[American Journal of Science, Vol. 301, February, 2001, P. 182–204]

GEOCARB III: A REVISED MODEL OF ATMOSPHERIC CO_2 OVER PHANEROZOIC TIME

ROBERT A. BERNER and ZAVARETH KOTHAVALA

Department of Geology and Geophysics, Yale University,
New Haven, Connecticut 06520-8109

ABSTRACT. Revision of the GEOCARB model (Berner, 1991, 1994) for paleolevels of atmospheric CO_2, has been made with emphasis on factors affecting CO_2 uptake by continental weathering. This includes: (1) new GCM (general circulation model) results for the dependence of global mean surface temperature and runoff on CO_2, for both glaciated and non-glaciated periods, coupled with new results for the temperature response to changes in solar radiation; (2) demonstration that values for the weathering-uplift factor $f_R(t)$ based on Sr isotopes as was done in GEOCARB II are in general agreement with independent values calculated from the abundance of terrigenous sediments as a measure of global physical erosion rate over Phanerozoic time; (3) more accurate estimates of the timing and the quantitative effects on Ca-Mg silicate weathering of the rise of large vascular plants on the continents during the Devonian; (4) inclusion of the effects of changes in paleogeography alone (constant CO_2 and solar radiation) on global mean land surface temperature as it affects the rate of weathering; (5) consideration of the effects of volcanic weathering, both in subduction zones and on the seafloor; (6) use of new data on the $\delta^{13}C$ values for Phanerozoic limestones and organic matter; (7) consideration of the relative weathering enhancement by gymnosperms versus angiosperms; (8) revision of paleo land area based on more recent data and use of this data, along with GCM-based paleo-runoff results, to calculate global water discharge from the continents over time.

Results show a similar overall pattern to those for GEOCARB II: very high CO_2 values during the early Paleozoic, a large drop during the Devonian and Carboniferous, high values during the early Mesozoic, and a gradual decrease from about 170 Ma to low values during the Cenozoic. However, the new results exhibit considerably higher CO_2 values during the Mesozoic, and their downward trend with time agrees with the independent estimates of Ekart and others (1999). Sensitivity analysis shows that results for paleo-CO_2 are especially sensitive to: the effects of CO_2 fertilization and temperature on the acceleration of plant-mediated chemical weathering; the quantitative effects of plants on mineral dissolution rate for constant temperature and CO_2; the relative roles of angiosperms and gymnosperms in accelerating rock weathering; and the response of paleo-temperature to the global climate model used. This emphasizes the need for further study of the role of plants in chemical weathering and the application of GCMs to study of paleo-CO_2 and the long term carbon cycle.

INTRODUCTION

In 1991 a new model for the evolution of the carbon cycle and of atmospheric CO_2 over Phanerozoic time was presented based on inputs of geological, geochemical, biological, and climatological data (Berner, 1991). This model was later revised in 1994 and given the name GEOCARB, whereupon the revised model was labelled as GEOCARB II (Berner, 1994). The purpose of the present paper is to amend the model to include findings in the earth, biological, and climatological sciences that have occurred over the past seven years. Most of the findings are related to chemical weathering on the continents.

The long-term carbon cycle.—On a multimillion year time scale the major process affecting atmospheric CO_2 is exchange between the atmosphere and carbon stored in rocks. This long-term, or geochemical carbon cycle is distinguished from the more familiar short-term cycle that involves the transfer of carbon between the oceans, atmosphere, biosphere, and soils (see Berner, 1999 for a comparison of the two cycles). In the long-term cycle loss of CO_2 from the atmosphere is accomplished by photosynthesis and burial of organic matter in sediments and by the reaction of atmospheric CO_2 with Ca and Mg silicates during continental weathering to form, ultimately, Ca and Mg carbonates on the ocean floor (after transport of the weathering-derived Ca, Mg, and carbon to the sea by rivers). Release of CO_2 to the atmosphere in the long-term carbon cycle takes place via the oxidative weathering of old organic matter and by the thermal breakdown of buried carbonates and organic matter (via diagenesis, metamorphism and volcanism) resulting in degassing to the earth surface.

The above description can be represented by succinct overall chemical reactions. The reactions (Ebelmen, 1845; Urey, 1952; Holland, 1978; Berner, 1991) are:

$$CO_2 + CaSiO_3 \leftrightarrow CaCO_3 + SiO_2 \tag{i}$$

$$CO_2 + MgSiO_3 \leftrightarrow MgCO_3 + SiO_2 \tag{ii}$$

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O \tag{iii}$$

The arrows in reactions (i) and (ii) refer to Ca-Mg silicate weathering plus sedimentation of marine carbonates when reading from left-to-right. These two weathering reactions summarize many intermediate steps including photosynthetic fixation of CO_2, root/mycorrhizal respiration, organic litter decomposition in soils, the reaction of carbonic and organic acids with primary silicate minerals, the conversion of CO_2 to HCO_3^- in soil and ground water, the flow of riverine HCO_3^- to the sea, and the precipitation of oceanic HCO_3^- as Ca-Mg carbonates in bottom sediments. Reactions (i) and (ii) reading from right-to-left represent thermal decomposion of carbonates at depth resulting in degassing of CO_2 to the surface. The double arrow in reaction (iii) refers to weathering (or thermal decomposition plus atmospheric oxidation of reduced gases) when reading from left to right and burial of organic matter (the net of global photosynthesis over respiration) when reading from right to left.

GEOCARB modeling of the long term carbon cycle consists of equations expressing carbon and carbon isotope mass balance along with formulations for rates of weathering and degassing and how these rates have changed over time. Details of the derivation of these equations can be found in GEOCARB I and II (Berner, 1991, 1994), and they are simply presented here in appendix 1. (For discussion of models similar to GEOCARB; see Kump and Arthur, 1997; Tajika, 1998, Gibbs and others, 1999; and Wallmann, 2001). Any modification of the equations from GEOCARB II to III are discussed in the present paper.

It should be emphasized that GEOCARB modeling has only a long time resolution. Data are input into the model at 10 my intervals with linear interpolation between. In the case of rock abundance data, averages for up to 30 my time slices are sometimes used. Thus, shorter term phenomena occurring over a few million years or less are generally missed in this type of modeling.

The GEOCARB II paper ended with suggestions for future research that included a need for better input data on (1) the quantitative effects of plants on weathering; (2) the quantitative effect of changes in relief, as it affects physical erosion and silicate weathering, including independent checks on the use of Sr isotopes as a proxy for continental relief and erosion; (3) changes in continental size and position as they affect weathering by way of changes in runoff and land temperature; (4) the application of GCM modeling, based on past and not just present geography, to the deduction of the effects of changes in atmospheric CO_2 on global temperature and runoff. These problems are now addressed in the present paper.

CHANGES TO THE MODELING

Application of new GCM results to $f_B(T,\ CO_2)$.—The weathering feedback parameter $f_B(T, CO_2)$ reflects the effects of changes in CO_2 and global temperature on the rate of weathering of Ca-Mg silicates. Factors considered that affect temperature are the evolution of the sun, the atmospheric greenhouse effect (relating temperature to CO_2), and changes in paleogeography. In addition, the direct effect of CO_2 on weathering in the presence and absence of vascular plants is included in this parameter. Appropriate expressions (see Berner, 1994, for further discussion) are:

$$f_B(T, CO_2) = f(T)f(CO_2) \tag{1}$$

$$f(T) = \exp\{ACT[T(t) - T(0)]\} \times \{1 + RUN[T(t) - T(0)]\}^{0.65} \tag{2}$$

$$T(t) - T(0) = \Gamma \ln RCO_2 - Ws(t/570) + GEOG(t) \tag{3}$$

$$f(CO_2) = (RCO_2)^{0.5} \text{ for pre-vascular plant weathering} \tag{4}$$

$$f(CO_2) = [2RCO_2/(1 + RCO_2)]^{FERT} \text{ for weathering affected by vascular plants} \tag{5}$$

where: T = global mean temperature
t = time
RCO_2 = the ratio of mass of CO_2 at time t to that at present (t = 0)
Γ = coefficient derived from GCM modeling that expresses the response of global mean temperature to change in atmospheric CO_2 due to the atmospheric greenhouse effect
Ws = factor expressing the effect on global mean temperature of the increase in solar radiation over geological time
GEOG(t) = the effect of changes in paleogeography on temperature
ACT = E/RT^2 = coefficient expressing the effect of mineral dissolution activation energy E on weathering rate (R = gas constant)
RUN = coefficient expressing the effect of temperature on global river runoff
FERT = exponent reflecting the proportion of plants globally that are fertilized by increasing CO_2 and that accelerate mineral weathering

Similar expressions are derived for the weathering feedback parameter $f_{BB}(T, CO_2)$ for carbonates but with different activation energies and a different formulation for runoff (Berner, 1994). Changes from GEOCARB II are the addition of the expression for the effect of changes in paleogeography on temperature GEOG(t) to the expression for f(T) and the allowance of variation of the CO_2 fertilization factor FERT which was previously assumed to be equal to 0.4 (equivalent to 35 percent of plants globally responding to CO_2 fertilization).

Values of GEOG(t), the greenhouse and solar response factors Γ and Ws, and the river runoff factor RUN can be obtained from the application of general circulation models (GCM) to paleo-environments. In GEOCARB II the results of Marshall and others (1994) and Manabe and Bryan (1985) for the present Earth were used to obtain Γ, Ws and RUN for all times. Recently GCM work, covering a large range of CO_2 values, has shown a lower sensitivity of temperature and runoff to CO_2 and solar forcing (Kothavala, Oglesby, and Saltzman, 1999, 2000). Therefore, we decided to use the new Kothavala, Oglesby, and Saltzman results for the present and also for times of similarly low temperatures and continental glaciation (340-260 Ma and 40-0 Ma). For warmer periods, representing the rest of Phanerozoic history, we have used results from the same GCM model (CCM-3—see below) applied to mid-Cretaceous (80 Ma) paleogeography (Hay and others, 1999). We use global mean temperature for weathering rate expressions (2) and (3) rather than land temperature, because it is probable that most weathering on land takes place in wet regions affected by on-shore winds and sea surface temperature. Global mean land temperature is inordinately affected by very low temperatures due to continental ice sheets and very high temperatures due to deserts. In both places there is very little chemical weathering.

