

## 3GEOCARB II: A REVISED MODEL OF ATMOSPHERIC CO<sub>2</sub> OVER PHANEROZOIC TIME

ROBERT A. BERNER

Department of Geology and Geophysics,  
Yale University, New Haven, Connecticut 06511

**ABSTRACT.** Revisions of the parameters in the model of Berner (1991) (henceforth GEOCARB I) for the long term geochemical carbon cycle have been made. Principal changes are: (1) inclusion of the effects of the variation of solar radiation in the feedback functions for continental weathering; (2) distinction between the feedback function for silicate weathering and that for carbonate weathering; (3) exclusion of land area from the expression for Ca-Mg silicate weathering and its replacement by an uplift factor calculated from changes in the strontium isotopic composition of the oceans; (4) consideration in the expression for carbonate weathering of changes in land area underlain by carbonate rocks; (5) use of new data on the rate of seafloor subduction and spreading over the past 150 my; (6) use of new data on the temperature coefficient of silicate dissolution and the relation between river runoff and rates of silicate weathering; (7) application of a new parameterization of global runoff over time; (8) consideration of an alternate model where total crustal carbon (organic C plus carbonate C) is allowed to vary with time.

Results indicate that: (1) increase in the solar constant over the past 570 my has brought about a gradual drop in atmospheric CO<sub>2</sub> from values much higher during the early Paleozoic than today. Superimposed on this are large fluctuations which in general are similar to those calculated by the previous model; (2) high CO<sub>2</sub> values during the Mesozoic and a decrease in CO<sub>2</sub> during the Cenozoic are due largely to low Mesozoic relief and Cenozoic mountain uplift combined with decreasing metamorphic/volcanic degassing of CO<sub>2</sub> during the Cenozoic; (3) changes in river runoff and carbonate land area are relatively unimportant, compared to other factors, as major controls on CO<sub>2</sub>; (4) variable degassing, due to changes in seafloor spreading rate, was not a major control on atmospheric CO<sub>2</sub> during the Paleozoic; (5) calculated Phanerozoic CO<sub>2</sub> is sensitive to the proportion of carbonate deposition in shallow water versus the deep sea as this affects the probability that the carbonate will be deeply buried and thermally degassed; (6) letting total crustal carbon vary by not tracking the masses of organic C and carbonate C with time has little effect on results.

Over Phanerozoic time a major control on global climate has been the CO<sub>2</sub> greenhouse effect, and changes in CO<sub>2</sub> have been a consequence of a combination of geological, biological, and astronomical factors.

### INTRODUCTION

Any model of the long term carbon cycle must take into account the latest findings in the geological, biological, and atmospheric sciences. Since publication of my model for atmospheric CO<sub>2</sub> over Phanerozoic time (Berner, 1991) several things have been called to my attention that

have caused me to attempt a revision of this model. These include: (1) the effect of changing solar radiation on rates of weathering over Phanerozoic time (Caldeira and Kasting, 1992); (2) new results of general circulation modeling (GCM) of the effect of changes in the amount of solar radiation and of CO<sub>2</sub> levels on global mean air surface temperature (Oglesby and Saltzman, 1990; Oglesby and Marshall, 1992); (3) new estimates of the rate of seafloor subduction over the past 150 my (Engelbreton and others, 1992); (4) estimates of the temperature effect on the rate of Ca-Mg silicate mineral dissolution during weathering (Brady, 1991; Velbel, 1993); (5) the use of the Sr isotopic composition of paleoseawater as a measure of enhanced continental weathering due to mountain uplift (Raymo, 1991; Francois and Walker, 1992; Richter, Rowley, and DePaolo, 1992); (6) field measurements of the effect of river runoff on the concentration of dissolved species derived from silicate weathering (Dunne, 1978; Peters, 1984); (7) new GCM estimates of river runoff over Phanerozoic time (Otto-Bliesner, 1993); (8) a new formulation of the effect of the transfer of CaCO<sub>3</sub> from the continents to the deep sea floor (Caldeira, 1992); and (9) estimates of the percentage of land area underlain by carbonates versus silicates over the Phanerozoic (Bluth and Kump, 1991).

It is the purpose of the present paper to revise the earlier model (Berner, 1991), which I now designate as GEOCARB I, to include the above findings, and to add some additional considerations. As a result the revised model presented here is designated as GEOCARB II. Use of the GEOCARB terminology considerably simplifies reference to this type of modeling and clearly distinguishes it from the older, and distinctly different, BLAG model with which the GEOCARB model is often confused.

#### THE MODEL

The model used here, GEOCARB II, is based on the long term carbon cycle. The long term cycle involves the transfer of carbon between rocks and the ocean/atmosphere/biosphere system. This includes: (1) the weathering of Ca and Mg silicates and carbonates and sedimentary organic matter on the continents; (2) the burial of organic matter and Ca-Mg carbonates in sediments; and (3) the thermal breakdown of carbonates and organic matter at depth with resultant CO<sub>2</sub> degassing to the atmosphere. In GEOCARB modeling a whole host of geological and biological factors that affect the rates of weathering and degassing are considered. In addition, values for the carbon isotopic composition of carbonates in the geological record are used to calculate carbon burial rates.

As a review and to point out clearly any changes in the modeling, the major expressions used in the GEOCARB I model are repeated here. Further details and discussion of the general modeling approach can be

found in the GEOCARB I paper (Berner, 1991). The major expressions are:

$$F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg} \quad (1)$$

$$\delta_c(F_{wc} + F_{mc}) + \delta_g(F_{wg} + F_{mg}) = \delta_{bc}F_{bc} + [\delta_{bc} - \alpha_c]F_{bg} \quad (2)$$

$$F_{wc} = f_{BB}(\text{CO}_2)f_{LA}(t)f_D(t)f_E(t)k_{wc}C \quad (3)$$

$$F_{wg} = f_D(t)f_R(t)k_{wg}G \quad (4)$$

$$F_{mc} = f_G(t)f_C(t)F_{mc}(0) \quad (5)$$

$$F_{mg} = f_G(t)F_{mg}(0) \quad (6)$$

$$dC/dt = F_{bc} - (F_{wc} + F_{mc}) \quad (7)$$

$$dG/dt = F_{bg} - (F_{wg} + F_{mg}) \quad (8)$$

$$d(\delta_c C)/dt = \delta_{bc}F_{bc} - \delta_c(F_{wc} + F_{mc}) \quad (9)$$

$$d(\delta_g G)/dt = (\delta_{bc} - \alpha_c)F_{bg} - \delta_g(F_{wg} + F_{mg}) \quad (10)$$

$$F_{wsi} = F_{bc} - F_{wc} = f_B(\text{CO}_2)f_R(t)f_E(t)f_D(t)^{0.65}F_{wsi}(0) \quad (11)$$

where:

$F_{wc}$ ;  $F_{wg}$  = rate of release of carbon to the ocean/atmosphere/biosphere system via the weathering of carbonates (c) and organic matter (g)

$F_{mc}$ ;  $F_{mg}$  = rate of release of carbon to the ocean/atmosphere/biosphere system via the metamorphic/volcanic/diagenetic breakdown of carbonates (c) and organic matter (g)

$F_{bc}$ ;  $F_{bg}$  = burial rate of carbon as carbonates (c) and organic matter (g) in sediments

$F_{wsi}$  = rate of uptake of atmospheric  $\text{CO}_2$  via the weathering of Ca and Mg silicates followed by precipitation of the Ca and Mg as carbonates (Urey reaction)

$f_{BB}(\text{CO}_2)$  = dimensionless feedback function for carbonates expressing the dependence of weathering on atmospheric  $\text{CO}_2$

$f_B(\text{CO}_2)$  = dimensionless feedback function for silicates expressing the dependence of weathering on atmospheric  $\text{CO}_2$

$f_{LA}(t)$  = carbonate land area (t)/carbonate land area (0) equal to  $f_A(t)f_L(t)$  where  $f_A(t)$  = total land area(t)/total land area(0) and  $f_L(t) = [\text{carb}/\text{total}](t)/[\text{carb}/\text{total}](0)$

$f_D(t)$  = river runoff (t)/river runoff (0) due to changes in paleogeography. Runoff is per unit area. (Dependence of runoff on atmospheric  $\text{CO}_2$  is included in  $f_B(\text{CO}_2)$ )

$f_R(t)$  = uplift factor; mean continental relief (t)/mean continental relief(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)/degassing rate (0) due to tectonics

$f_c(t)$  = dimensionless parameter expressing the dependence of degassing rate on the relative proportions of carbonates deposited in shallow water and in the deep sea ( $f_c(t) = 1$  at present)

$\delta = \delta^{13}\text{C}$  value (permil);  $\delta_c$  average value for all carbonates,  $\delta_g$  average value for all organic matter, and  $\delta_{bc}$  value for carbonates being buried at time  $t$  ( $\approx$  shallow oceanic value)

$\alpha_c$  = isotope fractionation factor between organic matter and carbonates (in permil)

$k_{wc}$ ;  $k_{wg}$  = rate constants for weathering of carbonates and organics

$C$ ;  $G$  = masses of carbon as carbonates and as organic matter

Here  $(t)$  refers to some time in the geological past and  $(0)$  to the present (average for the past 1 my).

Detailed discussion of the  $f(t)$  parameters used in these equations is presented in the next section. It is the change in these parameters that represents the core of the revisions in GEOCARB II. Otherwise the general philosophy and principles of the modeling, as represented by the above expressions, are maintained.

#### WEATHERING PARAMETERS

*Continental land area and relief.*—In the present model there are two important changes from the earlier model (GEOCARB I). They involve  $f_A(t)$ , the ratio of land at some time in the past to that today, and  $f_R(t)$ , the parameter expressing changes in mean continental elevation, or more specifically, relief. First, the use of  $f_A(t)$  in the expression for Ca-Mg silicate weathering has been dropped. The reason for this is that changes in land area over Phanerozoic time have resulted from sealevel changes on the vertical scale of at most a few hundred meters. Changes in sealevel of this magnitude involve mainly the covering and exposure of continental shelves, coastal plains, and interior lowlands. Such areas are ordinarily underlain by sediments rich in relatively stable weathering products such as clay minerals (Stallard, 1985). Since clays do not weather readily, as far as the release of calcium, magnesium, and bicarbonate is concerned, one would not expect appreciable silicate weathering fluxes resulting from the uncovering of lowlands by falling sealevel. (In those lowlands receiving a constant supply of eroded relatively unweathered debris from nearby uplands, appreciable low elevation weathering can occur; however, this situation can be considered to be a consequence of mountain uplift and treated accordingly—see below.)

The same story is not true of Ca-Mg carbonates. Appreciable carbonate dissolution by weathering and ground water flow takes place in lowlands as attested to, for example, at present by the karst phenomena of Florida, a lowland barely above sealevel. Thus, in the case of carbonates, in contrast to the weathering of silicates,  $f_A(t)$  is retained in the weathering expression. To this I have added the proportion of land area underlain by carbonates,  $f_L(t)$  (Bluth and Kump, 1991), which when

multiplied by  $f_A(t)$  gives a new parameter, the land area underlain by carbonates relative to that at present  $f_{LA}(t)$ . A plot of  $f_{LA}(t)$  versus time is presented in figure 1.

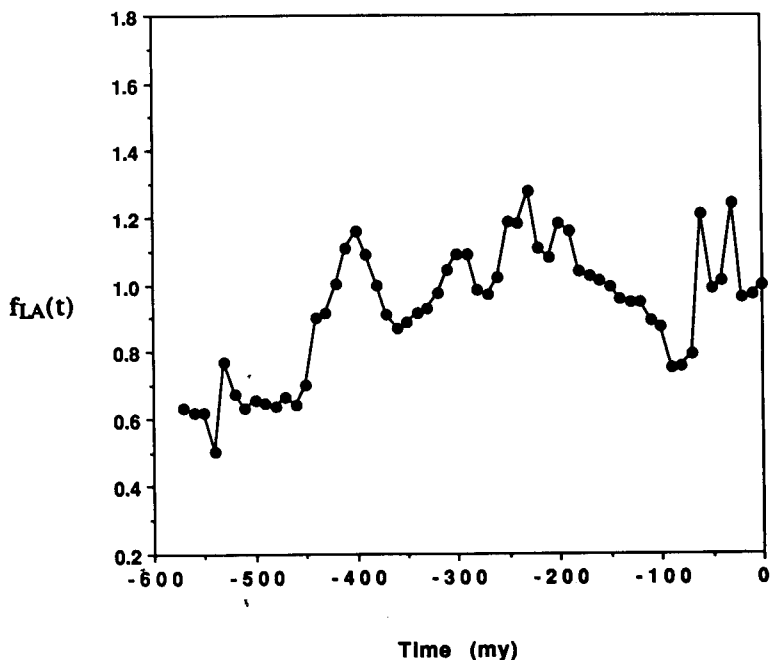


Fig. 1. Plot of the carbonate land area parameter  $f_{LA}(t)$  versus time.

