of sea-floor spreading at time t divided by the rate today. Values of $f_{SR}(t)$ are based on the sea level inversion calculations of Gaffin (*27*). Long-term eustatic sea level change has been shown to correlate with the rate of generation of sea floor or spreading rate [see references in (*27*)], and thus, can be used as an indicator of crustal turnover by plate tectonics. [The problem is complicated, however, by the effects of continental breakup and collision on sea level (*28*)—see Table 2.] The further assumption made here [see also (*6, 7*)] is that the global rate of CO_2 degassing is linearly related to crustal turnover rate, which is in turn indicated by long-term changes in sea level.

not arise until the Silurian (*12*) and angiosperms until the Cretaceous (*13*), some allowance in the weathering feedback mechanism for these evolutionary changes must be made. I assumed that before vascular land plants, from 570 to 350 Ma, the weathering response was directly proportional to the level of atmospheric CO_2 such that $f_B(CO_2)$ equals RCO_2. Little is known of how weathering proceeded at this time in the presence of primitive nonvascular plants, but a direct response to the atmospheric CO_2 level should represent the strongest possible feedback. On the basis of laboratory experiments on mineral dissolution (*14*) and the potential mediation by soil microflora, it is possible that the feedback during the early Paleozoic could have been much less than linear. (Use of feedbacks based on laboratory observations results in RCO_2 values ranging from 30 to 400.)

The date of 350 Ma represents the time when vascular plants had become widespread on dry land and important as weathering agents. In order to represent the changeover to vascular plant-affected weathering, a linear mix of weathering functions was used between 350 and 300 Ma. Angiosperms may induce faster weathering than more primitive plants (*15*), but did not arrive until approximately 130 Ma (*13*). To account for this an intermediate gymnosperm-pteridophyte feedback function was introduced between 300 and 130 Ma. From 130 to 80 Ma a linear mix of functions was employed, and from 80 Ma to the present the functionality of $f_B(CO_2)$ was assumed to be the same as that of today, that is Eq. 12.

Accompanying changes in $f_B(CO_2)$ over time the model also considers corresponding changes in $f_E(t)$, the parameter expressing the effects of soil biological activity on actual weathering rate. There is little doubt that plants and associated soil biota enhance chemical weathering by the production of CO_2 and organic acids in the soil. The question is how much. A study of waters draining lava flows in Iceland (*16*) showed a threefold enhancement of dissolved HCO_3^- concentration from vegetated to nonvegetated areas. However, much more work is needed to check this result. There is also a suggestion that angiosperms induce more rapid weathering than gymnosperms (*15*), and on this basis Volk (*17*) has constructed an appropriate global expression, which is incorporated in the present model (Table 2).

Results and Discussion

Model results showing sensitivity to some key parameters are shown in Fig. 4. One simulation is for the situation of no change in global tectonics, in other words for the same geographic, degassing, and general tectonic setting as at present. In this case $f_A(t) = 1$, $f_D(t) = 1$, $f_R(t) = 1$, $f_C(t) = 1$, and $f_G(t) = 1$ for all time. The curve expresses the residual effects of the burial rate of organic matter, as calculated from carbon isotopic data, plus the effect of the evolution of land plants. Another simulation is for no biological evolution. Here $f_E(t)$ is set equal to one for all time and the weathering feedback function $f_B(CO_2)$ is assumed equal for all time to that used for the present (Eq. 12). Here the curve reflects tectonics plus the burial rate of organic matter. (The result of setting all dimensionless parameters equal to one, such that the controlling factor is only organic burial rate, results in a curve similar to the no-tectonics situation except that CO_2 values before 350 Ma are about one-third those shown.) In either the no-tectonics or no-evolution cases the curves show a consistent trend of high atmospheric CO_2 levels during the Mesozoic (240 to 65 Ma) and early Paleozoic (570 to 350 Ma) and low levels during the late Paleozoic (330 to 260 Ma) and late Cenozoic (last 30 million years). Thus, neither geology nor biology dominate the trend in CO_2 levels for all times. It is a combination of factors that results in the calculated CO_2 values. This response comes about partly because some biological factors cancel each other and some tectonic factors cancel each other. For example,