The calculations in this paper take into consideration the improvements in general circulation modeling over the last six years. We use results from the simulation of the National Center for Atmospheric Research (NCAR) Community Climate Model, version 3 (CCM-3) which is described in Kiehl and others (1998). Improvements in the physical processes of CCM-3 over the GCM used for the rate-constants in GEOCARB I and II are attributed to: (1) higher spatial resolution, (2) greater number of vertical levels in the atmosphere, (3) a sophisticated land-surface scheme, (4) an enhanced parameterization of oceans and sea ice, and (5) changes in the radiation scheme. Carbon dioxide is a prescribed model parameter that directly enters into the longwave radiation computations. Herein lies a key difference between CCM-1 (used for GEOCARB II) and CCM-3 (used in this paper). In CCM-1, a broadband model evaluated at 15 micrometers is used to parameterize the absorption of radiation by CO_2. CCM-1 does not explicitly account for the weaker absorption bands of CO_2 whereas CCM-3 accounts for the radiative properties of two weak CO_2 bands located at 9.4 and 10.4 micrometers.

The hydrological cycle in CCM-3 is less sensitive to changes in global mean temperature than is the hydrological cycle in many other GCMs. Thus, because the reliability of GCM-derived runoff estimates is uncertain, and other models produce different results, the RUN values in the present study should be viewed only as one approach to the problem. Fortunately, final results for CO_2 are much less sensitive to changes in the value of the runoff parameter RUN than to changes in the value of the weathering activation energy factor ACT (see eq 2).

For the effect of changing paleogeography on the temperature of weathering, rather than use the results of our CCM-3 modeling here, we rely on the earlier data of Otto-Bliesner (1995). Her results are for flat, ice-free continents, computed at several times over the Phanerozoic, which provide a first-order guide to changes in land temperature as a result of changes in continental size and position. This approach allows for the exclusion of glacial and periglacial land areas, which affect global mean land temperature, but which exhibit very little chemical weathering.

The weathering-uplift parameter $f_R(t)$.—The dimensionless parameter $f_R(t)$ was initially introduced in GEOCARB I (Berner, 1991) as a measure of the enhanced exposure of primary silicate minerals to chemical weathering via the removal of overburden by physical erosion. It is defined as the effect on chemical weathering of mountain uplift (mean global relief) at some past time to the effect at present. Following the results of a number of studies (Raymo, 1991; Richter, Rowley, and DePaolo, 1992) the use of Sr isotopes was employed as a means of quantifying $f_R(t)$ in GEOCARB II. However, the approach used did not assume that the Sr isotopic composition of the oceans is a direct measure of the overall rate of silicate weathering, as was done by Raymo and partly by Richter, Rowley, and DePaolo. Instead the marine Sr isotope record was used as a measure of the radiogenicity or $^{87}Sr/^{86}Sr$ of rocks undergoing weathering on the continents. This latter point has been emphasized by subsequent studies (Derry and France-Lanord, 1996; Quade and others, 1997). In other words, uplift of old radiogenic rocks, as a result of tectonic processes (Richter, Rowley, and DePaolo, 1992), would result in the input to the ocean of Sr that was more radiogenic. The uplift does not necessarily infer a greater rate of input of total Sr to the sea because other factors such as global climate, not recorded by Sr isotopes, also affect the rate of chemical weathering. Unfortunately this latter point was ignored by Raymo and Richter, Rowley, and DePaolo. In GEOCARB II the difference between the actual $^{87}Sr/^{86}Sr$ of seawater and the value calculated for submarine volcanic-seawater reaction alone, was used to deduce the relative importance of radiogenic Sr input from

TABLE 1

Terrigenous sedimentary rock abundance (10^6 km^3/my) over the Phanerozoic. $f_{erosion}(t)$ = [meas($\Delta V/\Delta t$)/expon($\Delta V/\Delta t$)] where expon represents the value calculated from an exponential fit to the $\Delta V/\Delta t$ data (see fig. 1). $f_R(t) = [f_{erosion}(t)/1.58]^{2/3}$ (see text). $\Delta V/\Delta t$ values from Ronov (1993). The value for the Pliocene is not used in the modeling (see text). Ages from Gradstein and Ogg (1996)

	Midpoint age (Ma)	Meas. $\Delta V/\Delta t$	Expon. $\Delta V\Delta/t$	$f_{erosion}$ (t)	$f_R(t)$
Pliocene	3.6	8504	2046	4.16	1.91
Miocene	14.6	3141	1992	1.58	1.00
Oligocene	28.8	3384	1926	1.76	1.07
Eocene	44.3	1681	1855	0.91	0.69
Paleocene	59.9	1092	1787	0.61	0.53
Late Cretaceous	82	1726	1695	1.02	0.75
Early Cretaceous	120.5	1531	1545	0.99	0.73
Late Jurassic	150.7	1365	1437	0.95	0.71
Middle Jurassic	169.8	730	1372	0.53	0.48
Early Jurassic	192.9	578	1298	0.45	0.43
Late Triassic	216.6	685	1227	0.56	0.50
Middle Triassic	234.6	590	1175	0.5	0.47
Early Triassic	245	1326	1146	1.16	0.81
Late Permian	252.1	1580	1126	1.4	0.92
Early Permian	273	511	1071	0.48	0.45
Middle & Late Carboniferous	306.5	619	988	0.63	0.54
Early Carboniferous	338.5	595	915	0.65	0.55
Late Devonian	362	1098	865	1.27	0.86
Middle Devonian	380.5	724	827	0.87	0.67
Early Devonian	404	585	782	0.75	0.61
Late Silurian	420	1701	753	2.26	1.27
Early Silurian	433	691	729	0.95	0.71
Late Ordovician	450.5	860	699	1.23	0.85
Middle Ordovician	464	1553	677	2.29	1.28
Early Ordovician	482.5	588	648	0.91	0.69
Late Cambrian	500	943	621	1.52	0.97
Middle Cambrian	511.5	901	604	1.49	0.96
Early Cambrian	531.5	436	576	0.76	0.61

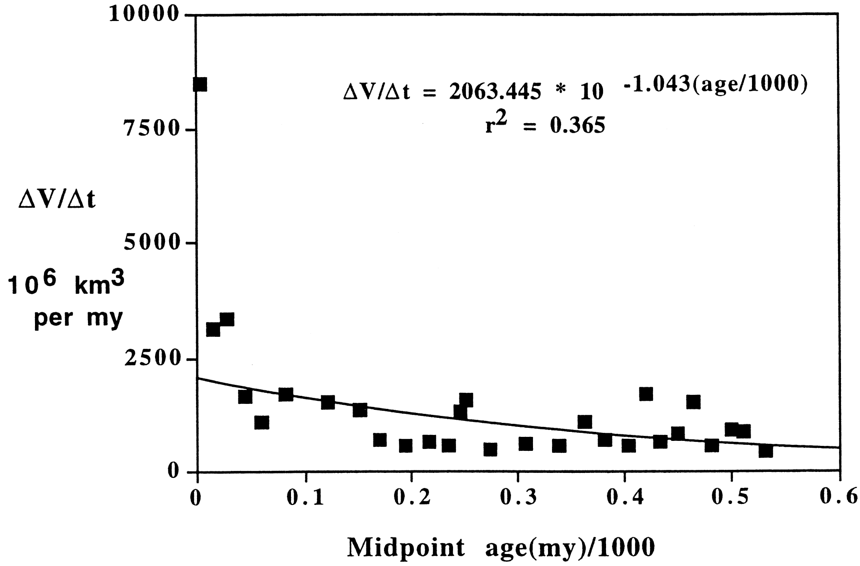

Fig. 1. Exponential fit to the terrigenous sediment abundance data of Ronov (1993) presented in Table 1. $\Delta V/\Delta t$ refers to the volume of sediment for each time period divided by its duration.

uplift-affected weathering. This isotopic ratio difference was related to $f_R(t)$ by way of an arbitrary fitting factor L (Berner, 1994). The best fit to independently deduced CO_2 values was found, in the GEOCARB II study, for L = 2.

Since variations in the strontium isotopic composition of seawater can also be due to changes in the relative input of weathering from granites versus basalts versus limestones (Brass, 1976; Bluth and Kump, 1991; Berner and Rye, 1992; Taylor and Lasaga, 1999), it is imperative to try to develop an independent method for estimating the quantitative effect of uplift and erosion on the rate of silicate chemical weathering. Because terrigenous (for example non-carbonate, non-evaporite) sedimentary rocks form as a result of physical erosion, one can use estimated abundances of such sediments over time as a measure of paleo-erosion. This is now possible using the sediment abundance data of Ronov (1993) based on his exhaustive study of a great many samples and geologic maps. Further, Gaillardet and others (1999) have shown that for the major world rivers the chemical weathering of silicates (not total weathering dominated by carbonates) is correlated well with physical erosion, as measured by suspended sediment transport. (Of course there are outstanding exceptions, for example the Huang He, but such unusually muddy rivers often owe their excessive suspended load to disturbances by humans.) It is the results of these two studies that enable an independent calculation of $f_R(t)$.

The abundance of terrigenous sediments, as a function of time, over the Phanerozoic is shown in table 1. The raw volume data are divided by the time span for each epoch so as to get average rates of survival. The decrease in sediment volume with age is mainly due to loss by subduction and erosion of the sediments themselves. This loss can be modelled as an exponential decrease with time (Gregor, 1970, 1992; Wold and Hay, 1990), and the $\Delta V/\Delta t$ data of table 1 are fit by an exponential curve in figure 1. According to the model of Wold and Hay, values lying above and below the exponential curve reflect, respectively, greater and lesser original depositional rate than that at present. Although this is a very simplistic model it is a first attempt to get at rates of paleo-deposition and, therefore, paleo-erosion. According to Wold and Hay:

$$R_{depn}(t) = [\Delta V/\Delta t(\text{measured})/\Delta V/\Delta t(\text{exponential})] \times R_{depn}(0) \quad (6)$$

where R_{depn} = rate of deposition in volume (or mass) per unit time, and $R_{depn}(0)$ represents the t = 0 intercept of the exponential curve. Since global erosion is equal to global deposition, eq (6) can be recast as:

$$f_{erosion}(t) = R_{erosion}(t)/R_{erosion}(0) = [\Delta V/\Delta t(\text{measured})/\Delta V/\Delta t(\text{exponential})] \quad (7)$$

Now, Gaillardet and others (1999) have shown that there is a good log-log correlation between the rates of silicate chemical weathering and physical erosion for the major world rivers. Their data can be represented by the expression:

$$R_{weathering} = k(R_{erosion})^{2/3} \quad (8)$$

where k is a constant, and R is rate in terms of mass flux per unit time for each major river. If this relation can be applied globally to all rivers and all erosion, then normalizing by letting $f_R(t) = R_{weathering}(t)/R_{weathering}(0)$ due to erosion, and assuming that k does not change over time, we obtain:

$$f_R(t) = [f_{erosion}(t)]^{2/3} \quad (9)$$

Before calculating $f_R(t)$, values of $f_{erosion}(t)$ were normalized to the value for the Miocene (see table 1), and the Miocene value used for $f_R(0) = 1$. This excludes the excessive erosion and deposition for the Pliocene and Quaternary due to extensive continental glaciation. (Note in fig. 1 the great distance of the Pliocene data point, from the exponential curve, as compared to all the other data points).