The principal new factor introduced to the weathering expression for silicates is a greater emphasis on the uplift of mountain belts and, consequently, of changes in continental relief as expressed by the parameter  $f_R(t)$ . (In GEOCARB I  $f_R(t)$  was merely set proportional to the logarithm of continental land area). Increased continental relief should lead to enhanced erosion and quite likely to the enhanced weathering of silicates (Holland, 1978; Stallard, 1985; Berner and Berner, 1987). The idea is that enhanced stripping of the weathered mantle by physical erosion on steep slopes helps to expose fresh Ca and Mg silicate bedrock to further chemical weathering (the weathering-limited scenario of Stallard, 1985). Also, glacial erosion at very high elevations produces ground-up fresh rock debris that is available for weathering at the foot of the glaciers or in nearby lowlands. Furthermore, mountain belts on their windward sides experience orographic rainfall which should lead to enhanced runoff, enhanced erosion, and enhanced weathering (Raymo, Ruddiman, and Froelich, 1988). The relief parameter  $f_R(t)$  is applied only

to silicates and not to the weathering of carbonates, because relief appears not to be an important factor in carbonate dissolution (Holland, 1978) as exemplified by appreciable dissolution in even flat lowland areas such as Florida.

It is difficult to establish values for  $f_R(t)$  because of a lack of knowledge of paleotopography and paleohypsography. As a result we are forced to adopt a proxy for elevation or relief. Here I use the strontium isotopic composition of seawater as recorded by limestones over the past 600 my (Burke and others, 1982). The ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  in the oceans is used as a measure of mountain uplift according to the following argument (Raymo, 1991; Francois and Walker, 1992; Richter, Rowley, and DePaolo, 1992; Edmond, 1992): The value of  $^{87}\text{Sr}/^{86}\text{Sr}$  of the oceans represents a balance between inputs of Sr from the continental weathering of silicates (high  $^{87}\text{Sr}/^{86}\text{Sr}$ ), the weathering of carbonates (intermediate  $^{87}\text{Sr}/^{86}\text{Sr}$  similar to that of seawater), and from basalt-seawater reaction (low  $^{87}\text{Sr}/^{86}\text{Sr}$ ), combined with the output of Sr from the oceans in sedimentary carbonates (same Sr isotopic composition as the oceans). Calculations (Richter, Rowley, and DePaolo, 1992) indicate that changes in continental weathering fluxes should have a much greater effect on oceanic Sr isotopic composition than changes in the rate of basalt-seawater reaction. In this way an increase in the silicate weathering flux, because of the relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$  of most silicates exposed to weathering, should result in an increase in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater. This is especially true of silicates in the core of collisional mountain belts which exhibit very high  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Edmond, 1992).

The problem with using Sr isotopes as a measure of the silicate weathering flux, however, is that such a flux must be constrained by other factors. Most importantly, the flux must not disturb carbon mass balance (eq 1). In other words, on the multimillion year time scale enhanced weathering of silicates with enhanced removal of atmospheric CO<sub>2</sub> must be accompanied by enhanced degassing. Otherwise, atmospheric CO<sub>2</sub> would be rapidly exhausted (Sundquist, 1991). Strontium isotopes cannot be used blindly in isolation to calculate weathering rates; the rates must also be constrained by carbon cycle modeling as well as by other factors (Caldeira, 1992; Berner and Rye, 1992). Furthermore, an enhanced radiogenic Sr signal can result from the uplift and weathering of silicates that are unusually rich in  $^{87}\text{Sr}$ , such as are found at present in Himalayan headwaters (Krishnaswami and others, 1992; Edmond, 1992), and not necessarily from an increase in the global Sr (and carbon) flux from a weathering source of constant isotopic composition as assumed in a number of Sr isotope models. As an extreme case one can consider that changes in oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$  are due solely to changes in the continental weathering of radiogenic versus non-radiogenic sources (granites versus basalts) (Brass, 1976; Kump, 1989; Berner and Rye, 1992) and not to changes in global weathering rates.

In this paper I take a noncommittal position. It is that changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the oceans are due to changes in the weathering of silicates,

and a higher  $^{87}\text{Sr}/^{86}\text{Sr}$  of the source is correlated with enhanced silicate weatherability. Uplift due to continental collision exposes deeply buried old, highly radiogenic silicate rocks to weathering, and there is also the potential for enhanced weathering as a result of the uplift. With this approach one can ignore the exact cause of Sr isotope variation as long as the uptake of  $\text{CO}_2$  by silicate weathering is constrained by the supply of  $\text{CO}_2$  from degassing or organic subcycle imbalance, and the Sr isotopic composition of the oceans is mainly affected by uplift-induced silicate weathering.

According to the above discussion I let the uplift parameter  $f_R(t)$  represent the effect of silicate weathering on the oceanic value of  $^{87}\text{Sr}/^{86}\text{Sr}$ . In order to do this we must first correct for the effect of basalt-seawater reaction on oceanic Sr isotopic composition. To do this the following model is constructed (see also Richter, Rowley, and DePaolo, 1992):

$$dM_{\text{Sr}}/dt = F_{\text{riv}} - F_{\text{Src}} \quad (12)$$

$$dR_{\text{oc}}(t)M_{\text{Sr}}/dt = [R_{\text{bas}} - R_{\text{oc}}(t)]F_{\text{bas}} + R_{\text{riv}}F_{\text{riv}} - R_{\text{oc}}(t)F_{\text{Src}} \quad (13)$$

where:

$R_{\text{oc}}(t)$  = calculated  $^{87}\text{Sr}/^{86}\text{Sr}$  of oceans for some time  $t$

$M_{\text{Sr}}$  = mass of total Sr in the oceans

$F_{\text{riv}}$  = flux of total Sr to oceans from rivers

$F_{\text{Src}}$  = flux of total Sr from oceans to carbonates in sediments

$F_{\text{bas}}$  = flux of total Sr between basalt and seawater (input and output hydrothermal fluxes of total Sr to the ocean are about equal)

$R_{\text{bas}}$  = average  $^{87}\text{Sr}/^{86}\text{Sr}$  of basalt

$R_{\text{riv}}$  = average  $^{87}\text{Sr}/^{86}\text{Sr}$  of rivers

Combining eqs (12) and (13):

$$dR_{\text{oc}}/dt = \{[R_{\text{bas}} - R_{\text{oc}}(t)]F_{\text{bas}} + [R_{\text{riv}} - R_{\text{oc}}(t)]F_{\text{riv}}\}/M_{\text{Sr}} \quad (14)$$

In order to isolate the effect of basalt-seawater reaction on seawater composition, I hold  $F_{\text{riv}}$  and  $R_{\text{riv}}$  constant over time and equal to present day values. In addition, I assume that  $M_{\text{Sr}}$  is constant over time and that  $F_{\text{bas}}$  is linearly proportional to changes in seafloor spreading rate. In other words:

$$F_{\text{bas}} = f_{\text{SR}}(t)F_{\text{bas}}(0) \quad (15)$$

where  $f_{\text{SR}}(t)$  = spreading rate(t)/spreading rate(0) ( $f_{\text{SR}}(t) = f_G(t)$ , see below), and 0 refers to the present. Using the values (Palmer and Edmond, 1989; Richter, Rowley, and DePaolo, 1992):  $F_{\text{riv}} = 3.3 \times 10^{16}$  mol/my;  $R_{\text{riv}} = 0.711$ ;  $F_{\text{bas}}(0) = 0.92 \times 10^{16}$  mol/my;  $R_{\text{bas}} = 0.703$ ,  $M_{\text{Sr}} = 12.5 \times 10^{16}$  moles, by numerical integration of eq (14) a plot of  $R_{\text{oc}}(t)$  versus time is calculated for the effects only of basalt-seawater reaction on oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$ . (The calculation is set up so as to arrive at the measured value for oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$  at present.)

Once the curve for basalt-seawater reaction alone,  $R_{ocb}(t)$ , is constructed, it is then plotted along with actual measured values of  $^{87}\text{Sr}/^{86}\text{Sr}$  for seawater,  $R_{ocm}(t)$ . This is shown in figure 2. It is assumed that the difference  $R_{ocm}(t) - R_{ocb}(t)$  at any given time is a measure of the effect of continental silicate weathering on  $R_{oc}(t)$ . This difference is then assumed to be (approximately) linearly proportional to the uplift parameter  $f_R(t)$ :

$$f_R(t) = 1 - L[(R_{ocb}(t) - R_{ocm}(t))/(R_{ocb}(t) - 0.7000)] \quad (16)$$

where  $L$  = uplift proportionality factor. By varying  $L$  one can see how strongly changes in oceanic Sr isotope composition affect  $f_R(t)$  and, ultimately, atmospheric CO<sub>2</sub>. This approach is admittedly preliminary and crude, and other equally plausible approaches using Sr isotopes are possible, but they await further development of a better understanding of factors controlling the strontium isotopic composition of seawater.

*Weathering feedback functions.*—An important overhaul of the weathering feedback function  $f_B(\text{CO}_2)$  used in GEOCARB I has been undertaken. Most fundamentally the response of silicate weathering to changes in global temperature has been separated from the response of carbonate

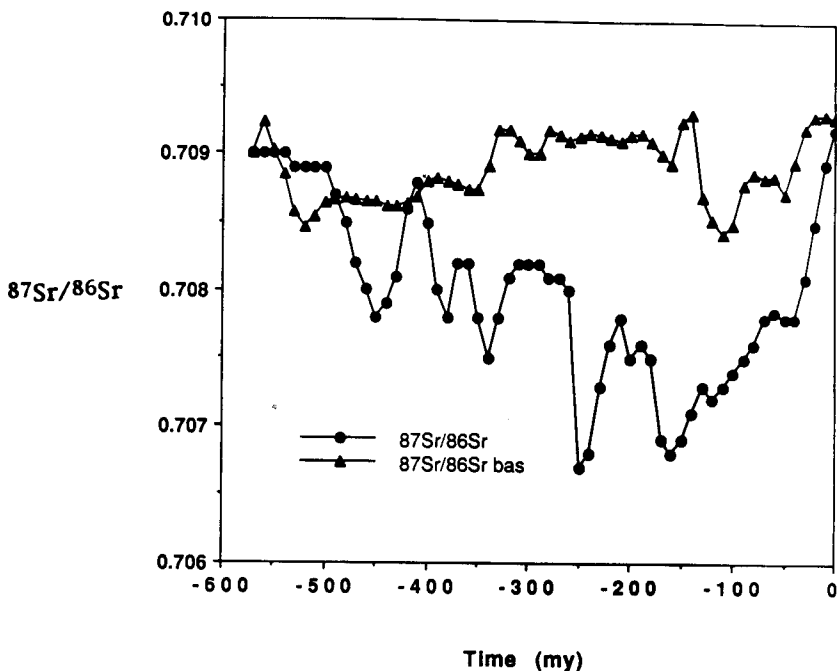


Fig. 2. Plots of  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater as a function of time. The upper curve represents values calculated for seawater-basalt reaction only. The lower curve represents actual measured data (Burke and others, 1982).



weathering. The feedback used previously for both silicates and carbonates (Berner, Lasaga, and Garrels, 1983; Berner, 1991) was based on the temperature dependence of the concentration of dissolved  $\text{HCO}_3^-$  in ground waters of limestones across North America (Harmon and others, 1975) and the temperature dependence of global runoff deduced from GCM modeling (Manabe and Stouffer, 1980; Gates, 1976). The result was then combined with the relation between global mean surface air temperature and atmospheric  $\text{CO}_2$  level derived from GCM modeling (Manabe and Stouffer, 1980) and the response of plant mediated weathering to  $\text{CO}_2$  fertilization. For carbonate weathering, this same approach is used in the present paper except that the alternative GCM result of Oglesby and Saltzman (1990) is used, and the effects of changes in solar radiation are introduced (see below). Because I now distinguish between feedbacks for silicate versus carbonate weathering, I introduce a new feedback parameter  $f_{\text{BB}}(\text{CO}_2)$  for carbonate weathering and separate it from  $f_{\text{B}}(\text{CO}_2)$  which is used now to refer only to silicates.

The situation for silicates is entirely different, and modeling is now based on a better understanding of the controls on silicate weathering. This includes new data on the temperature dependence of the rate of silicate dissolution based both on laboratory studies (summarized for Ca-Mg silicates by Brady, 1991) and field observations (Velbel, 1993) combined with knowledge concerning the relation between river runoff and dissolved  $\text{HCO}_3^-$  derived from Ca-Mg silicate weathering (Dunne, 1978; Peters, 1984; see also Bluth, 1990). For temperature dependence both the laboratory and field studies result in an activation energy for silicate dissolution of approx 15 kcal/mol which is used here.