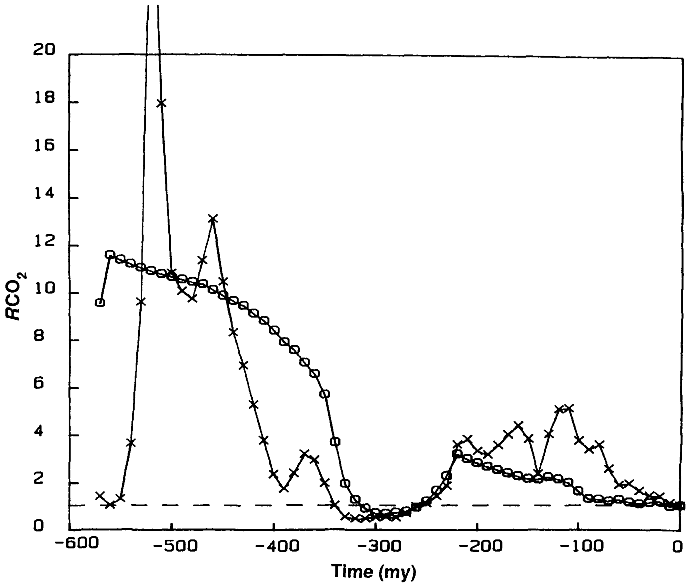

Fig. 4. Sensitivity plots versus time of RCO_2, the ratio of mass of CO_2 in the atmosphere at time t to that in the present atmosphere, illustrating the effects of major processes. (○) Situation for no change in tectonics over time; in other words for $f_A(t)$, $f_D(t)$, $f_R(t)$, $f_C(t)$, and $f_G(t)$ all equal to 1. (×) Situation for no biological evolution; in other words for $f_E(t) = 1$ and use for all time of the present-day formulation for the weathering feedback function $f_B(CO_2)$ (Eq. 12).

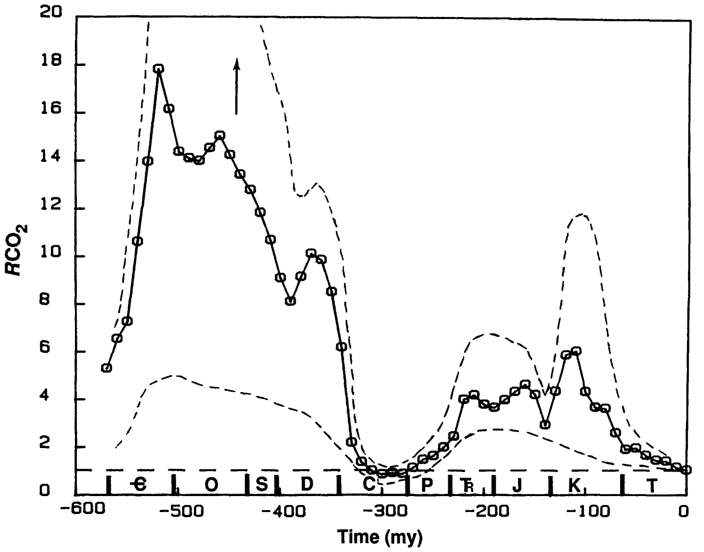

Fig. 5. Standard plot versus time of RCO_2, the ratio of mass of CO_2 in the atmosphere at time t to that in the present atmosphere, based on the carbon mass balance model of the present study. The curve represents the best estimate of the various parameters that go into the model. Dashed lines show the envelope of approximate error based on sensitivity analysis. The vertical arrow denotes that early Paleozoic CO_2 levels may have been even higher than those shown; see text for discussion. Values used (see Table 2): $C = 0.75$; $f_E(t) = 0.15$ for 570 to 350 Ma; $f_E(t) = 0.75$ for 300 to 130 Ma; $f_A(t)$ and $f_D(t)$ from Fig. 2; $f_G(t)$ from Fig. 3.

setting $f_E(t)$ equal to one during the early Paleozoic reduces the level of CO_2, but use of also the present-day formulation for $f_B(CO_2)$ at that time raises the level. Likewise, because changes in $f_D(t)$, representing CO_2 consumption, are generally parallel to changes in $f_G(t)$, representing CO_2 production (compare Figs. 2 and 3), holding both constant results in no great change in the trend of CO_2 levels with time.

Standard results for best estimates of all parameters are shown in Fig. 5 along with a crude estimate of the ranges in error from sensitivity analysis. (Because of a severe lack of knowledge of the role of primitive nonvascular land plants on weathering during the early Paleozoic, a wide range of error is shown for this time.) Again, the pattern of high CO_2 levels during the Mesozoic and early Paleozoic and low CO_2 levels during the late Paleozoic and late Cenozoic are apparent. Furthermore, use of the concept of rapid recycling (*18*) did not change the qualitative aspects of these results. Thus, although the curve shown in Fig. 5 represents only one choice of imperfectly known parameters, it can be used in a semiquantitative sense to represent the approximate levels of atmospheric CO_2 over Phanerozic time.

If the values of CO_2 calculated here are at all correct, then because of the atmospheric greenhouse effect one would expect warm global climates on the average during the Mesozoic and early Paleozoic and cold climates during the late Paleozoic and late Cenozoic. This conclusion is in agreement with independent estimates of paleoclimate (*19*) and the contention of Fischer (*20*) that Phanerozoic climates can be characterized as a succession of greenhouses and icehouses. The two most important glaciations during Phanerozic time occurred during the Permo-Carboniferous and the latest Cenozoic, precisely at times of minimum atmospheric CO_2 levels calculated by the model. (There is a problem with a smaller glaciation that occurred during the Ordovician, and this requires further refinement of the model.)