Values of $f_R(t)$ calculated from eqs (6) to (9) are listed in table 1 and fitted to a polynomial of the third order (cubic) in figure 2. Also, plotted on the diagram are values of $f_R(t)$ derived from Sr isotope data (for L = 2), taken from GEOCARB II. Note the amazingly good fit of the cubic curve to the Sr isotope-derived values. This agreement provides independent corroboration of the use of Sr isotopes to obtain $f_R(t)$. Thus, the $f_R(t)$ values derived in GEOCARB II are used again in the present paper.

Plant weathering.—The rise and evolution of vascular plants on the continents have proven to have exerted a major effect on the evolution of atmospheric CO_2 (Lovelock and Watson, 1982; Volk, 1987; Berner, 1994, 1998; Algeo and others, 1995; McElwain and Chaloner, 1995). Plants accelerate the uptake of CO_2 during weathering by a variety of mechanisms (Berner, 1998) including the secretion of organic acids by roots and associate symbiotic microflora, the recirculation of water by transpiration and accelerated rainfall, and the retention by roots of soil from removal by erosion. An important question is: how important quantitatively has the effect of the evolution of land plants been on CO_2? In GEOCARB II it was crudely estimated that the rise of deeply rooted large vascular plants (in other words, trees) during the Devonian led to an acceleration in weathering of a factor of 6.7. This was expressed in terms of the plant weathering parameter $f_E(t)$ which was set for the pre-Devonian rise of trees equal to 15 percent of the present value ($f_E(t) = 0.15$). However, this was based only on a few studies of modern weathering where strict controls of factors, other than the presence and absence of trees, were not held constant.

There are now data from a controlled study of the effects of trees on the release of Ca and Mg from basalt which can be applied to the present modelling. The results of Moulton and others (2000) from adjacent areas in Iceland with the same microclimate, aspect, slope, and basaltic lithology show an acceleration of the weathering release of Ca and Mg by a factor of about four for trees versus "bare" regions containing sporadic lichens and mosses. If lichens and mosses are considered representative of the pre-vascular land surface during the early Paleozoic (Wright, 1985; Schwartzman and

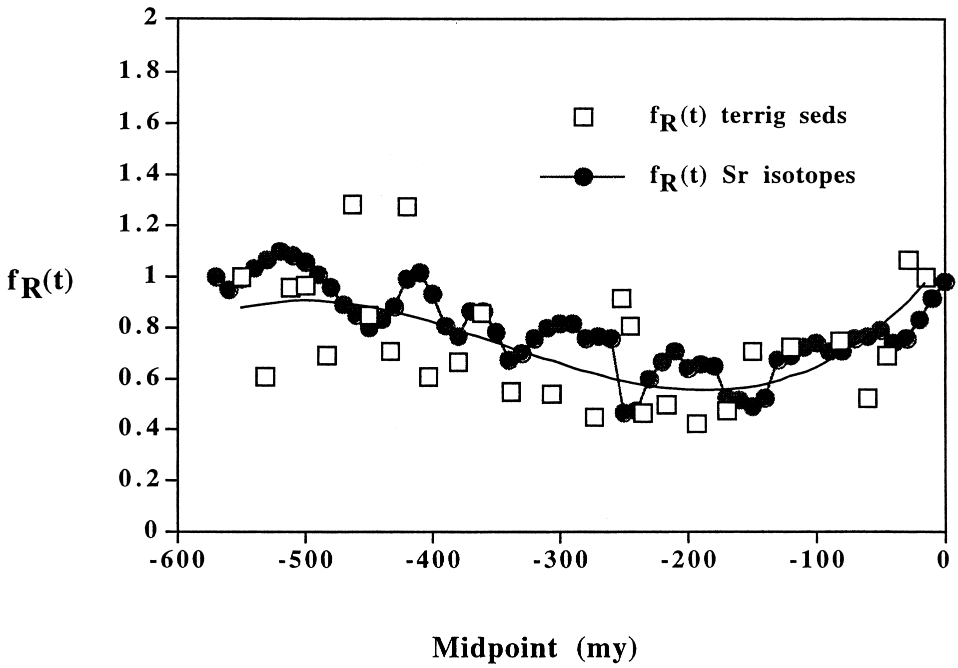

Fig. 2. The uplift/erosion weathering parameter $f_R(t)$ derived from Sr isotope data (Berner, 1994) compared to $f_R(t)$ derived from terrigenous sediment abundance data (Ronov, 1993), and the relation between physical erosion (as measured by river transport of suspended load) and the chemical weathering of silicates (Gaillardet and others, 1998). Note that the curved line, which is a 3rd order polynomial (cubic) fit to the sediment abundance data, agrees well with the Sr-isotope generated data.

Volk, 1989), then the Moulton data can be used, as a first approximation, for the effect on weathering of the rise of trees during the Devonian. This is done here, but because this is only one study and there are beginning to be others of similar nature (Bormann and others, 1998), we will examine the effects of varying $f_E(t)$ over a reasonably large range for the pre-vascular land surface. Also, we have revised the period when Devonian trees arose and affected weathering from 350 to 300 Ma as assumed in GEOCARB II to 380 to 350 Ma which is in better agreement with paleobotanical observations (Algeo and others, 1995).

Another factor in plant evolution is whether post-Devonian changes in flora brought about changes in the extent of the acceleration of weathering. Principally the question becomes whether the rise of angiosperms resulted in increased or decreased release of Ca and Mg relative to pre-existing gymnosperms. Since we have no good handle on the quantitative importance of gymnosperms versus angiosperms with regard to the acceleration of weathering, we vary their effects in our modeling to determine the effect on CO_2 concentration. Comparison of our results with recent field measurements on the effects of gymnosperms versus angiosperms on weathering is discussed below. As in GEOCARB II, we assume that angiosperms first arose at approx 130 Ma and were fully evolved and dominated weathering by 80 Ma.

It is now known that plant growth and carbon storage can be accelerated by an increase in atmospheric CO_2. If this is true, then it is likely that weathering by trees is also accelerated by CO_2. The question is by how much and to what extent globally? In GEOCARB II this effect was incorporated (see eq 5) in the feedback factor $f_B(T, CO_2)$ where plant productivity was assumed to be limited to no more than a doubling worldwide and that 35 percent of plants globally (FERT = 0.4) actually respond to increasing CO_2. However, because this value is poorly known, we have let the value of FERT vary in the modelling of the present paper to test its effect on CO_2.

Basalt weathering in the subdiction zones and on the seafloor.—Wallmann (2001) has pointed out that the subaerial weathering of basaltic rocks is dominated by that occurring in subduction zones, and this is affected by the rate of formation (eruption), as well as by the normal controls on weathering, such as climate and relief. With this in mind the expression for silicate weathering from GEOCARB II has been modified so as to separate basalt weathering from that of other silicates. The assumption is that all subaerial basalt weathering occurs in subduction zones, and the rate of basalt eruption over time is guided by the rate of seafloor spreading as represented by the parameter $f_{SR}(t)$ defined as $f_{SR}(t)$ = spreading rate (t)/spreading rate (0). (The CO_2 degassing parameter $f_G(t)$, defined in appendix 1, is equivalent to $f_{SR}(t)$—see Berner, 1991, 1994).

Thus, for the purpose of sensitivity analysis, the expression for Ca and Mg silicate weathering F_{wsi} (app. 1) is modified to read:

$$F_{wsi} = f_B(T,\ CO_2)f_R(t)f_E(t)f_{AD}(t)^{0.65}[F_{wothsi}(0) + f_{SR}(t)F_{wbas}(0)] \tag{10}$$

$$F_{wsi} = F_{wothsi} + F_{wbas} = F_{bc} - F_{wc} \tag{11}$$

where F_{wbas} represents the rate of basalt weathering; F_{wothsi} represents the rate of weathering of all other silicates; F_{bc} is the rate of burial of carbonates in the oceans, F_{wc} is the rate of weathering of carbonates, and (0) represents present values (the other terms are defined in app. 1). The relative proportions of the fluxes from the weathering of the two silicate rock types at present has been estimated by Gaillardet and others (1999) to be about 25 percent from basalt and 75 percent from other silicates. These proportions are assumed here but may well represent minima for basalt as mentioned by Gaillardet and others. This is especially true because Taylor and Lasaga (1999) have shown that basalt weathers distinctly faster than grantic rocks under the same conditions of climate and relief.

The importance of the effect of seafloor basalt "weathering" (the reaction of seawater with basalt at low temperatures) on the long term carbon cycle has been emphasized by Alt and Teagle (1999) and Wallmann (2001). If the uptake of CO_2 by the weathering of Ca and Mg silicate minerals on the seafloor proceeds identically to that on land (reactions (i) and (ii) above) then an additional term is necessary to take account of the effect of seafloor spreading on the rate of supply of submarine basalts for this type of weathering. In this case eq (11) is modified to:

$$F_{wsi} = F_{wothsi} + F_{wbas} = F_{bc} - F_{wc} - f_{SR}(t)F_{swbas}(0) \tag{12}$$

where F_{swbas} represents seafloor basalt "weathering" and (0) the present time. The term for $F_{swbas}(0)$ is negative because F_{wsi} as defined represents carbon removed from the atmosphere/ocean system only by subaerial Ca-Mg silicate weathering (eq 10), whereas the sediment burial term for carbonates (F_{bc}) includes carbon derived from both subaerial ($F_{wothsi} + F_{wbas}$) and seafloor (F_{swbas}) Ca-Mg silicate weathering as well as from subaerial carbonate weathering (F_{wc}). Note that here the other f(t) factors that modify weathering are not included in the F_{swbas} term because they apply only to subaerial weathering. Alt and Teagle state that the rate of C uptake to form interstitial $CaCO_3$ in weathered seafloor basalts is about 3.4×10^{18} mol C/my. However, based on strontium isotope results, they point out that 70 to 100 percent of Ca in this $CaCO_3$ is derived from seawater and not from basaltic minerals. Derivation of Ca from seawater means that the interstitial carbonate can be treated as if its carbon were derived only from subaerial weathering and eq (12) replaced by eq (11). However, for the purposes of sensitivity analysis, we will assume the Alt and Teagle maximum (30 percent) value for the derivation of Ca from basalt which gives $F_{swbas}(0) = 1 \times 10^{18}$ mol/my. That this a maximum effect is buttressed by the observation that, during alteration by seawater, Ca from basaltic minerals is commonly released in a one-for-one exchange for dissolved Mg, and this exchange has no effect on oceanic/atmospheric CO_2 (Alt and Teagle, 1999).