The study of Dunne (1978) shows that dissolved Ca plus Mg and the dissolved  $\text{HCO}_3^-$  associated with them in a large number of Kenyan rivers that drain only silicate rocks follow the relation:

$$C = k'R^{-0.4} \quad (17)$$

where:  $R$  = runoff,  $C$  is concentration of Ca + Mg, and  $k'$  is an empirical constant. (Runoff here refers to mean annual runoff for each river, not the seasonal variation within each river.) Likewise, from the data of Peters, for rivers of the United States (including Hawaii) which drain only silicates, it can be shown that a similar relation results:

$$C = k''R^{-0.3} \quad (18)$$

From these results I assume that a general relation for global rivers can be used:

$$C = k'''R^{-0.35} \quad (19)$$

This result is used as a guide along with the results for the temperature dependence of dissolution rate in a simple global weathering model.

It is assumed that the concentration of dissolved HCO<sub>3</sub><sup>-</sup> from Ca + Mg silicate weathering in a "global regolith" can be represented by the expression:

$$dC/dT = J - (Q/V)C \quad (20)$$

where:

C = concentration of HCO<sub>3</sub><sup>-</sup> in mass per unit volume

J = flux of HCO<sub>3</sub><sup>-</sup> into solution from Ca + Mg silicate weathering (mass per volume per unit time)

Q = global discharge (volume per unit time)

V = volume of water contained in the regolith

Now:

$$Q = RA \quad (21)$$

$$V = hA\Phi \quad (22)$$

where:

R = continental runoff (discharge per unit area)

A = surface area of that portion of the continents undergoing weathering

h = average thickness of the regolith

Φ = average regolith porosity

If it is assumed that in most regoliths the buildup of dissolved C is small such that there is negligible back-reaction (in other words, the water is far from equilibrium with the dissolving silicates), the term J can be considered to be only a function of temperature and not of concentration C. At steady state, dC/dt = 0, and substituting the above relations we obtain:

$$C = h\Phi J/R \quad (23)$$

Here the 1/R dependence of concentration C represents the situation of pure dilution for a constant input flux J. The direct dependence of C on h reflects the buildup in concentration for the longer water residence time that would accompany a larger (thicker) regolith water volume. As a check on this simple relation one can cite the inverse relation found between dissolved bicarbonate and runoff for seasonal variation of the Zaire River (Probst, Mortatti, and Tardy, 1993) which drains mainly silicates.

If we make the reasonable assumption that average regolith thickness (volume per unit area) from one area to another increases with mean annual runoff or in other words more runoff means more weathered rock due to increased flushing and enhanced vegetational effects, we can derive an expression from eq (23) that agrees with the observations of Dunne and Peters. The appropriate relation is:

$$h = kR^{0.65} \quad (24)$$

where  $k$  is a proportionality constant. Combining eqs (23) and (24) we obtain:

$$C = \Phi k J R^{-0.35} \quad (25)$$

which is functionally equivalent to the empirical relation (19). According to this model the empirically observed relation ( $R^{-0.35}$ ) for a variety of rivers represents a combination of pure dilution ( $R^{-1.00}$ ) and changes in average regolith thickness ( $R^{0.65}$ ).

Now the global weathering feedback, as a function of temperature  $f_B(T)$ , can be expressed as the ratio of weathering fluxes (Berner, Lasaga, and Garrels, 1983);

$$f_B(T) = [C(T)/C(T_0)] \times [R(T)/R(T_0)] \quad (26)$$

where  $T$  and  $T_0$  refer to global mean surface air temperature at some time in the past and at present, respectively. If we assume that  $k$  and  $\Phi$  do not change with time, then from eqs (25) and (26):

$$f_B(T) = [J(T)/J(T_0)] \times [R(T)/R(T_0)]^{0.65} \quad (27)$$

From the standard Arrhenius formulation of dissolution rate we obtain the relation:

$$\ln [J(T)/J(T_0)] = [\Delta E/R][(T - T_0)/TT_0] \quad (28)$$

where  $\Delta E$  = activation energy,  $T$  = temperature in  $^{\circ}\text{K}$ , and  $R$  = the gas constant ( $1.99 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ). Since changes in global mean temperatures over Phanerozoic time have been small, one can consider the product  $TT_0$  to be a constant for our purposes ( $=288^2$ ). Substituting the value  $\Delta E = 15,000 \text{ cal/mol}$  (Brady, 1991) and simplifying:

$$J(T)/J(T_0) = \exp [0.090(T - T_0)] \quad (29)$$

We also have the relation for runoff as a function of temperature (Berner, Lasaga, and Garrels, 1983) derived from GCM modeling (Manabe and Stouffer, 1980; Manabe and Bryan, 1985). (Changes in runoff due to factors other than temperature are included in the parameter  $f_D(t)$ ). The derived relation is:

$$R(T)/R(T_0) = 1 + 0.038(T - T_0) \quad (30)$$

Combining eqs (29) and (30) with eq (27):

$$f_B(T) = \{\exp [0.090(T - T_0)]\} \times [1 + 0.038(T - T_0)]^{0.65} \quad (31)$$

At this point we introduce the relation between global mean surface temperature and atmospheric  $\text{CO}_2$  level derived from GCM modeling. Further, because we are dealing with such long geological time scales we

must also introduce the effects on global temperature due to changes in solar radiation with time (Caldeira and Kasting, 1992). The appropriate expression is:

$$T(t) - T(0) = \Gamma \ln(\text{RCO}_2) - W_s(t/570) \quad (32)$$

where  $\text{RCO}_2$  is the ratio of the level of atmospheric CO<sub>2</sub> in the past at a given time to that at present,  $\Gamma$  is a constant derived from the GCM modeling,  $W_s$  is the sensitivity of temperature solely to changes in solar radiation (also derived from GCM modeling), and  $t$ , 570, and 0 refer to some time in the past, to the beginning of the Phanerozoic, and to the present, respectively. Substituting eq (32) in eq (31) and simplifying we obtain the relation between CO<sub>2</sub> and the rate of weathering which we will use as our feedback function due to changes in temperature:

$$f_B(\text{CO}_2)_T = \exp[-0.09W_s(t/570)] \times (\text{RCO}_2)^{0.09\Gamma} \times [1 + 0.038\Gamma \ln(\text{RCO}_2) - 0.038W_s(t/570)]^{0.65} \quad (33)$$

One last term needs to be added to this expression. It is the additional effect due to possible CO<sub>2</sub> fertilization of weathering rate. The same formulation used earlier is used here where it is assumed that the weathering response follows a Michaelis-Menton formulation (Volk, 1989), the maximum effect of fertilization is a doubling of weathering rate, and only about 35 percent of plants respond to CO<sub>2</sub> fertilization (see Berner, 1991 for further details). The complete CO<sub>2</sub> feedback expression is, thus:

*With vascular land plant fertilization:*

$$f_B(\text{CO}_2) = \exp[-0.09W_s(t/570)] \times (\text{RCO}_2)^{0.09\Gamma} \times [1 + 0.038\Gamma \ln(\text{RCO}_2) - 0.038W_s(t/570)]^{0.65} \times [2\text{RCO}_2/(1 + \text{RCO}_2)]^{0.4} \quad (34)$$

Eq (34) is used in the present work to apply to plant-mediated weathering for the past 300 my. This differs from the previous formulation in that no distinction is made now between the feedback by CO<sub>2</sub> on angiosperm versus gymnosperm mediated weathering. (Nevertheless, differences in *rates* of weathering as represented by  $f_E(t)$  for the two vegetation types are retained from the earlier model.) Before the time when vascular land plants became abundant in upland areas and could affect weathering, a different feedback formulation is made. Stronger feedback during this period is necessary in order to avoid excessively high values of CO<sub>2</sub>. In the absence of plants it is assumed that there is a direct response of both silicate and carbonate weathering to atmospheric CO<sub>2</sub>. The functional dependence should lie somewhere between  $f_B(\text{CO}_2) = \text{RCO}_2^{0.25}$  for the response to a weathering system open to exchange of gases with the atmosphere and  $f_B(\text{CO}_2) = \text{RCO}_2$  for a closed system where CO<sub>2</sub>-charged water enters the ground and reacts with minerals only

slowly at depth (Berner, 1992). Here I adopt an intermediate situation where  $f_B(\text{CO}_2) = \text{RCO}_2^{0.50}$ . To this I add the effects of changes in temperature due to changes in atmospheric  $\text{CO}_2$  and in solar radiation but exclude the expression for the  $\text{CO}_2$  fertilization of plant-mediated weathering because of the absence of higher plants. The overall expression for silicate weathering, thus, is:

*Before vascular land plants:*

$$\begin{aligned} f_B(\text{CO}_2) = & \exp[-0.09W_s(t/570)] \times (\text{RCO}_2)^{0.09\Gamma} \\ & \times [1 + 0.038\Gamma \ln(\text{RCO}_2) - 0.038W_s(t/570)]^{0.65} \\ & \times \text{RCO}_2^{0.50} \end{aligned} \quad (35)$$

For the period when vascular land plants were evolving and spreading to upland areas we introduce, as earlier, a linear mix of expressions. Thus, between 350 and 300 myBP we linearly mix eqs (34) and (35) which results in a smooth variation of  $\text{RCO}_2$ . Without it, as already pointed out (Berner, 1991), excessive values of  $\text{RCO}_2$  result for this period.

The changes applied to silicate weathering to account for changes in solar radiation are also applied to carbonate weathering. Otherwise the formulation of Berner, Lasaga, and Garrels (1983) is used where it is assumed that carbonates saturate the soil or ground water in contact with them so rapidly that changes in runoff do not result in appreciable dilution. In other words, the concentration  $C(T)$  is assumed to be independent of runoff  $R(T)$ . Accordingly the appropriate expressions for  $f_{\text{BB}}(\text{CO}_2)$ , the feedback function for carbonate weathering, are:

*With vascular land plant fertilization:*

$$\begin{aligned} f_{\text{BB}}(\text{CO}_2) = & [1 + 0.087\Gamma \ln(\text{RCO}_2) - 0.087W_s(t/570)] \\ & \times [2\text{RCO}_2/(1 + \text{RCO}_2)]^{0.4} \end{aligned} \quad (36)$$

*Before vascular land plants:*

$$f_{\text{BB}}(\text{CO}_2) + [(1 + 0.087\Gamma \ln(\text{RCO}_2) - 0.087W_s(t/570))\text{RCO}_2^{0.50} \quad (37)$$

In order to apply eq (34) to (37) to the model it is necessary to specify values of  $\Gamma$  and  $W_s$ , the parameters relating the response of global temperature to changes in atmospheric  $\text{CO}_2$  and solar radiation, respectively. The value of  $\Gamma = 6^\circ\text{C}$ , which is equivalent to a  $4^\circ\text{C}$  rise for a doubling of  $\text{CO}_2$ , is used here based on the GCM model of Oglesby and Saltzman (1990). For consistency the value of  $W_s = 12.9^\circ\text{C}$ , which is derived from similar GCM modeling (Oglesby and Marshall, 1992), and the change of solar flux with time (Caldeira and Kasting, 1992) is adopted. The Oglesby  $W_s$  result is equivalent to a linear increase of  $2.8^\circ\text{C}$  for each 1 percent increase in the solar radiation flux. Solar flux values used are based on a simplified expression fitted to the data of other

workers as reported by Caldeira and Kasting; it is  $\Delta S = -4.6(t/570)$ , where  $\Delta S$  is the percent change in solar flux, and  $t$  is time before the present in millions of years. Use of  $\Gamma$  and  $W_s$  each from different studies, for example  $\Gamma = 3.5^\circ\text{C}$  (Manabe and Bryan, 1985) and  $W_s = 12.9^\circ\text{C}$  (Oglesby and Marshall, 1992) was found to produce physically impossible results in the model including unreasonable values of atmospheric CO<sub>2</sub> in the early Paleozoic. By contrast different, but internally consistent,  $\Gamma$  and  $W_s$  values by the same author (Manabe) gave CO<sub>2</sub> results similar to those obtained here.

*Other weathering parameters.*—No changes have been made in the parameter  $f_E(t)$  that expresses the effects of the rise and evolution of vascular land plants on the rates of both silicate and carbonate weathering. As before, exploration of the effect on RCO<sub>2</sub> of varying the value of  $f_E(T)$  prior to the rise of plants is made. There is some evidence to support the use of the lowest value considered  $f_E(t) = 0.15$  as a standard reference point for the pre-plant situation, based on the data of Drever and Zobrist (1992). (See Results and Discussion.) As in GEOCARB I, I use a value of  $f_E(t) = 0.75$  for weathering by pteridophytes and gymnosperms (300-130 myBP) with a transition to angiosperm-controlled weathering taking place between 130 and 80 myBP. After 80 my the value of  $f_E(t)$  is set equal to one.