The model presented here is primarily an attempt to illustrate how one can use the geochemical carbon cycle as a means of exploring the various factors affecting atmospheric CO_2 over long geologic times. The results should be interpreted in the same manner as they are presented, as semi-quantitative trends. There are many problems with values of key parameters, but at least the modeling points to the importance of obtaining better estimates for them (*21*). For example, the parameterization of degassing rate as related to sea level is a crude assumption; other approaches are needed such as good estimates of the original abundance of igneous rocks as a function of time. Also, much more is needed on the quantitative role of land plants in chemical weathering. Nevertheless, the trend of changing CO_2 levels with time calculated with the model is consistent with paleoclimatic trends, and the greenhouse theory of climatic change, on a multimillion-year time scale, is supported by the results.

REFERENCES AND NOTES

1. J. M. Barnola, D. Raynaud, Y. S. Korotkevich, C. Lorius, *Nature* **329**, 408 (1987).
2. For a review of the geochemical carbon cycle consult H. D. Holland, *The Chemistry of the Atmosphere and Oceans* (Wiley, New York, 1978) or R. A. Berner and A. C. Lasaga, *Sci. Am.* **260**, 74 (March 1989).
3. H. C. Urey, *The Planets: Their Origin and Development* (Yale Univ. Press, New Haven, CT, 1952).
4. Two of the more complete mathematical models by other workers for changes over geologic time are those of M. I. Budyko, A. B. Ronov, and A. L. Yanshin [*History of the Earth's Atmosphere* (Springer-Verlag, Berlin, 1987)] and J. C. G. Walker, P. B. Hays, and J. F. Kasting [*J. Geophys. Res.* **86**, 9776 (1981)].
5. R. M. Garrels and A. Lerman, *Am. J. Sci.* **284**, 989 (1984).
6. R. A. Berner, A. C. Lasaga, R. M. Garrels, *ibid.* **283**, 641 (1983).
7. A. C. Lasaga, R. A. Berner, R. M. Garrels, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, E. T. Sundquist and W. S. Broecker, Eds. (*Geophys. Monogr. 32*, American Geophysical Union, Washington, DC, 1985), pp. 397–411.
8. J. F. Kasting, *Am. J. Sci.* **284**, 1175 (1984); L. R. Kump and R. M. Garrels, *ibid.* **286**, 337 (1986); A. C. Lasaga, *ibid.* **289**, 411 (1989).
9. T. Volk, *ibid.* **287**, 763 (1987).
10. E. K. Berner and R. A. Berner, *The Global Water Cycle: Geochemistry and Environment* (Princeton Univ. Press, Princeton, NJ, 1987).
11. E. R. Lemon, Ed., *CO_2 and Plants: The Response of Plants to Rising Levels of Atmospheric Carbon Dioxide* (Westview, Boulder, CO, 1983); D. M. Gates, in *Direct Effects of Increasing Carbon Dioxide on Vegetation*, B. R. Strain and J. D. Cure, Eds. (*DOE/ER-0238*, U.S. Department of Energy, Washington, DC, 1985), pp. 186–204.
12. W. N. Stewart, *Paleobotany and the Evolution of Plants* (Cambridge Univ. Press, Cambridge, 1983).
13. D. W. Taylor and L. J. Hickey, *Science* **247**, 702 (1990).
14. A. Blum and A. C. Lasaga, *Nature* **331**, 431 (1988).
15. M. A. Knoll and W. C. James, *Geology* **15**, 1099 (1987).
16. J. L. Cawley, R. C. Burruss, H. D. Holland, *Science* **165**, 391 (1969).
17. T. Volk, *Geology* **17**, 107 (1989).
18. R. A. Berner, *Am. J. Sci.* **287**, 177 (1987).
19. L. A. Frakes, *Climates Throughout Geologic Time* (Elsevier, Amsterdam, 1979).
20. A. G. Fischer, in *Catastrophes and Earth History*, W. A. Berggren and J. A. Van Couvering, Eds. (Princeton Univ. Press, Princeton, NJ, 1984), pp. 129–150.
21. Other processes, not included in the model, may also prove to be important. The suggested mechanism of direct uptake of CO_2 from seawater by sea-floor basalt [H. Staudigel, S. R. Hart, H.-U. Schminke, B. M. Smith, *Geochim. Cosmochim. Acta* **53**, 3091 (1989)] has been omitted from the model because its net effect on CO_2 levels should be minimal. This is because any increased uptake of CO_2 due to greater production of sea floor would be more or less balanced by increased degassing of CO_2 accompanying faster sea-floor spreading.
22. E. J. Barron, J. L. Sloan, C. G. A. Harrison, *Paleogeogr. Paleoclimatol. Paleoecol.* **30**, 17 (1980).
23. A. B. Ronov, *Geochem. Int. (transl. Geokhimiya)* **13**, 172 (1976).
24. Y. Tardy, R. N'Kounkou, J.-L. Probst, *Am. J. Sci.* **289**, 455 (1989).
25. T. Volk, *Nature* **337**, 637 (1989).
26. B. H. Wilkinson and J. C. G. Walker, *Am. J. Sci.* **289**, 525 (1989).
27. S. Gaffin, *ibid.* **287**, 596 (1987).
28. P. L. Heller and C. L. Angevine, *Earth Planet. Sci. Lett.* **75**, 417 (1985).
29. R. A. Berner, *Glob. Planet. Change* **1**, 97 (1989).
30. M. A. Arthur, personal communication.
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