Other changes from GEOCARB II to GEOCARB III.—Other changes include the updating of the land area parameter $f_A(t)$ where:

$$f_A(t) = \text{land area}(t)/\text{land area}(0) \tag{13}$$

based on the data of Ronov (1994). The results are used to calculate global discharge from global runoff $f_D(t)$ where:

$$f_D(t) = \text{runoff}(t)/\text{runoff}(0) \tag{14}$$

with values of $f_D(t)$ from Otto-Bliesner (1995). In GEOCARB II it was assumed that runoff, which is in terms of volume of water per unit area per time, should apply only to mountainous areas where most weathering is concentrated. However, the values of $f_D(t)$ are derived for whole continents, and we feel it better here to multiply $f_D(t)$ by $f_A(t)$ to obtain the combined parameter:

$$f_{AD}(t) = f_A(t)f_D(t) \tag{15}$$

Another change is the use of more recent data on the carbon isotopic composition of $CaCO_3$ and organic matter in Phanerozoic sediments. The values presented by Veizer and others (1999) and Hayes, Strauss, and Kaufman (1999) are used for both the $\delta^{13}C$ of carbonates being buried and for the isotope fractionation that occurs during the burial of sedimentary organic matter. A smoothed fit to the Veizer $\delta^{13}C$ data for carbonates was made to eliminate shorter-term variations, as was done previously for different data in GEOCARB II. For the final values of RCO_2, organic matter burial, et cetera to come out as closely as possible to present values at the end of each run, the initial $\delta^{13}C$ values for carbonates and organic matter undergoing weathering were varied, and the best-fit values found to be 3 and −27 permil, respectively.

Some other minor changes from GEOCARB II are: change in the timing of the beginning of the Cambrian from 570 to 550 Ma (although runs are still initiated at 570 Ma) and change of two values, at 140 and 150 Ma, for the effect of sea floor spreading rate on global degassing, $f_G(t)$, so as to allow a smooth transition between the data of Engebretson and others (1992) and Gaffin (1987). Otherwise, no changes have been made in the functionality or values for degassing parameters.

RESULTS AND DISCUSSION

To demonstrate the sensitivity of calculated CO_2 values to changes in various input parameters, a series of runs have been conducted. Results are expressed as RCO_2 which is defined as the ratio of mass of CO_2 in the atmosphere at time t divided by the mass at present, and the results are compared to a standard run, where best estimates of the various input parameters are used. To convert RCO_2 to CO_2 concentration, because of appreciable errors inherent in this kind of modeling, a rough value of 300 ppm can be used to represent "the present."

Phanerozoic timescale.—Figure 3 illustrates the effect on RCO_2 of changing the sensitivity of global mean temperature and global river runoff to changes in CO_2 and solar radiation (see eqs 1 and 2). The standard curve is based on the results of Kothavala, Oglesby, and Saltzman (1999, 2000) and our unpublished results for Cretaceous paleogeography at 80 Ma, from which are derived the values: greenhouse response factor $\Gamma = 4.0°$, and temperature-controlled runoff factor RUN = 0.045 for

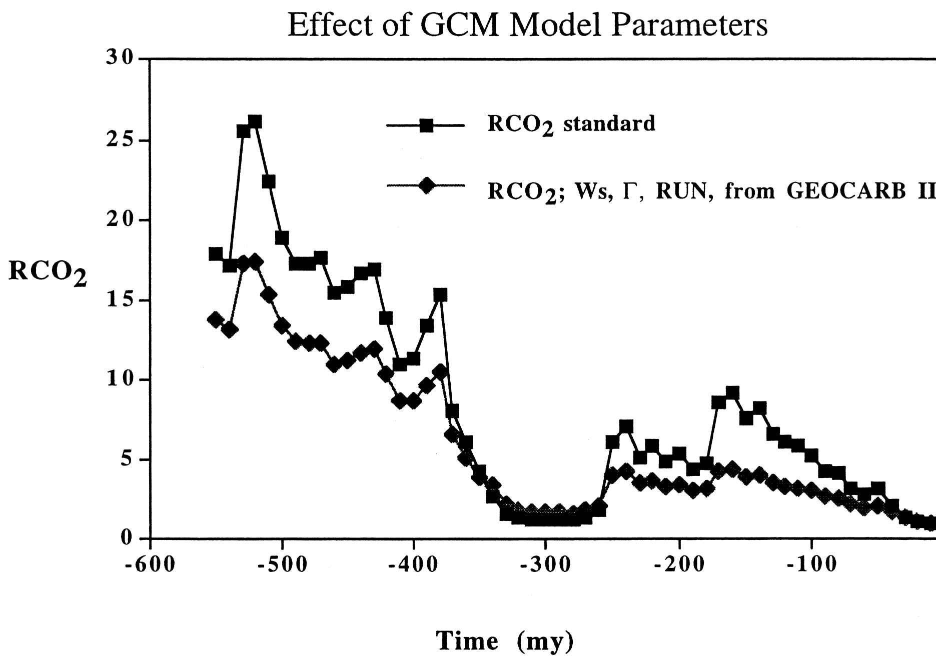

Fig. 3. Phanerozoic RCO_2 vs time for the standard formulation compared with that derived from the GCM data used in GEOCARB II. RCO_2 = mass of atmos. $CO_2(t)$/mass of $CO_2(0)$. Γ and Ws = response of global mean temperature to changes in CO_2 and solar radiation respectively; RUN = response of global river runoff to changes in global mean temperature. For the standard case Ws = 7.4°, Γ = 4.0°, RUN = 0.045 for colder periods (340-260 Ma and 40-0 Ma) and Ws = 7.4°, Γ = 3.3°, RUN = 0.025 for the warmer rest of the Phanerozoic. Values for the same parameters from GEOCARB II are Ws = 12.9°, Γ = 6.0°, and RUN = 0.038 for all times.

colder periods (340-260 and 40-0 Ma), and Γ = 3.3°, RUN = 0.025 for the warmer rest of the Phanerozoic. For all the Phanerozoic we use a new solar response factor Ws = 7.4°. The earlier results of Marshall and others (1994) (Γ = 6° and Ws = 12.9° for all time) and the results of Manabe and Bryan (1985) for runoff (RUN = 0.038 for all time), as used by GEOCARB II, are combined with the other new parameter values to construct the comparison curve. As can be seen, our new GCM results bring about enhanced variations in RCO_2 for the standard curve as compared to the CCM-1-based curve. This is a consequence of the fact that the latest CCM-3 model shows only about a 2.5° temperature change for a doubling of CO_2 as opposed to a 4° change as found in the earlier work. Another way to visualize this result is that for a given temperature and runoff change, driving mineral weathering, a larger change in CO_2 is needed, using the new Γ, Ws, and RUN values, to bring about this temperature change. The use of new GCM parameter values is one of the most important factors bringing about the differences between GEOCARB II and GEOCARB III results.

The use of two different sets of values for Γ and RUN is in accord with climate modeling in general. The higher value of Γ for cold periods incorporates the effects of ice albedo feedback, which is appropriate for 340 to 260 and 40 to 0 Ma at which times there were numerous epochs of extensive continental glaciation. Also, the higher RUN value for colder periods reflects the greater sensitivity of runoff to temperature when ice formation and melting are involved. Ideally, different values for Ws should have been used for cold and warm periods because climate sensitivity to solar forcing should be greater in cold periods. However, these data are not available at the present time.

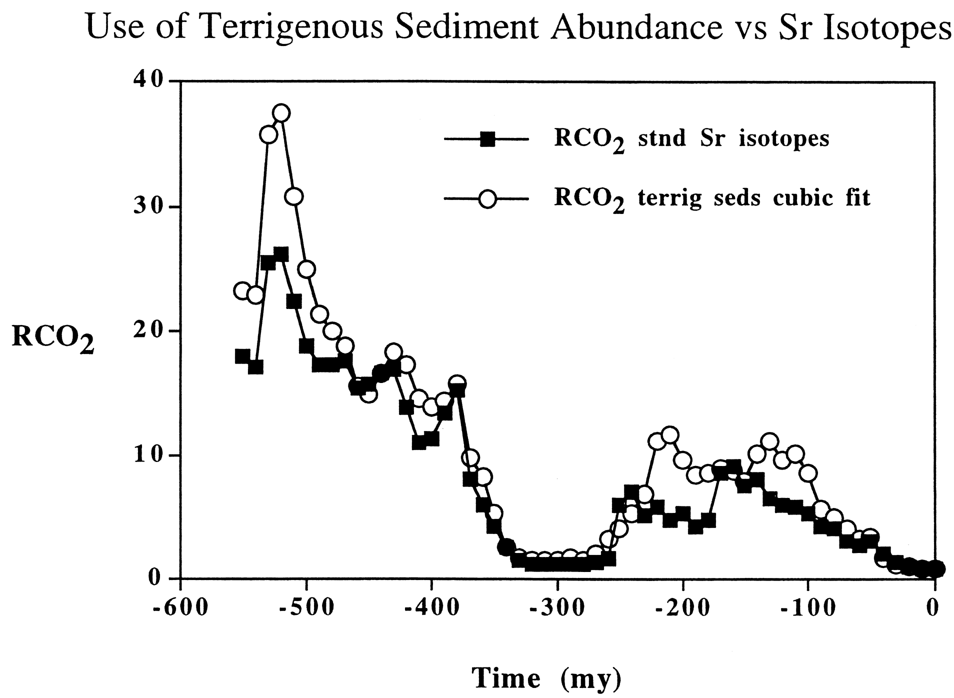

Fig. 4. Phanerozoic RCO_2 vs time derived from the uplift/erosion weathering factor $f_R(t)$ based on Sr isotopes (standard) and based on a cubic fit to the sediment abundance data of Ronov (1993).

Included in our RCO_2 calculation is a new term GEOG(t) expressing the effect of changes in paleogeography on global mean temperature (see eq 3). However, as stated earlier, the use of global mean land temperature is probably incorrect for this purpose. Global mean land temperature is inordinately biased by the inclusion of areas associated with continental-scale glaciers, where little chemical weathering takes place. For example, comparison of ice-free conditions (for example, the Cretaceous) with appreciable continental glaciation (such as the present) from our GCM modeling results in such large changes in GEOG(t) that calculated CO_2 values for the very warm Mesozoic become LOWER than that at present, and the greenhouse effect loses all meaning. To avoid this problem we have used land temperatures calculated by Otto-Bliesner (1995) for flat ice-free continents over time to obtain GEOG(t), but this is only a crude first-order approach. What is needed is to use temperatures only for land that is undergoing appreciable weathering. This points to the need in future modeling to consideration of the geographic distribution of temperature (and rainfall), as it affects weathering, rather than using global mean values.