The values used for the river runoff factor  $f_D(t)$  based on the study of Tardy, N'Koukou, and Probst (1989) have been replaced by values furnished to the writer by Bette Otto-Bliesner of the University of Texas at Arlington (Otto-Bliesner, 1993). Otto-Bliesner's values for twelve different times spanning the Phanerozoic are based on GCM modeling of paleocontinents without topographic relief, and ratios are taken here to her value for the present continents also calculated for the case of no relief. Use of GCM modeling is preferable to the approach used by Tardy, N'Koukou, and Probst. The Tardy approach, although good as a first approximation, is based on the assumption of constant latitudinal belts of P-E (precipitation minus evaporation) for all time, equal to those today. The continents then move under these belts as the result of continental drift over geologic time. Otto-Bliesner's approach, in addition to latitudinal changes, includes the effects of changes in such things as continental size as it affects the degree of monsoonal development, changes in the distribution of water around continents, et cetera.

Use of  $f_D(t)$  in the expression for the weathering of silicates is raised to the 0.65 power to account for dilution, as described in the section on weathering feedbacks. By comparison,  $f_D(t)$  is applied linearly to the weathering of carbonate because of the reasonable assumption that ground waters in limestone/dolostone terrains attain saturation with respect to the surrounding carbonate minerals.

An additional problem involving runoff is that eliminating the land area parameter  $f_A(t)$  in the expression for the weathering of Ca-Mg silicates (eq 11) leaves out the multiplication of  $f_D(t)$ , which is expressed per unit land area, by  $f_A(t)$  to get the proper flux units. To correct for this,

the present formulation inherently assumes that changes in the land area of actively weathering (that is high relief) regions, as well as their elevation, is reflected by changes in  $^{87}\text{Sr}/^{86}\text{Sr}$  as they are incorporated in the relief parameter  $f_R(t)$ . Also, implied in this is the assumption that changes in total global runoff are in the same proportion as changes in runoff from only the actively weathering regions.

#### DEGASSING PARAMETERS

The parameters  $f_G(t)$  and  $f_C(t)$  that express changes in  $\text{CO}_2$  degassing rate have undergone some revision from values used in GEOCARB I. First of all, the data of Engebretson and others (1992) for the past 150 my is now used for  $f_G(t)$ , the parameter that expresses changes in degassing due to changes in global tectonics. Engebretson and others calculate rates of seafloor subduction over time using a fixed hot spot reference frame. This provides data that are an improvement over the formulation of GEOCARB I which used sealevel as a proxy for seafloor spreading rate according to the inversion by Gaffin (1987) of paleo-sealevel estimates. Subduction is a major process whereby Ca-Mg carbonates in sediments are carried downward to higher temperatures and transformed to silicates by metamorphism or by volcanism with the consequent release of  $\text{CO}_2$ . Thus, use of direct subduction estimates in calculating  $f_G(t)$  is a preferable approach. However, this approach does not include  $\text{CO}_2$  from mantle plume volcanism, and parameterization of this process requires further modeling.

For the remainder of geologic time (570-150 myBP) I am forced to continue to use the sealevel inversion method of Gaffin to calculate  $f_G(t)$  because of a lack of direct subduction data. The method rests on the idea that sealevel changes reflect changes in rates of seafloor spreading, which in turn correlate with subduction and global degassing rate (Berner, Lasaga, and Garrels, 1983). In other words, with increased spreading rate the volume of the mid-oceanic ridges increases, displacing sealevel upward, and at the same time there is increased subduction (and degassing) to conserve seafloor area. This approach isn't quite as crude as it first appears. For one thing sealevel rise also results from continental breakup, and during such breakup one would again expect both sealevel rise and increased degassing, in this case because of new extension-zone volcanism. Furthermore, for the past 150 my there is an excellent correlation of sealevel calculated from subduction (spreading) rate and that estimated by independent methods (Engebretson and others, 1992). A plot of  $f_G(t)$  versus time based on the Gaffin model for 570 to 150 my and the Engebretson subduction results for 150 my to the present is presented in figure 3.

The other degassing parameter  $f_C(t)$  expresses the effect of the relative amount of deposition of Ca-Mg carbonates in shallow water versus that in the deep sea. Changes in the distribution of carbonates affect degassing because deep sea carbonates have a higher probability of being thermally decomposed. (The distribution of deep sea carbonate

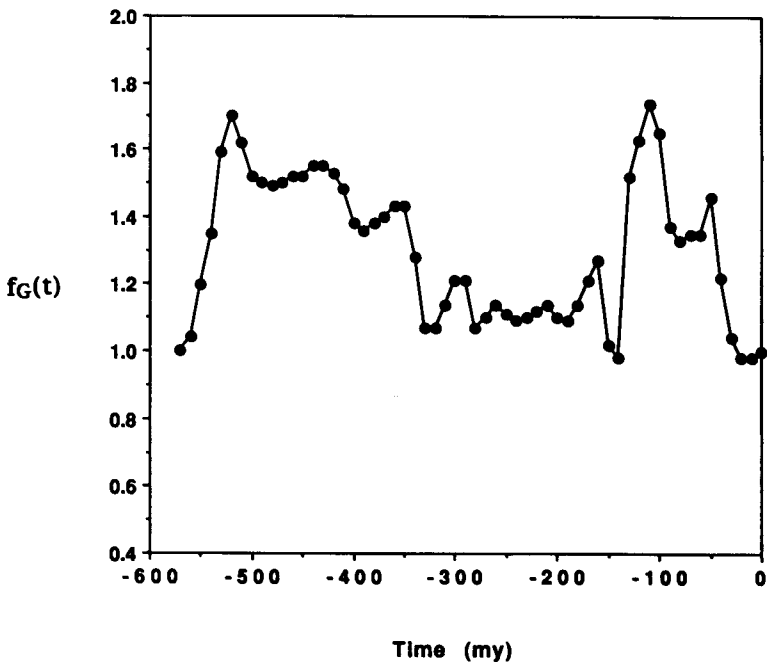


Fig. 3. Plot of the tectonic degassing parameter  $f_G(t)$  versus time.  $f_G(t)$  is assumed equal to the parameter  $f_{SR}(t) = \text{spreading rate}(t)/\text{spreading rate}(0)$ .

between subducting and non-subducting seafloor is an additional complication.) Deep sea carbonates are carried atop oceanic sea floor as it plunges down subduction zones where they may undergo metamorphic breakdown or be dragged downward into the mantle with further heating. By contrast, carbonates deposited on continental shelves or shallow platforms are thermally decomposed only by the diagenesis and metamorphism that accompanies deep burial in sedimentary basins.

There are two approaches to calculating  $f_G(t)$ . The first is based on the hypothesis that during the Jurassic and Cretaceous periods (about 150-100 my ago) plankton, such as foraminifera and coccolithophorids, arose that could secrete calcium carbonate in the waters of the open ocean and thus deliver their skeletal debris to deep sea sediments upon death. Subsequently, the evolution of calcareous plankton has resulted in the gradual transfer of carbonate to the deep sea over Cretaceous and Cenozoic time. Before 150 my virtually all carbonate is believed to have been deposited in shallow water because there is no evidence for calcareous planktonic fossils in older sedimentary rocks. With this approach  $f_G(t)$  is assumed to have been lower and constant prior to 150 myBP and to have increased linearly with time over the past 150 my to the present value of one. This is the approach used by Wilkinson and Walker (1989)



and Caldeira (1992) and also that adopted here for the standard situation. In GEOCARB I a similar approach was used, but it was assumed that the value of  $f_C(t)$  increased more rapidly during the earlier part of the 150 my period with the present value of one approached asymptotically.

There is an alternative way to formulate  $f_C(t)$ . The reasoning is that carbonate is deposited in the deep sea when sealevel is low and shallow platforms and shelves are emergent and not available for deposition. Conversely, when sealevel is high, large areas of the continents are flooded by shallow epeiric seas, and benthic organisms secrete large amounts of calcium carbonate on the continents and thereby "rob" the deep sea floor of carbonate. The lack of fossil evidence for calcareous plankton prior to 150 myBP is ignored because it is assumed that the evidence has been erased by diagenesis or that carbonate falling to the deep sea floor was originally precipitated by a nonbiological process. (Rare evidence for calcareous plankton prior to 150 my has been described for upper Triassic sediments; for example, see Bralower, Brown, and Siesser, 1991.) Using this as an alternative approach, I let  $f_C(t)$  correlate positively with  $f_A(t)$ , the total land area parameter. The idea behind this is that a rise in sealevel should both reduce land area and lower the proportion of  $\text{CaCO}_3$  deposited in the deep sea by providing more shallow water sites for deposition. The response of  $f_C(t)$  to changes in land area, as reflected by  $f_A(t)$ , is unknown, but for the sake of sensitivity analysis I arbitrarily set  $f_C(t) = f_A(t)$  or  $f_C(t) = f_A(t)^2$ . These formulations are compared to the standard formulation (for change only from 150 my to the present) in figure 4.

#### OTHER PARAMETERS

An additional change from GEOCARB I is the omission of the masses of organic carbon  $G$  and carbonate carbon  $C$  as well as the kinetic rate constants for degassing  $k_{mg}$  and  $k_{mc}$ , from the expressions for the metamorphic/volcanic degassing fluxes  $F_{mg}$  and  $F_{mc}$ . By contrast, inclusion of  $G$  and  $C$ , along with the corresponding rate constants, is retained in the expressions for weathering. The reason for this distinction is that during transfer of carbonates to the deep sea over the past 150 my the amount of carbonate available for continental weathering would have diminished while the amount subjected to metamorphism and volcanism would not have changed. Therefore, this change in mass should be accounted for in the weathering expressions for  $F_{wc}$  and  $F_{wg}$  but not in those for the degassing fluxes. In order to express this the degassing parameters  $f_C(t)$  and  $f_C(t)$  in the new formulation are simply multiplied by the degassing rates at present,  $F_{wg}(0)$  and  $F_{wc}(0)$ , to obtain  $F_{wg}$  and  $F_{wc}$  in the past. (This change makes little difference in results for  $\text{RCO}_2$ , but it is more correct physically.)

One can extend this approach to remove  $G$  and  $C$  and  $k_{wg}$  and  $k_{wc}$  also from the weathering expressions. As a result the mass of each type of carbon and its isotopic composition is not tracked, nor is total carbon in

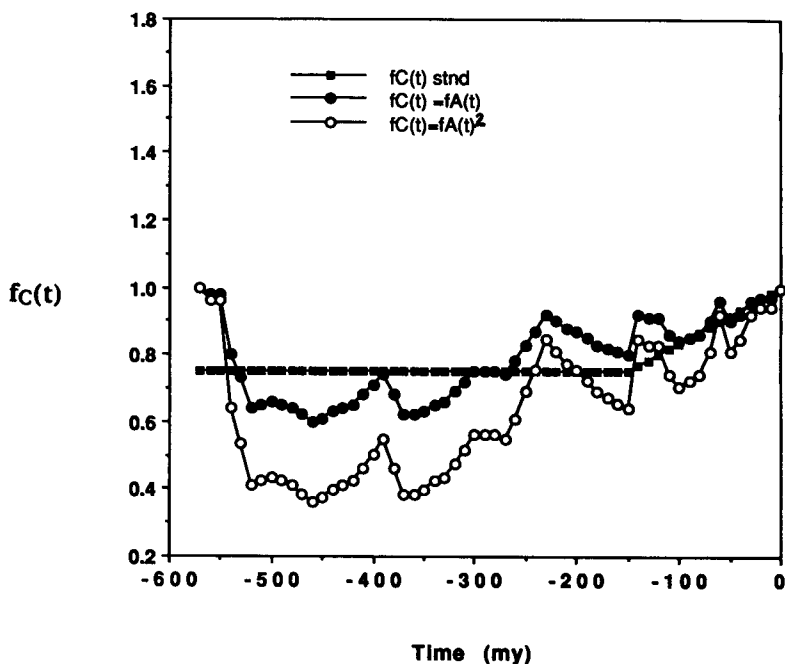


Fig. 4. Plot of the carbonate transfer parameter  $f_C(t)$  versus time for different formulations.  $f_A(t)$  = total land area(t)/total land area(0).

the surficial system held constant. In this case, the weathering expressions simply multiply the  $f(t)$  parameters by  $F_{wg}(0)$  and  $F_{wc}(0)$ , the present day weathering fluxes. In addition division of the thermal breakdown flux of CO<sub>2</sub> into carbonate and organic sources is not done. Rather *total* degassing ( $F_m = F_{mg} + F_{mc}$ ) at present is simply multiplied by  $f_C(t)$  and  $f_C(t)$  to obtain degassing rates in the past. This approach I refer to as the simplified "mantle" model, the results of which are used to test sensitivity to relaxation of the assumption of total crustal carbon. (The parameter  $f_C(t)$  is left in the model to restrict results to this sensitivity.) The idea behind it is that if much degassing is mantle derived, it is impossible to track the origin of the CO<sub>2</sub>, and possible inequalities between rates of mantle degassing of carbon and subduction of carbon into the mantle do not need to be addressed. In the standard model and in GEOCARB I, it is assumed that these rates balance one another so that there is no long term loss of carbon to or gain of carbon from the mantle, and the total carbon in the crustal system as a result remains essentially constant over time. The simplified "mantle" model assigns isotopic values to organic carbon ( $\delta = -23$  permil), carbonate carbon ( $\delta = 2$  permil), and the "mantle" ( $\delta = -3$  permil) which are held constant over time. The "mantle" value represents the mean  $\delta$  value for crustal carbon (80 percent carbon-

ate C with  $\delta = 2$  permil and 20 percent organic C with  $\delta = -23$  permil at present). Use of a different value for the mantle requires that proportionately different values be assigned to the abundance and/or isotopic composition of the two crustal carbon reservoirs and to the rate of silicate weathering, at present  $F_{si}(0)$ ; otherwise present day fluxes are not obtained.