In figure 4 the results for alternative formulations of $f_R(t)$, the weathering-erosion-relief factor, are shown. Occasional enhanced CO_2 excursions are found with the use of the cubic polynomial fit to the terrigenous sediment abundance data. Because the sediment data are subject to probably large sampling error, as compared to the rather well established curve of oceanic $^{87}Sr/^{86}Sr$ over time (Burke and others, 1982), we have decided to use the Sr isotope-based $f_R(t)$ for our standard runs. Nevertheless the two formulations give overall similar results.

The effect of varying $f_E(t)$, the parameter reflecting the quantitative effect on weathering of vascular land plants, for the early Paleozoic is shown in figure 5. The

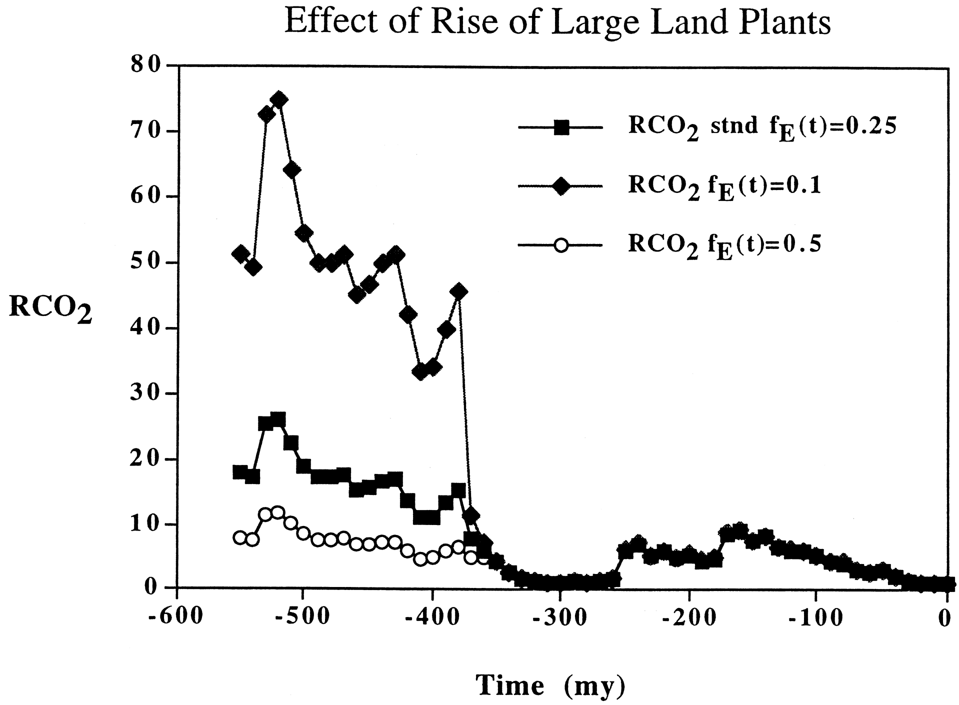

Fig. 5. Effect on RCO_2 of variation of the quantitative effect of the Devonian rise of large vascular land plants on continental weathering. The standard value for the early Paleozoic of the plant weathering factor $f_E(t) = 0.25$ is based on the field results of Moulton, West, and Berner (2000). Note enlarged vertical scale compared to other figures.

standard curve is based on an early Paleozoic value of $f_E(t) = 0.25$ from the results of Moulton, West, and Berner (2000) whereas the other $f_E(t)$ values are chosen to include the estimates of others on the role of plants in weathering. In all cases there is a big drop in CO_2 during the Devonian due to the rise of large vascular plants on the continents. This drop is the most dramatic for all of the Phanerozoic and illustrates the importance of biological evolution to the evolution of the atmosphere. As emphasized in earlier work (Berner, 1994, 1998) knowledge of this parameter is essential for deducing levels of CO_2 during the early Paleozoic. Use of the value $f_E(t) = 0.10$, based on the study of Bormann and others (1998), appears to lead to excessive early Paleozoic levels of CO_2 (note the enlarged vertical scale) which suggests that the actual $f_E(t)$ value was less than this.

The temperature dependence of the rate of dissolution of minerals during weathering has a major influence on the CO_2 result obtained from GEOCARB-type modelling (Brady, 1991). In figure 6 the effects on CO_2 of using three values of the activation energy (temperature dependence) for the weathering of Ca-Mg silicate minerals are shown. The value used for the standard 15 kcal/mole (ACT = 0.09) is the same as that used in GEOCARB II, and this value has been verified more recently by the field studies of basalt weathering over a large range of climates by Louvat (1997). The other values (10 kcal/mol and 20 kcal/mol) are based on the field study of Brady and others (1999) where temperature dependence was deduced from the etching of plagioclase and olivine esposed to weathering at different elevations on the Hawaiian island mountain Hualalai. As can be seen, knowledge of activation energy is important

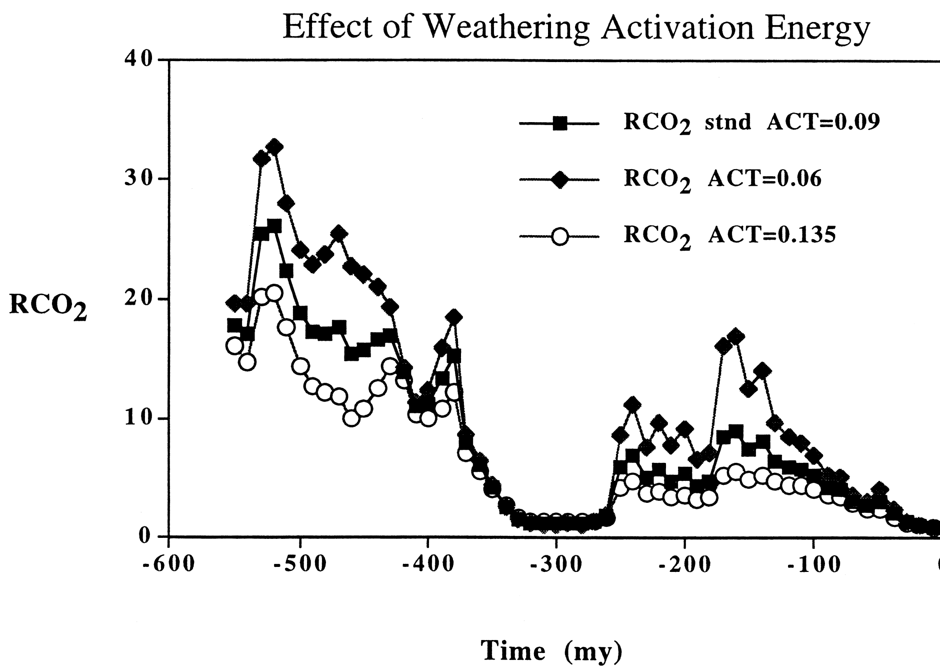

Fig. 6. Effect on RCO_2 of changes in the activation energy (temperature dependence) for Ca-Mg silicate weathering. ACT = activation energy (kcal/mol)/RT^2.

to results, but values of RCO_2 are better constrained here than they are for those resulting from variations of the plant weathering factor, $f_E(t)$.

The sensitivity of RCO_2 to including separate terms for the weathering of subduction zone volcanics and seafloor basalt in the overall weathering expression for silicates is shown in figure 7. As can be seen there is only a minor effect compared to the effects of varying other parameters such as $f_E(t)$ or ACT. Since it is assumed in this approach that all subaerial volcanic weathering occurs in subduction zones and that the maximum value of 30 percent of the Ca in seafloor basalt-included $CaCO_3$ comes from basalt mineral dissolution instead of from seawater or Mg-Ca exchange (Alt and Teagle, 1999), the effect shown should be maximal.

As was done in GEOCARB II, a smoothed first-order fit to values of $\delta^{13}C$ for sedimentary carbonates has been used here for calculating carbon burial rates in the standard runs, the difference being that the newer $\delta^{13}C$ data of Veizer and others (1999) have been used along with data on $\delta^{13}C$ for sedimentary organic matter to obtain values of the fractionation parameter α_c (Hayes, Strauss, and Kaufman, 1999). To examine the effect of smoothing on RCO_2, an additional run has been conducted using the actual mean data tabulated for $\delta^{13}C$ over Phanerozoic time by Veizer and others. Results are shown in figure 8. Except for an occasional sharp excursion, there is reasonably good agreement between the two approaches. Thus, it is justifiable to use the smoothed isotope data because the time resolution of GEOCARB modeling is only good to about 10 to 20 my.

Mesozoic-Cenozoic timescale.—Because of a better knowledge of factors affecting the long term carbon cycle (for example, seafloor spreading rate, the rise of angiosperms, the rise of calcareous plankton, better-known paleogeography, et cetera), it is of special interest to focus on the past 250 my when calculating paleo-CO_2. Here, because

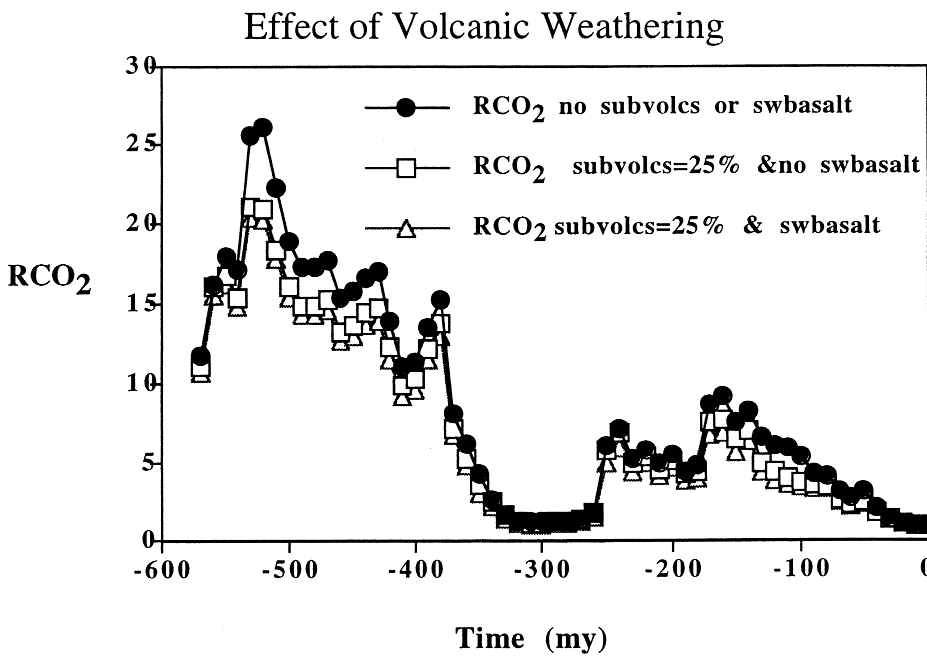

Fig. 7. Effect of distinguishing weathering of volcanics in subduction zones (subvolcs) from the weathering of other silicates and of adding seafloor basalt weathering (swbasalt) to total silicate weathering.

of less attention being paid to it, and because of the rather coarse time resolution of the GEOCARB modeling, emphasis is placed mainly on the longer time span, the Mesozoic (250-65 Ma).

One of the least known parameters in GEOCARB modeling is the relative importance of gymnosperms versus angiosperms as they affect silicate weathering rate. This is an important question because the angiosperms did not exist before about 130 Ma. In GEOCARB II it was assumed that the rise of angiosperms in the Mesozoic between 130 and 80 Ma led to an increase in the global plant effect on weathering $f_E(t)$ from 0.75 to 1, with the latter representing the present value. However, this presumed increase is controversial. Knoll and James (1987) and Volk (1989) state that present-day angiosperms release more cations, and therefore accelerate weathering, more than gymnosperms. However, Robinson (1991) has pointed out that some of the data used by Knoll and James was from areas underlain by limestones and not silicates, and $CaCO_3$ is well known to weather much faster than silicates. In addition, Quideau and others (1996) from studies of experimental ecosystems have come to the conclusion that gymnosperms release Ca and Mg faster than angiosperms. By contrast, the work of Moulton, West, and Berner (2000) shows a similar release rate of Ca and Mg from basalt by conifers and by birch trees. However, the birches are stunted, very slow growing "bushes" because of the harsh Icelandic climate, and it may be possible that more actively growing birches would weather faster. (On a per unit of biomass basis the birches weather faster than the conifers.) Another problem is that the data of Quideau and others (1996), and Moulton, West, and Berner (2000) are both derived from extreme climates: the first a dry chapparal and the other a cold maritime climate. There is a need for more studies of this type from more typical environments of extensive chemical weathering such as tropical rainforests.

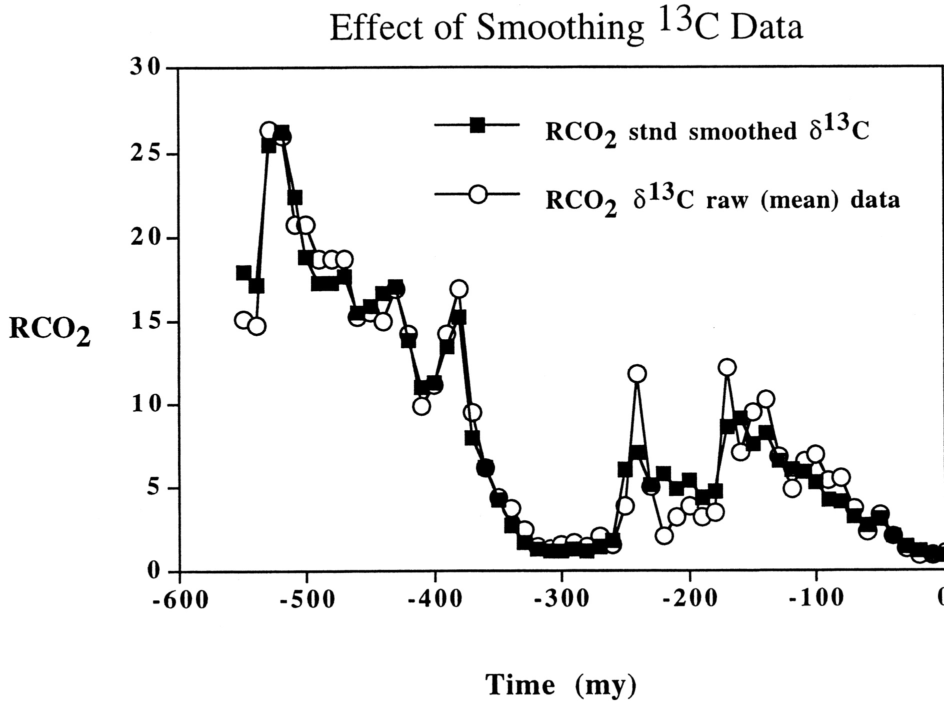

Fig. 8. Effect of using raw mean data for $\delta^{13}C$ vs time (Veizer and others, 1999) vs first order smoothing of the same data as used in the standard formulation.

Figure 9 shows plots of RCO_2 versus time for three values of the ratio of the plant weathering factor $f_E(t)$ for gymnosperms to that for angiosperms. Also plotted are independent estimates of RCO_2, based on the study of paleosols, by Ekart and others (1999) (plotted as the letter E in figure 9 with some plotted E's representing the average for several analyses for similar times). Since no firm conclusion can be given as to the best value for the $f_E(t)$ ratio, our approach here is to use the ratio that gives the best fit to the Ekart and others (1999) data. In this case the best value is about 0.875. Thus, for our standard runs we have used this value for $f_E(t)$ applied to a gymnosperm-dominated world prior to 130 Ma, a linear rise in $f_E(t)$ between 130 and 80 Ma, and the value of $f_E(t) = 1$ for an angiosperm-dominated world from 80 Ma up to the present.

Ekart and others (1999) have plotted their data in terms of a running five-point weighted average with an error estimate equivalent to ± 2 in RCO_2. This average, as well as the raw data shown in figure 9, shows a definite downward trend in CO_2 during the Mesozoic from about 170 to 65 Ma. Both GEOCARB II and III modelling show a similar trend, and we believe that it is real. The question then becomes: is this decrease with time matched by global cooling? This is an important question that needs to be addressed by future paleoclimatological research.

Another poorly known land plant parameter is the proportion of trees worldwide that undergo fertilization of growth by increasing CO_2 and that weather faster as a result. This effect is parameterized in terms of the exponent FERT in eq (5), and actual values of FERT for the present, not to mention the geological past, are essentially unknown (see Volk, 1987; Berner, 1994). Certainly there are plants that do respond, in terms of carbon storage, to CO_2 fertilization as shown by many experimental greenhouse studies (see Bazzaz, 1990), but the problem is how much does increased growth

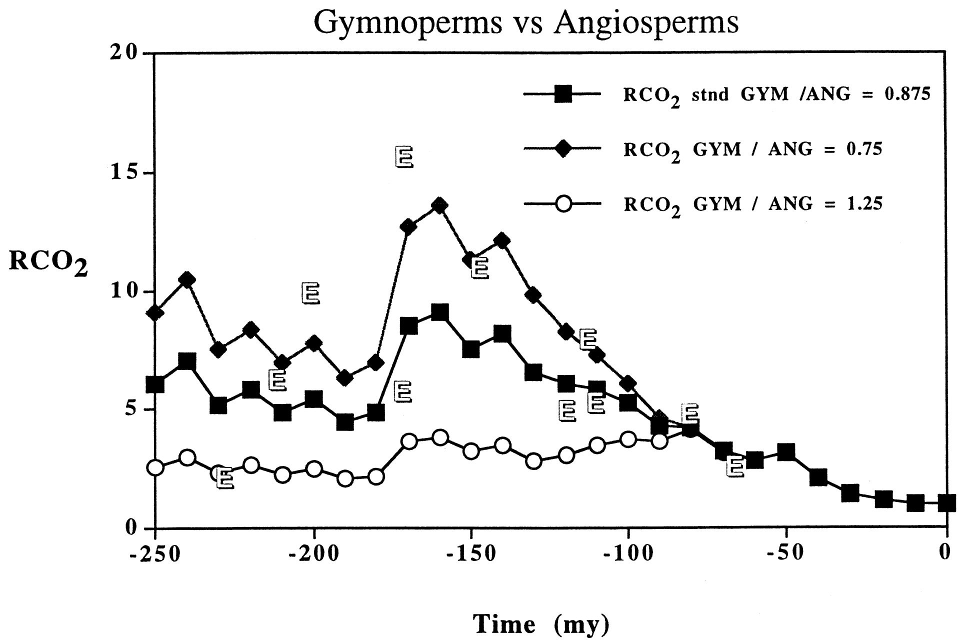

Fig. 9. Effect of the ratio of the plant weathering factor $f_E(t)$ for angiosperms vs gymnosperms on RCO_2 vs time over the Mesozoic and Cenozoic. By definition $f_E(t) = 1$ for angiosperms. The pre-angiosperm $f_E(t)$ value for the standard curve (0.875) is derived from the best fit, of calculated RCO_2, to the independently derived Mesozoic CO_2 data of Ekart and others (1999), The Ekart and others data are represented by the letter E and have error ranges of RCO_2 of about ± 2.

bring about increased weathering and whether tree growth is limited by nutrients, light, or water availability, and thus not affected by changes in CO_2. That some trees should bring about faster weathering under higher CO_2 is suggested by the results of Godbold, Berntson, and Bazzaz (1997) who have found greater root mass and ectomycorrhizal colonization for seedlings grown under elevated CO_2. Roots and their associated symbiotic microflora are the principal agents of plant-induced weathering.

Recent work of Andrews and Schlesinger (2000) has shown that an increased CO_2 level does in fact result in enhanced chemical weathering. In their study a natural pine forest was fumigated with excess CO_2, and they found that an increase of CO_2 from 360 to 570 ppm resulted in a 33 percent increase in the flux of dissolved bicarbonate from mineral weathering. This value is reasonably close to what is predicted by eq (5) with FERT = 0.4 (23 percent increase), which suggests some validity to the Michaelis-Menton functionality that is assumed in GEOCARB II and in the present paper. In addition, recent paleo-productivity modeling of D.J. Beerling (personal communication) indicates a maximum productivity increase, at very high CO_2 levels, of a factor of two, which is also in agreement with eq (5).