The "mantle" model, although simpler mathematically, has not been adopted as a standard in the present paper, because I believe that most degassing comes from volcanic breakdown of recently subducted material, metamorphism, and diagenesis, and that the relative masses of crustal organic and carbonate carbon and their isotopic composition should be tracked over time. Furthermore, results from the mantle model are very similar to those for the standard model which makes the whole exercise rather academic as far as  $CO_2$  is concerned.

The values for other parameters used in GEOCARB I are also used here. This includes the total masses of organic carbon G and carbonate carbon C at present, the rate constants for weathering  $k_{wg}$  and  $k_{wc}$ , present day burial flux values for organic carbon  $F_{bg}(0)$  and carbonate carbon  $F_{bc}(0)$ , the present day weathering flux for Ca-Mg silicates  $F_{wsi}(0)$ , the smoothed curve of  $\delta^{13}C$  of carbonates undergoing burial as a function of time  $\delta_{bc}$ , mean  $\delta^{13}C$  values for organic matter and carbonates at present  $\delta_G(0)$  and  $\delta_C(0)$ , and the marine fractionation factor for carbon isotopes  $\alpha_c$ . The reader is referred to Berner (1991) for actual values of these parameters.

#### RESULTS AND DISCUSSION

Results for atmospheric carbon dioxide expressed as  $RCO_2$ , the ratio of atmospheric  $CO_2$  mass at any time  $t$  to that at present, are shown in figures 5 to 16. The purpose of these plots is to illustrate the sensitivity of the modeling to a variety of input parameters and, in several cases to investigate the response to alternate parameter formulations. Figure 17, a plot of organic carbon burial rate  $F_{bg}$  versus time, serves as a check on the results of the modeling. Figure 18 compares results between GEOCARB I and GEOCARB II. Finally, figure 19 represents my best estimate of  $RCO_2$  based on choices of the various parameters discussed in the previous section. It is used as a standard for comparison and is shown in all  $RCO_2$  plots where it is labeled as "stdn."

Figure 5 shows the effect of including changes in solar radiation in the feedback for weathering,  $f_B(CO_2)$ . As can be seen inclusion of solar evolution makes a considerable difference in values of  $RCO_2$  calculated for the early and middle Paleozoic (570-300 myBP). The solar "constant" has increased by about 5 percent since the beginning of the Cambrian period, and its effect on weathering and  $RCO_2$  is significant. Figure 6 shows that simply to maintain a constant earth surface temperature equal to that of today it was necessary for  $CO_2$  levels over much of Phanerozoic time to have been appreciably higher than that at present. This is in keeping with the results of Walker, Hays, and Kasting (1981) and

## Effect of Change in Solar Flux

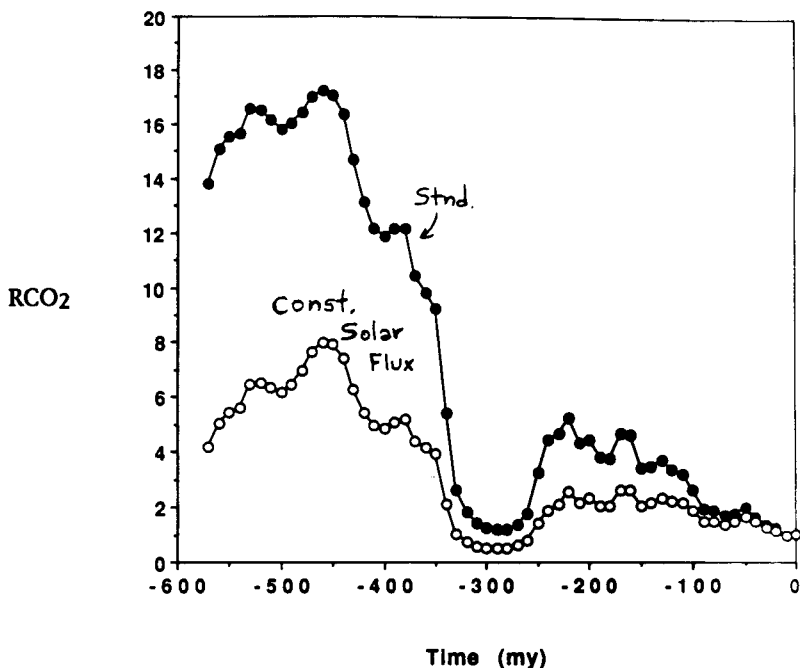


Fig. 5.  $RCO_2$  for constant solar flux over time compared to that for the standard situation.  $RCO_2$  = mass of atmospheric  $CO_2$  at time  $t$  divided by that at "present" (= 300 ppmv).

## Constant Temperature Earth

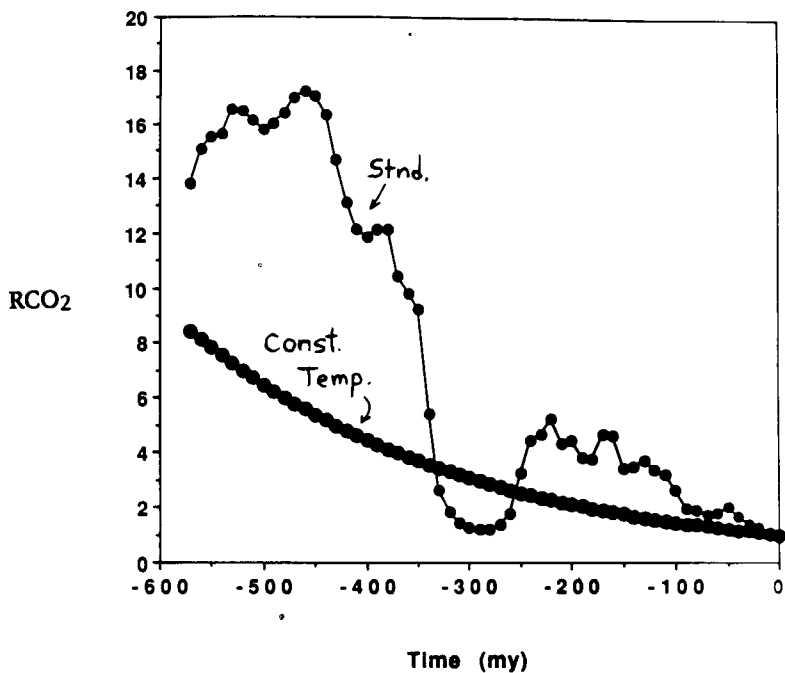


Fig. 6.  $RCO_2$  for constant mean surface air temperature versus that for the standard situation. For the constant temperature case temperature variations due to changing  $CO_2$  are balanced by variations due to changing solar flux.

Caldeira and Kasting (1992) who have suggested that increases in solar luminosity over geologic time have been met with general decreases in atmospheric  $\text{CO}_2$ , due to the negative weathering feedback effect, in order to maintain a constant earth surface temperature. Variations of the standard curve about the constant temperature curve in figure 6 illustrate the effects of the long term carbon cycle on  $\text{RCO}_2$  beyond that due to solar radiation increase.

Figure 7 illustrates the effects of varying the value of  $f_E(t)$  before the rise of vascular land plants. This value is poorly known (Berner, 1992), but recent results of Drever and Zobrist (1992) suggest that the adopted standard value of  $f_E(t) = 0.15$ , representing a sevenfold enhancement of the rate of weathering by higher plants, is reasonable. Drever has shown that silicate mineral weathering in a region of the southern Swiss Alps, as evidenced by water chemical composition, shows about a sevenfold increase in rate (once correction is made for temperature differences) going from unvegetated higher elevation portions to vegetated lower elevation portions of the same watersheds. In addition, results of field studies of the effect of higher plants on the rate of weathering of basalt in Hawaii (Cochran and Berner, 1993) indicate that there is a large effect of plant rootlets on the initial (centuries to millenia) dissolutive attack of the basalt. (However, there are insufficient data at present to establish a longer term effect.)

Judging from figure 7 there is no doubt that plant evolution could have had a major effect on the evolution of atmospheric carbon dioxide, at least during the Paleozoic. An idea of the importance of biological evolution is shown in figure 8 where the standard curve is compared to the situation where  $f_E(t) = 1$  for all time, in other words for the same effect of plants on weathering rate for all time as at present. The especially large effect on  $\text{CO}_2$  of plant evolution during the Paleozoic, as has been stated before (Berner, 1991), is believed to be due to both the effect of vascular plants on weathering and the supply by these plants of new forms of refractory organic matter (for example, lignin and its decomposition products) for burial and preservation in sediments. An idea of the independent importance of organic burial is shown in figure 9. Here the standard curve is compared to the situation where organic burial rate is greatly diminished during the Permo-Carboniferous by holding  $\delta_{bc}$  constant for all time at 1 permil. (See Berner and Canfield, 1989 for further discussion.) Note the resulting decreased deepening of the Permo-Carboniferous  $\text{RCO}_2$  "trough."

The effect of continental relief, or mountain uplift, as represented by the Sr isotopic composition of the oceans, is portrayed in figure 10. Since there is no a-priori method for estimating the value of  $L$ , the proportionality factor relating  $^{87}\text{Sr}/^{86}\text{Sr}$  to  $f_R(t)$  in eq (16), several values of  $L$  are investigated. (A value of  $L = 0$  corresponds to no change in relief, or  $f_R(t) = 1$  for all time.) The major effect of varying  $L$  is shown by high  $\text{RCO}_2$  values during the Mesozoic, when the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the oceans was lowest, and a general decrease in  $\text{RCO}_2$  during the Cenozoic. The value

## Effect of Vascular Land Plants

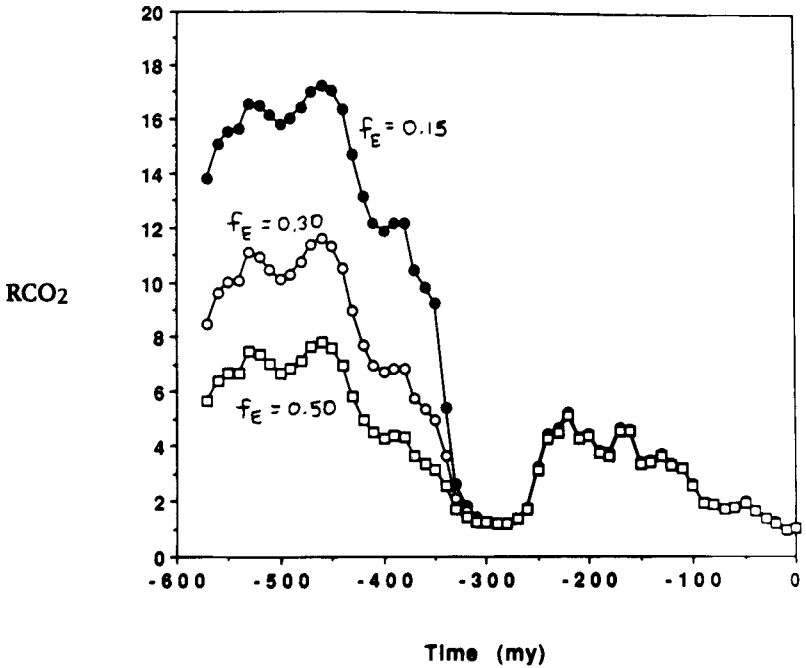


Fig. 7.  $RCO_2$  for different values of  $f_E(t)$  prior to the rise of vascular land plants. A lower  $f_E(t)$  value represents a greater effect of vascular plants on weathering.