Even if our assumed functional response of plant induced weathering to CO_2 may be correct, there is still no idea of what proportion of plants globally respond to CO_2. Thus, in figure 10 the value of the CO_2-fertilization factor FERT is varied from the extreme values of zero (no direct effect of CO_2 on plant-mediated weathering) and one (all plants globally behave like the pine trees in the forest of Andrews and Schlesinger). The "best guess" of FERT = 0.4, equivalent to 35 percent of plants responding to CO_2 globally, is used here, as was the case also for GEOCARB II. As can

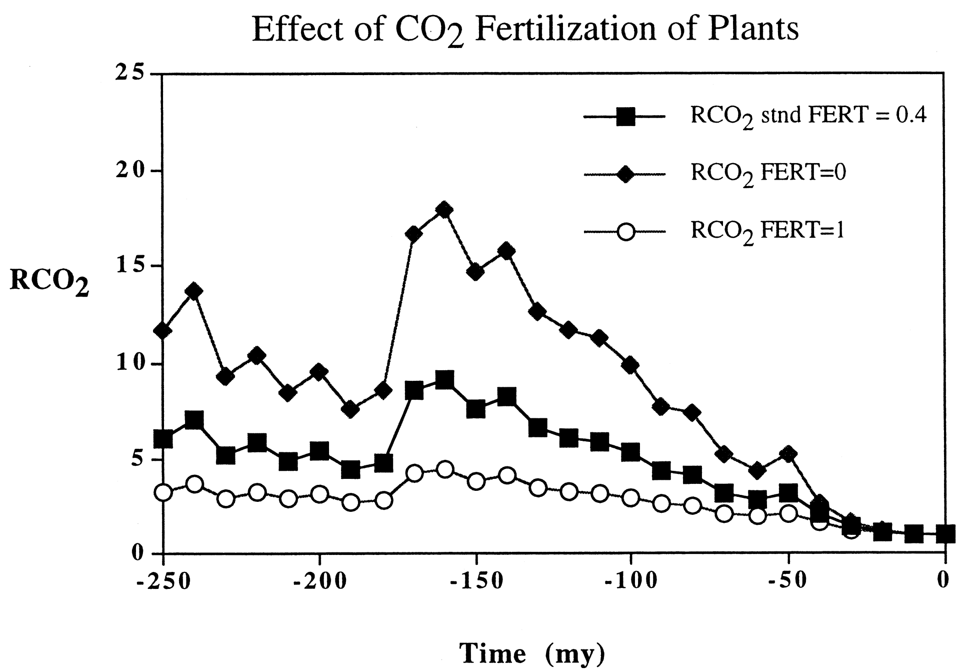

Fig. 10. The effect of varying the global proportion of plants that respond to changes in atmospheric CO_2 and thereby affect weathering rate for the Mesozoic-Cenozoic. FERT = 0 means no plants respond to CO_2; FERT = 1 means all plants respond.

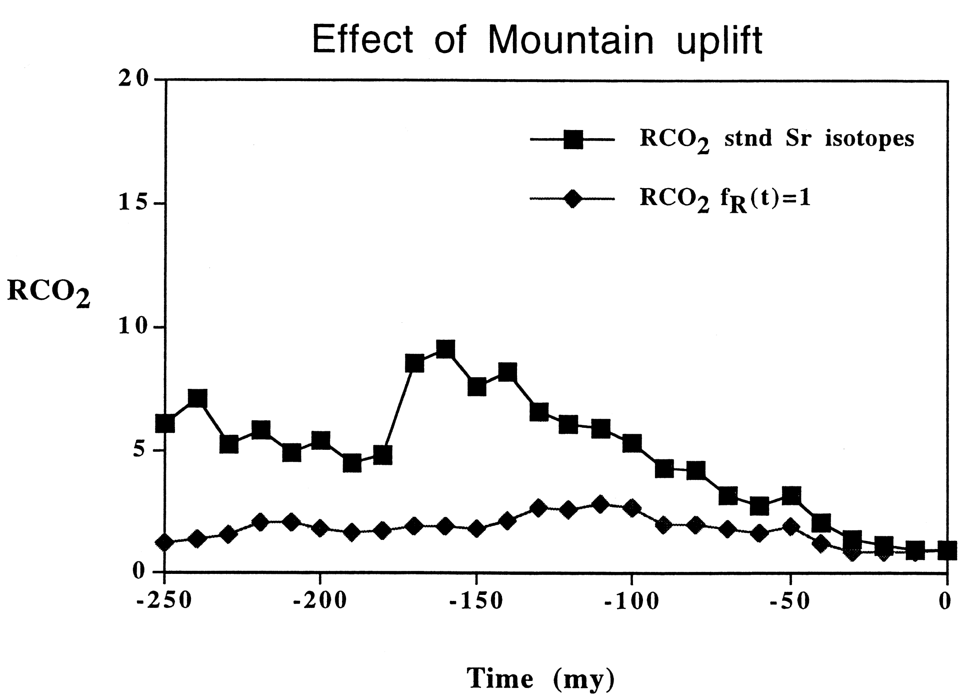

Fig. 11. Effect of mountain uplift on RCO_2 versus time for the Mesozoic-Cenozoic. $f_R(t) = 1$ means no change in mean global relief over time.

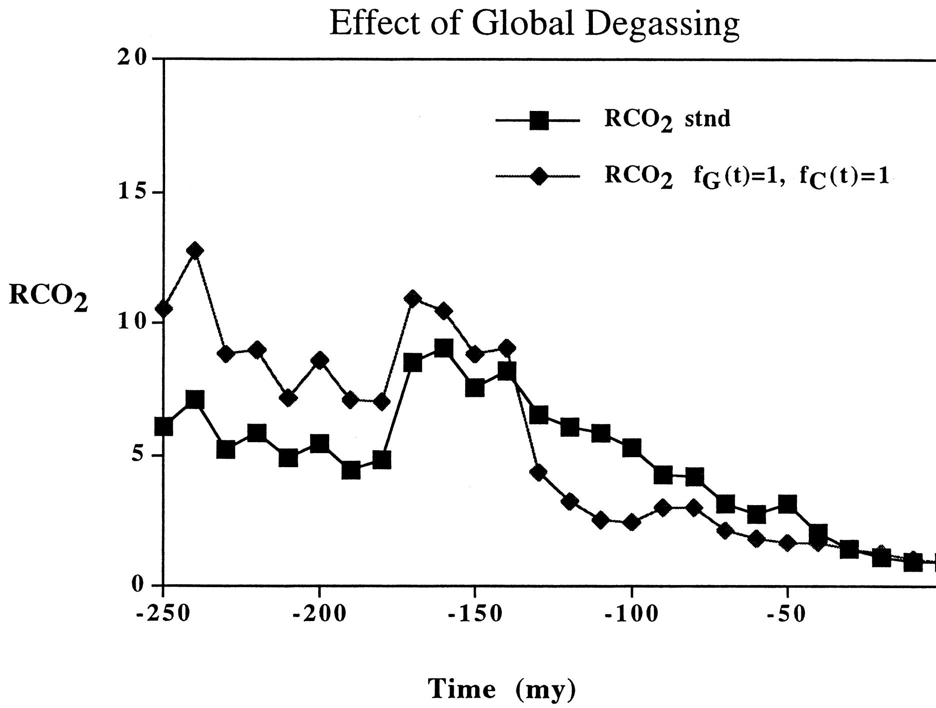

Fig. 12. Effect of global degassing on RCO_2 vs time for the Mesozoic-Cenozic. $f_G(t) = 1$ and $f_C(t) = 1$ means no change in degassing rate over time.

be seen from figure 10 knowledge of the FERT value has a major effect on calculated CO_2 levels for the Mesozoic and early Cenozoic.

Besides the plant-related factors that affect calculated CO_2 levels during the Mesozoic and Cenozoic, there are other factors included in GEOCARB modeling that have a measurable effect on CO_2, especially during the Mesozoic. Two, $f_R(t)$ and $f_G(t) + f_C(t)$, are shown in figures 11 and 12. If the uplift/erosion weathering factor $f_R(t)$ is held equal to that today ($f_R(t) = 1$) then much of the high values of RCO_2 found for the Mesozoic disappear. Likewise if global degassing, as represented by the factors $f_G(t)$ and $f_C(t)$, are both held equal to one, there is appreciable change in CO_2.

Many papers in the literature cite that high values of CO_2 (and temperature) during the Mesozoic were due predominantly to increased global degassing at that time (Fischer, 1984; Larson, 1991). However, if one compares figures 9 through 12, it is obvious that many factors, some of which were possibly more important than degassing, also could have affected CO_2 during this period. This points to the importance of considering ALL factors affecting CO_2 when modelling the long term carbon cycle and not concentrating only one cause.

CONCLUSION

Results for GEOCARB III, as presented in the present paper, are compared to those for GEOCARB II in figure 13. As one can see the modeling has retained its overall trend, and the GEOCARB II curve falls within the error margins for GEOCARB III, based on the sensitivity analysis of the present paper. This means that there appears to have been very high early Paleozoic levels of CO_2, followed by a large drop during the Devonian, and a rise to moderately high values during the Mesozoic, followed by a

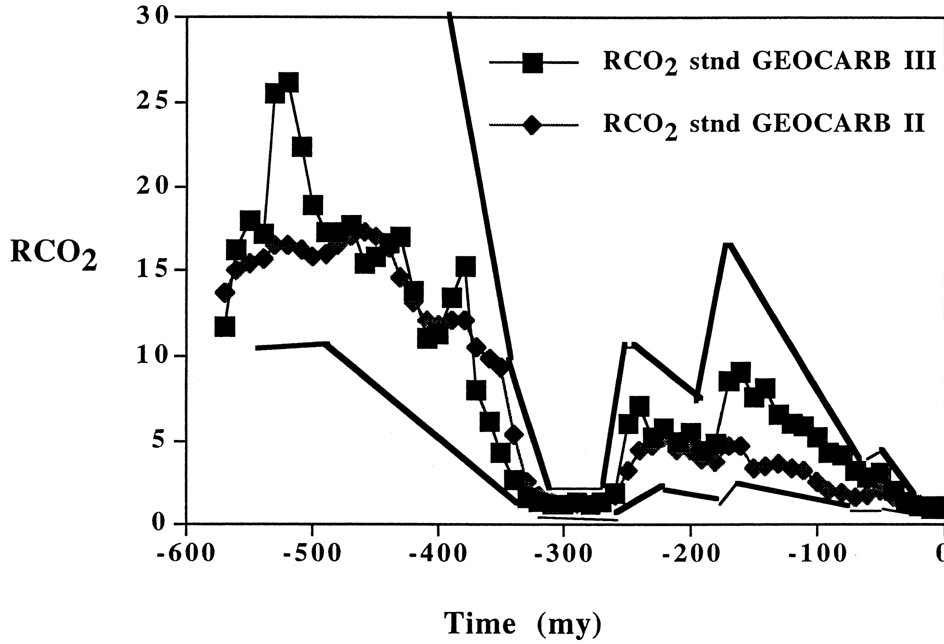

Fig. 13. Comparison of standard curves of RCO_2 vs time for GEOCARB II and III. The outer lines represent an estimate of errors in the present GEOCARB III model.

gradual decline through both the later Mesozoic and Cenozoic. This type of modeling is incapable of delimiting shorter term CO_2 fluctuations (Paleocene-Eocene boundary, late Ordovician glaciation) because of the nature of the input data which is added to the model as 10 my or longer averages. Thus, exact values of CO_2, as shown by the standard curve, should not be taken literally and are always susceptible to modification. Nevertheless, the overall trend remains. This means that over the long term there is indeed a correlation between CO_2 and paleotemperature, as manifested by the atmospheric greenhouse effect.