## Effect of Organic Evolution

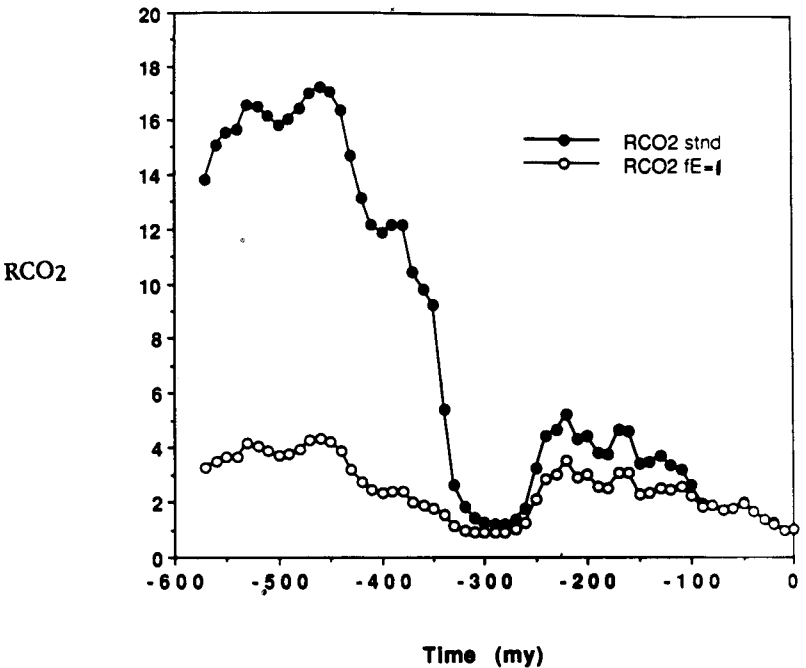


Fig. 8. Effect of organic evolution on  $CO_2$ . Holding  $f_E(t) = 1$  assumes that the present day effect of vascular plants on weathering applies to the entire Phanerozoic.

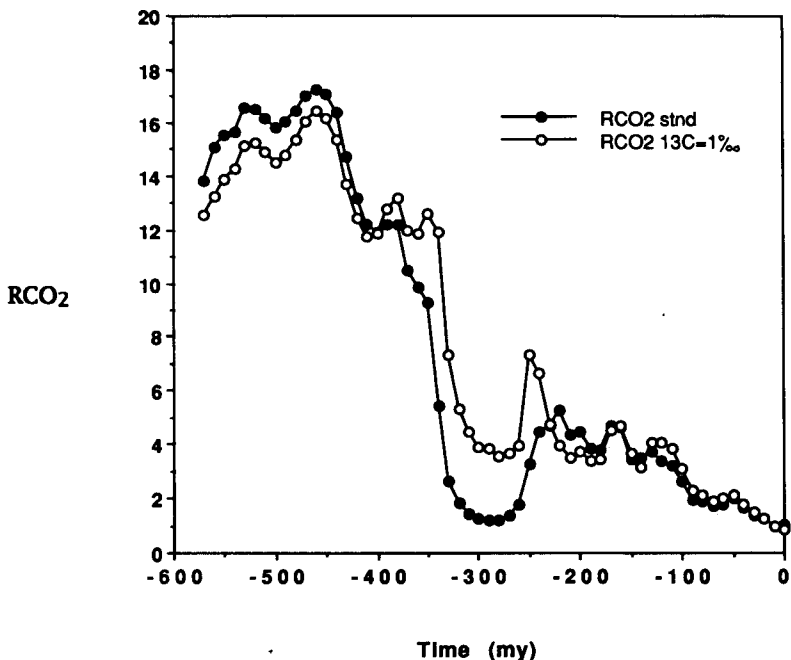


Fig. 9. Effect on  $\text{CO}_2$  of holding  $\delta^{13}\text{C}$  of carbonates being buried ("the oceans") constant (=1 permil) for all time.

### Effect of Uplift (Using Sr Isotopes)

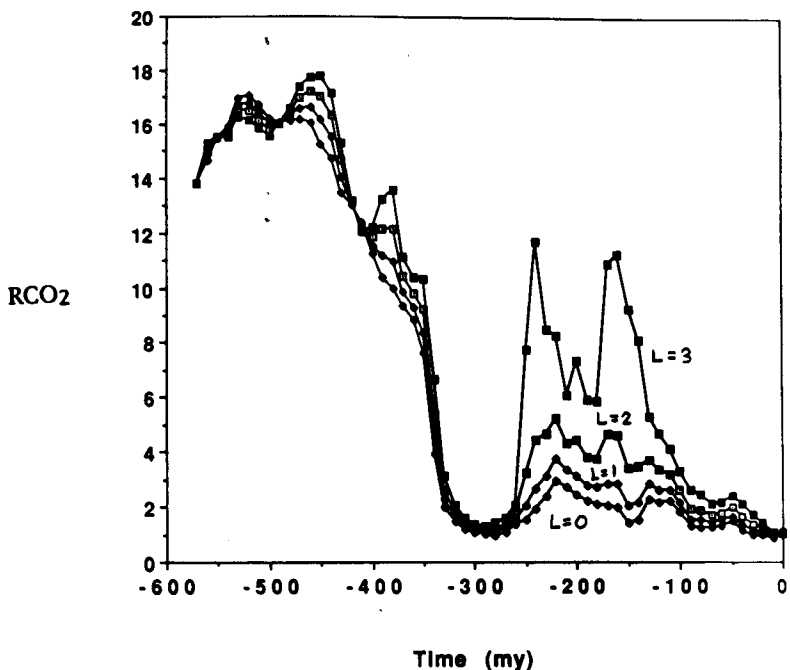


Fig. 10. Effect on  $\text{CO}_2$  of uplift (relief) as calculated via a Sr isotope model (see text). The parameter  $L$  is an intensity factor that relates the uplift parameter  $f_R(t)$  to the difference between the oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$  calculated for basalt-seawater reaction alone and the actual measured value (see fig. 2).

of  $L = 2$  is chosen for the standard situation so that the peak values of  $\text{RCO}_2$  during the Triassic ( $\approx 230$  my) and Jurassic ( $\approx 160$  my) do not become too much greater than values for the mid-Cretaceous ( $\approx 110$  my). This is in keeping with the common assumption of extreme mid-Cretaceous warming. Also, the  $\text{RCO}_2$  curve for  $L = 2$  agrees well with independent Mesozoic and Cenozoic values of  $\text{RCO}_2$  determined by Freeman and Hayes (1992).

The effect of different formulations of the parameter  $f_C(t)$ , which expresses the effect on degassing of changes in the distribution of  $\text{CaCO}_3$  sediments between shallow water and the deep sea, is shown in figures 11 and 12. Figure 11 shows the effect of varying the  $f_C(t)$  value for times prior to 150 my. As might be expected  $\text{RCO}_2$  prior to 150 my is sensitive to the value chosen for  $f_C(t)$  at that time. Since there is no a-priori method of directly estimating  $f_C(t)$ , I am forced to use indirect methods to narrow the probable range. If one lowers the pre-150 my value of  $f_C(t)$  to less than 0.50, there are severe consequences. Values of  $\text{RCO}_2$  during the Permo-Carboniferous minimum become impossibly low (below the photosynthetic limit for  $\text{C}_3$  plants), and some even go negative, and Triassic and Jurassic peaks greatly overshadowing the mid-Cretaceous appear, which, as mentioned above, is an unlikely situation. Because of this problem, I restrict the value of  $f_C(t)$  to lie between 0.50 and 1.00, using 0.75 arbitrarily for the standard situation.

Figure 12 shows that letting  $f_C(t) = f_A(t)$  or  $f_C(t) = f_A(t)^2$  results in a major response of  $\text{RCO}_2$  to this formulation only for the early Paleozoic. If a higher order dependence is used, values of  $\text{RCO}_2$  again go negative during the Permo-Carboniferous. Thus, if this alternate approach is correct, stronger response of  $f_C(t)$  to  $f_A(t)$  exerts its effect mainly over Cambrian-Devonian time.

The response of  $\text{RCO}_2$  to changes in  $f_D(t)$  and  $f_{LA}(t)$  were found to be minimal and are not plotted. Use of  $f_D(t) = 1$  gives results very similar to that for the standard formulation based on the new data of Otto-Bliesner (1993). There are two reasons for this. The first is that  $f_D(t)$  is now raised to the 0.65 power for the weathering of silicates (instead of the first power as in GEOCARB I) to account for the effects of riverine dilution as discussed above. Second, the  $f_D(t)$  values derived from the Otto-Bliesner data show a smaller amplitude of variation over time than the  $f_D(t)$  values of GEOCARB I which were based on the data of Tardy, N'Koukou, and Probst (1989). These two changes diminish the relative importance of runoff as a major factor affecting atmospheric  $\text{CO}_2$ .

Figure 13 shows the result of applying the alternate simplified "mantle" model. In this model the dependence of both weathering and degassing on the amounts of organic and carbonate carbon is removed, and, as a result, total crustal carbon is allowed to vary. As can be seen there is very little effect. This is important. It shows that results of the standard formulation are not dependent upon having a constant mass of total crustal carbon (organic C plus carbonate C) or dependent on the proportion of  $\text{CO}_2$  that is supplied by mantle degassing versus that



### Effect of Carbonate Transfer

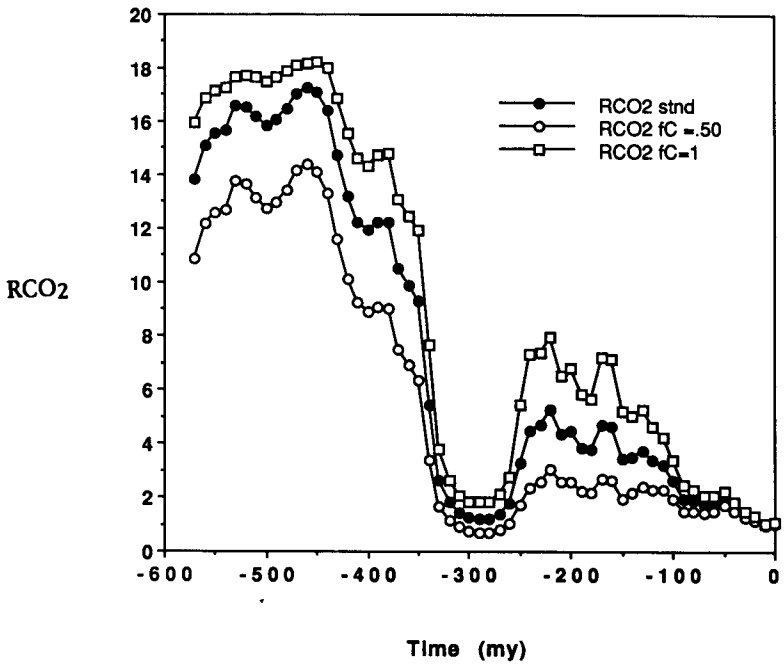


Fig. 11. Effect on CO<sub>2</sub> of the transfer of carbonate deposition from shallow water to the deep sea as represented by the parameter  $f_C(t)$ . Plots are for different  $f_C(t)$  values prior to the rise of planktonic carbonate secreting organisms in the pelagic realm (here assumed to be before 150 myBP).

### Effect of Carbonate Transfer

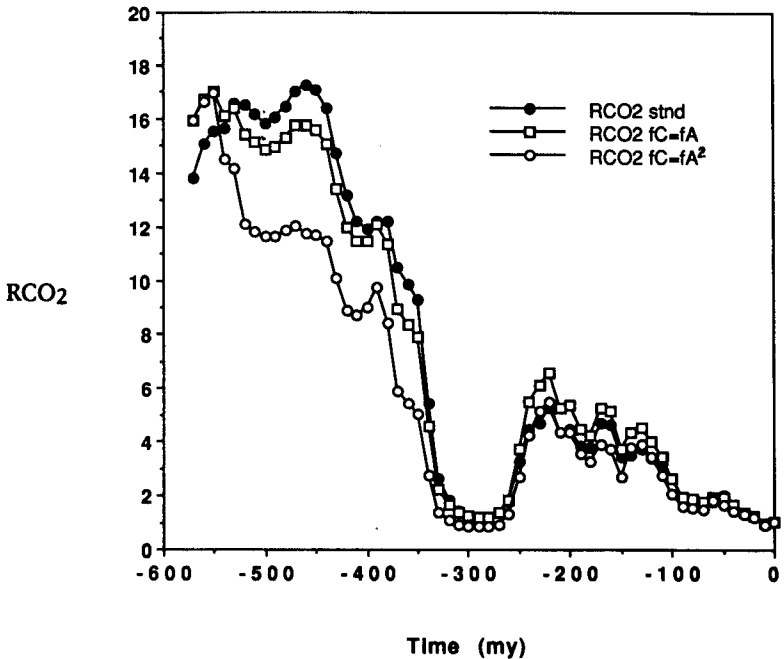


Fig. 12. Effect on CO<sub>2</sub> of different formulations of the carbonate transfer parameter  $f_C(t)$ . (See fig. 4.).

## Simplified "Mantle" Model

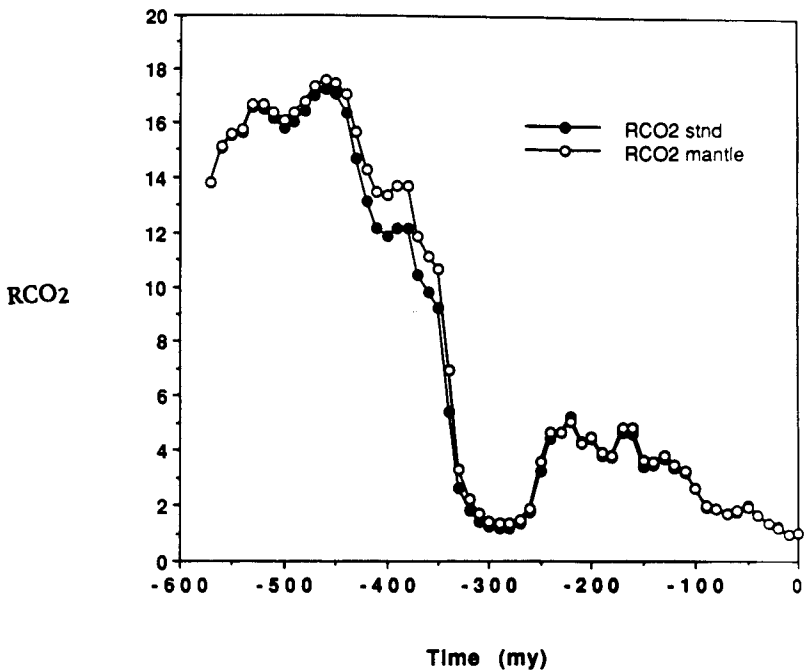


Fig. 13. Effect on  $\text{CO}_2$  of use of an alternative "mantle" model where masses of organic C and carbonate C are not tracked, degassing is mantle derived with constant isotopic composition, and total crustal carbon is not held constant.

derived from diagenesis or metamorphism. The  $f(t)$  parameters are the principal guides to weathering and degassing, not the masses of carbon involved.

Figure 14 shows the total effect of tectonics on  $\text{CO}_2$ . By tectonics I mean the combination of mountain uplift as represented by  $f_R(t)$  and seafloor spreading as represented by  $f_G(t)$ . Both  $f_R(t)$  and  $f_G(t)$  are set equal to one to compare this no-tectonics situation with the standard situation. The most dramatic effect is a considerable diminution of  $\text{RCO}_2$  during the Mesozoic and Cenozoic (240 my to the present) due mainly to holding  $f_R(t)$  constant. This indicates that tectonics was an important control of atmospheric  $\text{CO}_2$  during this time. By contrast, changes in  $\text{RCO}_2$  during the Paleozoic are relatively less. This indicates that something besides tectonics was important during this period. As shown in figure 7 the culprit is the rise and evolution of vascular land plants.

In figure 15 the situation of no change in seafloor spreading rate with time is examined. In this case  $f_G(t)$  is held equal to one for all time

### Effect of Tectonics

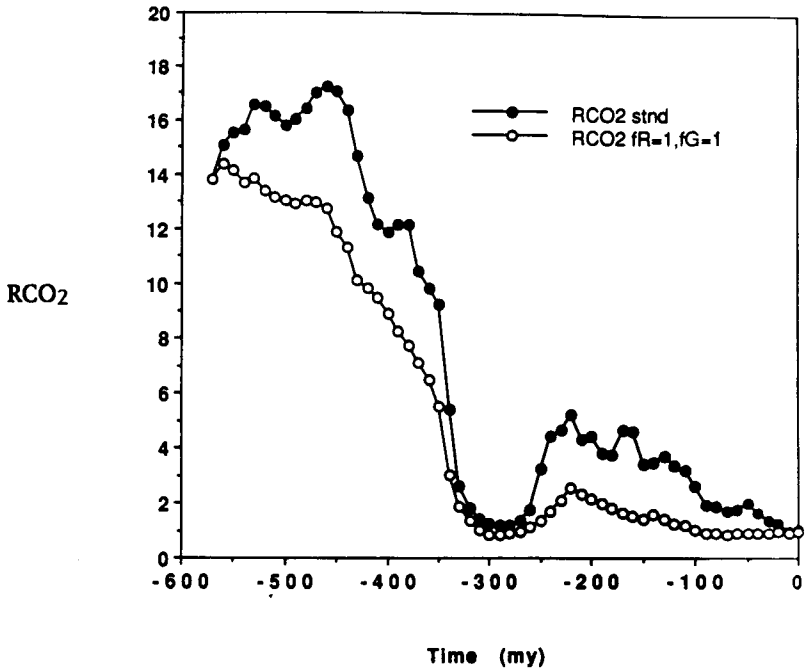


Fig. 14. Effect on CO<sub>2</sub> of tectonics for the situation of no change in continental relief,  $f_R(t) = 1$ , and no change in the rate of global degassing,  $f_G(t) = 1$ .

### Effect of Spreading Rate

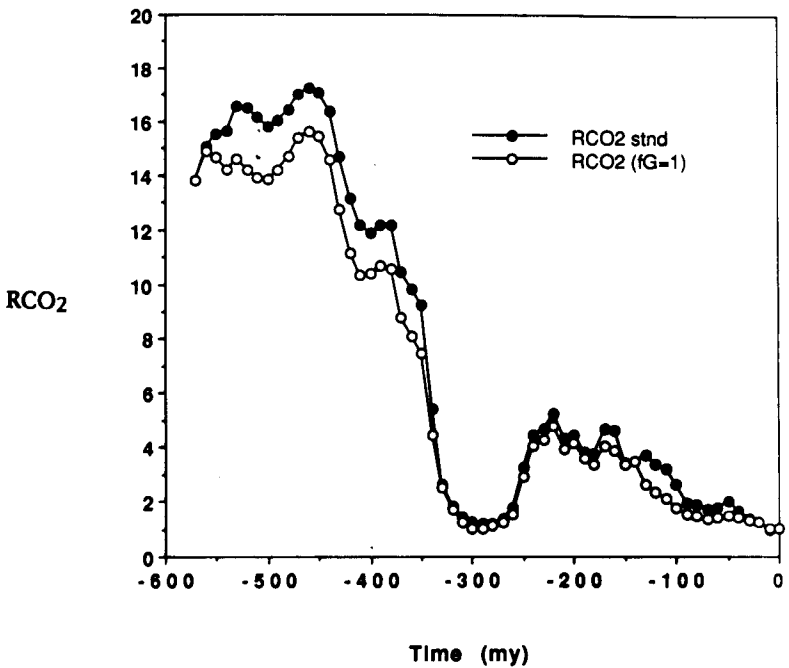


Fig. 15. Effect on CO<sub>2</sub> of global degassing alone.  $f_G(t) = 1$  represents the situation of no change with time in degassing. The standard formulation is based on seafloor spreading (subduction) rate as a proxy for degassing.

which means that metamorphic/volcanic degassing is assumed not to be a function of spreading rate. Rather surprisingly there is little change from the standard. Our original work (Berner, Lasaga, and Garrels, 1983) emphasized the role of spreading as a major factor controlling degassing rate and consequently atmospheric  $\text{CO}_2$ . Now it appears, that, *on a long term Phanerozoic time scale*, it is much less important than other factors, such as changes in solar radiation, land plant evolution, mountain uplift, and transfer of carbonates between shallow and deep water deposition. By contrast, on a Cenozoic time scale detailed analysis over this shorter time shows that degassing rate, based on the subduction estimates of Engebretson and others (1992), produces an important secondary maximum during the Eocene which was not present in GEOCARB I and which essentially disappears with  $f_G(t)$  set equal to one.

Figure 16 illustrates a dramatic situation. This is for all  $f(t)$  parameters set equal to one. In other words,  $f_A(t) = 1$ ,  $f_L(t) = 1$ ,  $f_D(t) = 1$ ,  $f_R(t) = 1$ ,  $f_E(t) = 1$ ,  $f_C(t) = 1$ ,  $f_C(t) = 1$ . There is still a ghost of the general trend

### Effects of Biology and Tectonics

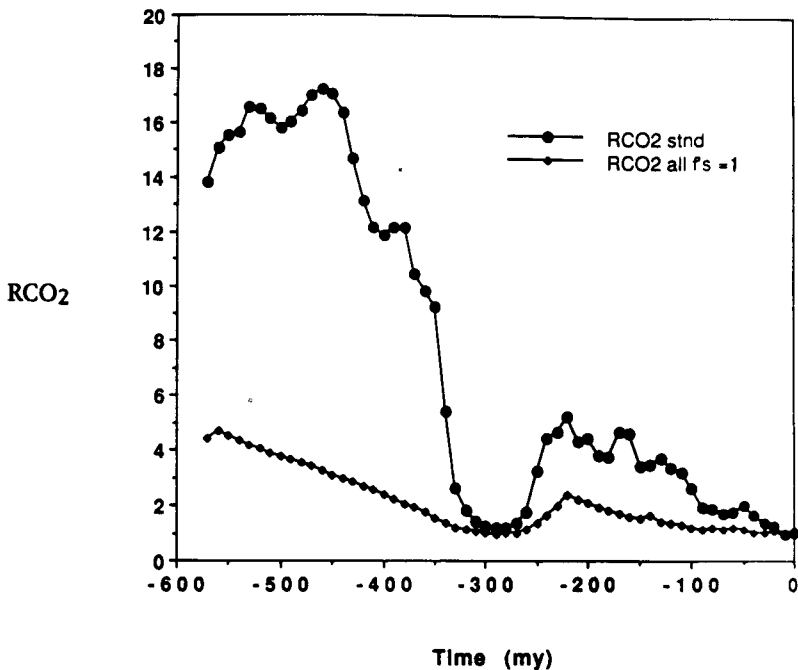


Fig. 16. Effect on  $\text{CO}_2$  of both biology and tectonics. The lower curve is for the situation where all weathering and degassing parameters are held constant equal to one. In other words,  $f_G(t) = 1$ ,  $f_C(t) = 1$ ,  $f_D(t) = 1$ ,  $f_{LA}(t) = 1$ ,  $f_R(t) = 1$ , and  $f_E(t) = 1$ .

for the standard curve. This is due to changes in the rate of burial of organic carbon as controlled by the carbon isotopic composition of seawater (indicated by  $\delta_{bc}$ ).

Figure 17 shows a plot of  $F_{bg}$ , the rate of burial of organic carbon, predicted by the model. Also plotted is a burial rate curve (Berner and Canfield, 1989) based on independent estimates of the abundance of organic carbon and different kinds of sedimentary rocks as a function of time. The reasonably close agreement, considering all the possible errors in both calculations, suggests that the standard model is somewhere near an approximation to reality.

### Org C Burial--Model vs Rock Data

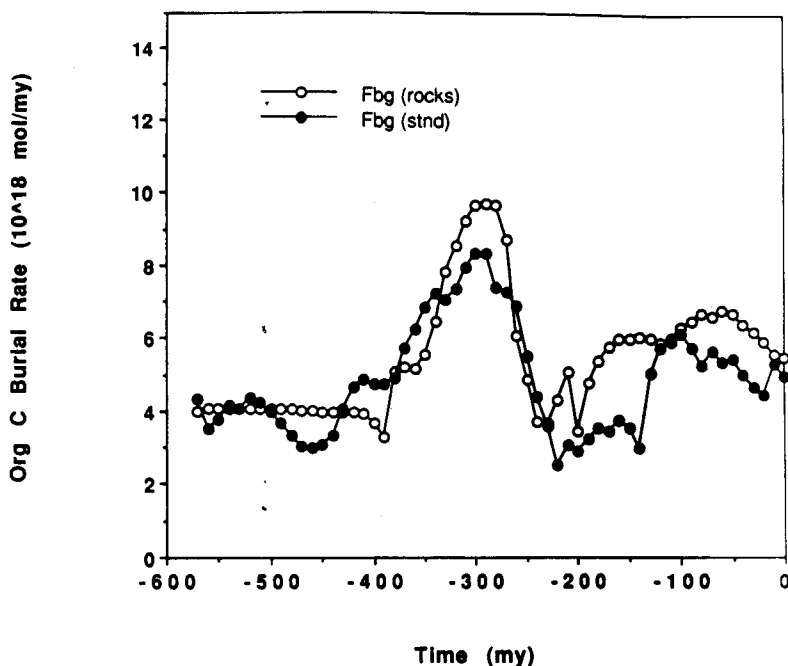


Fig. 17. Rate of burial of organic carbon calculated for the standard situation compared to burial rate derived independently from the abundance of organic carbon in different types of sedimentary rocks (Berner and Canfield, 1989).

To compare results of the present study with those of the earlier work (Berner, 1991), figure 18 is presented. Here the standard formulations for GEOCARB I AND GEOCARB II are shown. It is really quite amazing to see general agreement considering all the changes that have been made in the present paper. The major difference is loss of the

## GEOCARB 2 vs GEOCARB 1

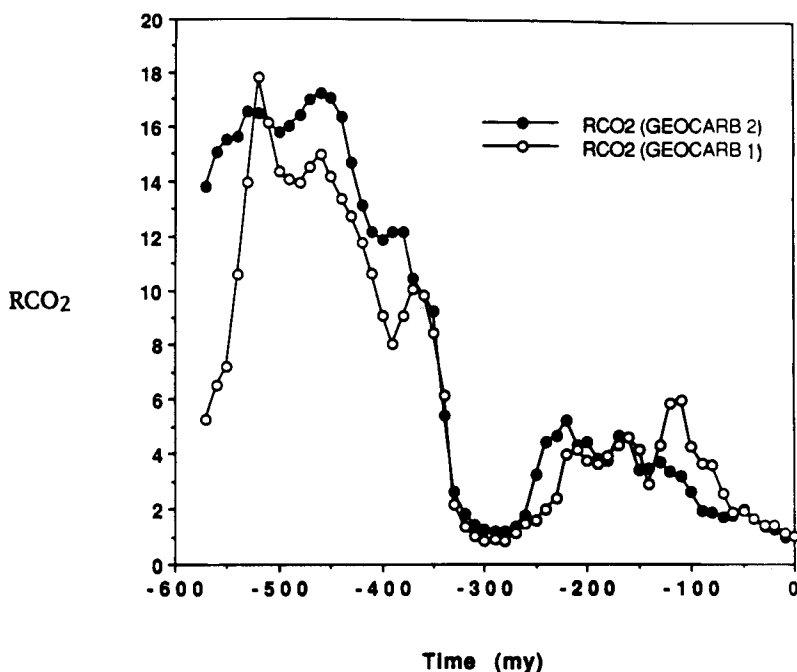


Fig. 18. Comparison of results for standard formulations for GEOCARB I (Berner, 1991) and GEOCARB II (present paper).

mid-Cretaceous peak at 110 to 120 my exhibited in GEOCARB I and the much higher values of RCO<sub>2</sub> during the early Cambrian in GEOCARB II.

Finally in figure 19 the "standard" situation is shown by itself including the geological time scale and a crude estimate of range in error based on the sensitivity analysis shown in the previous diagrams. This is the "best estimate" based on the present modeling, in other words GEOCARB II, and it also serves as standard for comparison in sensitivity analysis.

## SUMMARY AND CONCLUSIONS

Figure 19 shows the result of the present recalculations based on the GEOCARB modeling approach. From the sensitivity analysis the general trend of high CO<sub>2</sub> during the Mesozoic and early Paleozoic and low CO<sub>2</sub> during the Permo-Carboniferous and late Cenozoic appears to be robust. This is in agreement with the conclusions of the earlier work (Berner, 1991). The major *new* results are: (1) Changes in the solar "constant" over Phanerozoic time affect the degree of feedback during weathering and

## NEW STANDARD (GEOCARB 2)

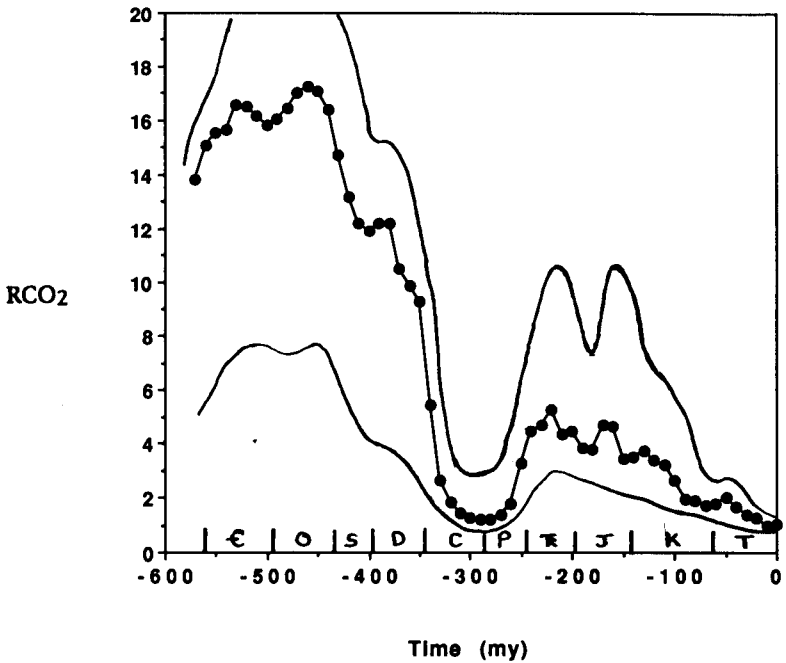


Fig. 19. Standard formulation according to the GEOCARB II model for  $RCO_2$  as a function of time.  $RCO_2$  is the mass of atmospheric  $CO_2$  at time  $t$  divided by that at "present" (=300 ppmv). Upper and lower lines represent crude error estimates based on the sensitivity analysis.

therefore have caused atmospheric  $CO_2$  levels to follow a generally downward path with time. (2) Lower continental relief helped to bring about elevated atmospheric  $CO_2$  during the Mesozoic, and mountain uplift combined with decreasing seafloor subduction helped to bring about a drop in  $CO_2$  during the Cenozoic. (3) Transfer of  $CaCO_3$  deposition between shallow and deep water environments affected the degassing of  $CO_2$  and the level of  $CO_2$  over the Phanerozoic. (4) Overall results are little affected by removing the constraint of tracking the masses of organic and carbonate carbon and thereby having constant total crustal carbon. (5) The effects of changes in runoff on  $CO_2$  are less than previously believed. (6) The effects on  $CO_2$  of changes in seafloor spreading rate, as it affects degassing during the Paleozoic, are less than previously believed.

Added to the above results is verification of the previous finding (Berner, 1991, 1992) of the importance of land plant evolution as it

affected atmospheric CO<sub>2</sub> during the early and mid-Paleozoic. From the present sensitivity analysis, the large mid-Paleozoic drop in CO<sub>2</sub> was mainly a consequence of enhanced silicate weathering and (secondarily) enhanced burial of organic matter as a consequence of the rise and spread of vascular land plants. (This drop has been corroborated by independent estimates of Paleozoic CO<sub>2</sub> levels based on the study of paleosols; see Berner, 1993, for a summary).

From what has been said here, CO<sub>2</sub> over Phanerozoic time was controlled by a mixture of geologic and biologic processes, combined with a warming sun, with geology dominating at certain periods and biology at others. As emphasized before (Berner, 1991), a purely geologic or purely biologic approach to the long term carbon cycle is overly simplistic.

Figure 20 shows a plot of global mean air surface temperature versus time for the Phanerozoic as calculated by the model. The temperature is

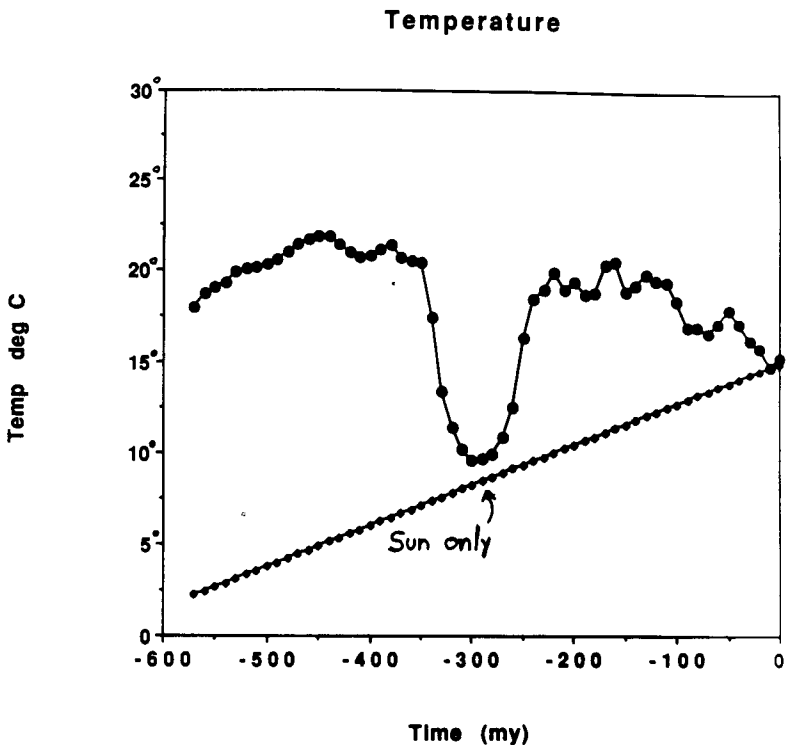


Fig. 20. Global mean surface air temperature calculated from CO<sub>2</sub> results for the standard formulation combined with GCM results for the effect of CO<sub>2</sub> and solar constant changes on temperature (Oglesby and Saltzman, 1990; Oglesby and Marshall, 1992).



based on eq (32), derived from the GCM calculations of Ogelsby and Saltzman (1990) and Oglesby and Marshall (1992), and RCO<sub>2</sub> values for the standard formulation. For comparison the temperature calculated for the situation of constant CO<sub>2</sub> but increasing solar radiation is also shown. As can be seen, the general warming of the early and mid-Paleozoic is a consequence of much higher levels of CO<sub>2</sub> at that time than at present. Further, the Permo-Carboniferous and late Cenozoic glaciations can be explained, at least partly, by a considerable lowering of CO<sub>2</sub> and, therefore, of temperature. Finally, the approximately same temperatures for the Mesozoic and early Paleozoic are due to a combination of very high CO<sub>2</sub> plus a lower solar "constant" during the early Paleozoic and lower CO<sub>2</sub> plus a higher solar "constant" during the Mesozoic. During these periods the two climate forcing mechanisms apparently balanced themselves against one another, but during the Permo-Carboniferous and late Cenozoic changes in the carbon cycle upset this balance to help bring about glaciations. At any rate based on modeling results, I still firmly believe that the atmospheric CO<sub>2</sub> greenhouse effect has been a major control on climate over Phanerozoic time.

#### FUTURE RESEARCH

Many of the parameterizations in the present paper are, by necessity, first approximations. Doing this research has led to the realization that there is a great need for obtaining reliable data on: (1) the quantitative effects of plants on weathering and the effects on plant activity of the rise of herbivorous animals; (2) the quantitative effects of changes in relief on the rate of weathering of Ca and Mg silicates; (3) independent estimates of the magnitude of past changes in continental relief (to check the many assumptions accompanying the Sr isotope model); (4) the timing and extent of past transfers of carbonates between shallow platforms and the deep sea; and (5) independent ways for estimating past rates of CO<sub>2</sub> degassing especially when plume-type volcanism is involved. Added to these is the almost totally unanswered question of how past paleolevels of atmospheric methane, in addition to CO<sub>2</sub>, may have affected climate via the greenhouse effect.

Besides the necessity of including in future carbon cycle modeling the latest thinking on the subjects cited above, it will be necessary in future work to consider also the effects of changes in continental size/position and ocean circulation on the weathering feedback functions used here. For example, changes in ocean heat transport or in the latitudinal distribution of continents should affect continental temperatures which should in turn affect the rate of global weathering. Further, the effect of changes in CO<sub>2</sub> and solar radiation on runoff and global temperature is calculated in the present paper from GCM modeling results that are based on present day geography, and this functionality may change with changing paleogeography. What is really needed is to intimately interface carbon cycle modeling with climate modeling, espe-

cially concerning the latitudinal distribution of continents, with the output of a climate model used in an accompanying C cycle model and the output of the C cycle model (atmospheric CO<sub>2</sub> level) used in turn in the climate model. Only in this way will a truly complete model of the long term carbon cycle and its effect on climate be possible.

## ACKNOWLEDGMENTS

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