As for suggested future carbon cycle modelling work, besides the usual plea for more data from all sources, there is a special need, in both carbon cycle and climate modelling, to consider only those land areas that have sufficient rain and are sufficiently warm to exhibit appreciable chemical weathering. This entails closer interaction between GCM models and carbon cycle models, with an attempt to look at weathering on a paleogeographic, not just global, basis. In addition, because of the importance of plants to weathering, many more experimental studies under natural conditions are needed to determine how much different plants accelerate weathering and how the plants respond to change in atmospheric CO_2. If nothing else, it is hoped that papers such as this one will act as a spur to more interaction between geologists, geochemists, geophysicists, biologists, and climatologists. The long term carbon cycle demands a multidisciplinary approach.

ACKNOWLEDGMENTS

We have benefitted immensely from discussions about erosion and weathering with Bill Hay and Jerome Gaillardet, about paleogeography with Chris Scotese, about paleoclimate modeling with Bob Oglesby and Bette Otto-Bliesner, and about plants and weathering with David Beerling, Bill Schlesinger, Leo Hickey, Katherine Moulton and Jennifer Robinson. Helpful reviews of the manuscript were provided by Bill Hay and Ken Caldeira. Supercomputing resources were provided by Bette Otto-Bliesner. Research of Berner is supported by DOE Grant DE-FGO2-95ER14522 and NSF Grant EAR-9804781. Kothavala's work is supported by NSF grant ATM-9530914 (to Barry Saltzman). Musical inspiration to Berner was supplied by being able to play his own compositions on a grand piano for a few days in a serene rural setting in the south of France (courtesy of the Treilles Foundation).

Appendix 1
Equations used in GEOCARB modeling

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

$$\delta_c(F_{wc} + F_{mc}) + \delta_g(F_{wg} + F_{mg}) = \delta_{bc}F_{bc} + (\delta_{bc} - \alpha_c)Fbg$$

$$Fwc = f_{BB}(T,\ CO_2)f_{LA}(t)f_{AD}(t)f_E(t)k_{wc}C$$

$$Fwg = f_R(t)f_{A_D}(t)k_{wg}G$$

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

$$F_{mg} = f_G(t)F_{mg}(0)$$

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

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

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

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

$$F_{wsi} = F_{bc} - F_{wc} = f_B(T,\ CO_2)f_R(t)f_E(t)f_{AD}(t)^{0.65}F_{wsi}(0)$$

Definitions

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 degassing release of carbon to the ocean, atmosphere, and biosphere system via the metamorphic, volcanic, and 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 CO_2 via the weathering of Ca and Mg silicates followed by precipitation of Ca and Mg carbonates (Ebelmen-Urey reaction). $F_{wsi}(0)$ represents rate at present.

$f_{BB}(T, CO_2)$ = dimensionless feedback factor for carbonates expressing the dependence of weathering on temperature and on CO_2

$f_B(T, CO_2)$ = dimensionless feedback factor for silicates expressing the dependence of weathering on temperature and on CO_2

$f_{LA}(t)$ = carbonate land area(t)/carbonate land area(0) derived from $f_A(t)$ = land area(t)/land area(0) times [carb/total land(t)]/[carb/total land(0)]

$f_{AD}(t)$ = river discharge(t)/river discharge(0) due to changes in paleogeography. It is obtained from the product of $f_A(t)$ and $f_D(t)$ = runoff(t)/runoff(0). The power of 0.65 in the expression for F_{wsi} reflects dilution at high runoff.

$f_R(t)$ = mountain uplift factor = mean land relief(t)/mean land relief(0)

$f_E(t)$ = factor expressing the dependence of weathering on soil biological activity due to land plants ($f_E(t) = 1$ at present)

$f_G(t)$ = global degassing rate(t)/global degassing rate(0)

$f_C(t)$ = dependence of degassing rate on the proportions of carbonate in shallow water and in deep sea sediments

δ = $\delta^{13}C$ value (‰); subscripts are c for average of all carbonates, g for average of all organic matter and bc for the burial of carbonates at each past time

α_c = carbon isotope fractionation between organic matter and carbonates during burial

k_{wc}; k_{wg} = rate constants for weathering of carbonates and organic matter

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

References

Algeo, T.J., Berner, R.A., Maynard, J.B., and Scheckler, S.E., 1995, Late Devonian oceanic anoxic events and biotic crises: "Rooted" in the evolution of vascular land plants? GSA Today, v. 5, p. 64–66.

Alt, J.C., and Teagle, D.A.H., 1999, The uptake of carbon during alteration of oceanic crust: Geochimica et Cosmochimica Acta, v. 63, p. 1527–1536.

Andrews, J.A., and Schlesinger, W.H., 2000, Soil CO_2 dynamics, acidification and chemical weathering in a temperate forest with experimental CO_2 enrichment: Global Biogeochemical Cycles (in press).

Bazzaz, F.A., 1990, The response of natural ecosystems to the rising global CO_2 levels: Ann. Rev. Evolution and Systematics: v. 21, p. 167–196.

Berner, R.A., 1991, A model for atmospheric CO_2 over Phanerozoic time: American Journal of Science, v. 291, p. 339–376.

—— 1994, GEOCARB II: A revised model of atmospheric CO_2 over Phanerozoic time: American Journal of Science, v. 294, p. 56–91.

—— 1998, The carbon cycle and CO_2 over Phanerozoic time: the role of land plants: Philosophical Transactions of the Royal Society, Series B, v. 353, p. 75–82.

—— 1999, A new look at the long-term carbon cycle: GSA Today, v. 9, p. 1–6.

Berner, R.A., and Rye, D.M., 1992, Calculation of the Phanerozoic strontium isortope record of the oceans from a carbon cycle model: American Journal of Science, v. 292, p. 136–148.

Bluth, G.J.S., and Kump, L.R., 1991, Phanerozoic paleogeology: American Journal of Science, v. 291, p. 284–308.

Bormann, B.T., Wang, D., Bormann, F.H., Benoit, G., April, R., and Snyder, R., 1998, Rapid, plant-induced weathering in an aggrading experimental ecosystem: Biogeochemistry, v. 43, p. 129–155.

Brady, P.V., 1991, The effect of silicate weathering on global temperature and atmospheric CO_2: Journal of Geophysical Research, v. 96, p. 18,101–18,106.

Brady, P.V., Dorn, R.I., Brazel, A.J., Clark, J., Moore, R.B., and Glidewell, T., 1999, Direct measurement of the combined effects of lichen, rainfall, and temperature on silicate weathering: Geochimica et Cosmochimica Acta, v. 63, p. 3293–3300.

Brass, G.W., 1976, The variation of the marine $^{87}Sr/^{86}Sr$ ratio during Phanerozoic time: interpretation using a flux model: Geochimica et Cosmochimica Acta, v. 40, p. 721–730.

Burke, W.H., Dension, R.E., Heatherington, E.A., Koepnik, R.B., Nelson, H.F., and Otto, J.B., 1982, Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time: Geology, v. 109, p. 516–519.

Derry, L.A., and France-Lanord, C., 1996, Neogene Himalayan weathering history and river $^{87}Sr/^{86}Sr$ impact on the marine Sr record: Earth and Planetary Science Letters, v. 142, p. 59–74.

Ebelmen, J.J., 1845, Sur les produits de la decomposition des especes minerales de la famille des silicates: Annales des Mines, v. 7, p. 3–66.

Ekart, D., Cerling, T.E., Montanez, I.P., and Tabor, N.J., 1999, A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide: American Journal of Science, v. 299, p. 805–827.

Engebretson, D.C., Kelley, K.P., Cashman, H.J., and Richards, M.A., 1992, 180 million years of subduction: GSA Today, v. 2, p. 93–95, 100.

Fischer, A.G., 1984, The two Phanerozoic supercycles, in Berggren, W.A., and Van Couvering, J.A., editors. Catastrophes and Earth History: Princeton, New Jersey, Princeton University Press, p. 129–150.

Gaffin, S., 1987, Ridge volume dependence of seafloor generation rate and inversion using long term sea-level change: American Journal of Science, v. 287, p. 596–611.

Gaillardet, J., Dupre, B., Louvat, P., and Allegre, C.J., 1999, Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers: Chemical Geology, v. 159, p. 3–30.

Gibbs, M.T., Bluth, G.J.S., Fawcett, P.J., and Kump, L.R., 1999, Global chemical erosion over the last 250 my: variations due to changes in paleogeography, paleoclimate, and paleogeology: American Journal of Science, v. 299, p. 611–651.

Godbold, D.L., Berntson, G.M., and Bazzaz, F.A., 1997, Growth and mycorrhizal colonization of three North American tree species under elevated atmospheric CO_2: New Phytologist, v. 137, p. 433–440.

Gradstein, F.M., and Ogg, J., 1996, A Phanerozoic time scale: Episodes, v. 19, p. 3–5.

Gregor, B., 1970, Denudation of the continents: Nature, v. 228, p. 273–275.

Gregor, B., 1992, Rock cycle: Encyclopedia of Earth System Science, v. 4, p. 21–30.

Hay, W.W., DeConto, R.M., Wold, C.N., Wilson, K.M., Voight, S., Schulz, M., Wold-Rossby, A., Dullo, W.-C., Ronov, A.B., Balukhovsky, A.N., and Soding, E., 1999, Alternative global Cretaceous paleogeography, Barrera, E., and Johnson, C.C., editors, Evolution of the Cretaceous Ocean-Climate System: Boulder, Colorado, Geological Society of American Special Paper 332, p. 1–48.

Hayes, J.M., Strauss, H., and Kaufman, A.J. 1999, The abundance of ^{13}C in marine organic matter and isotope fractionation in the global biogeochemical cycle of carbon during the past 800 Ma: Chemical Geology, v. 161, p. 103–125.

Holland, H.D., 1978, The chemistry of the atmosphere and ocean. New York: Wiley Interscience, 351 p.

Kiehl, J.T., Hack, J.J., Bonan, G., Boville, B.A., Williamson, D., and Rasch, P., 1998, The National Center for Atmospheric Research Community Climate Model: CCM3: Journal of Climate, v. 11, p. 1151–1178.

Knoll, M.A., and James, W.C., 1987, Effect of the advent and diversification of vascular plants on mineral weathering through geologic time: Geology, v. 15, p. 1099–1102.

Kothavala, Z., Oglesby, R.J., and Saltzman, B., 1999, Sensitivity of equilibrium surface temperature of CCM3 to systematic changes in atmospheric CO_2: Geophysical Research Letters, v. 26, p. 209–212.

—— 2000, Evaluating the climatic response to changes in CO_2 and solar luminosity, in 11th Symposium on Global Change Studies, Long Beach, California, American Meteorological Society, p. 348–351.

Kump, L.R., and Arthur, M.A., 1997, Global chemical erosion during the Cenzooic: weatherability balances the budgets, *in* Ruddiman, W.F., editor, Tectonic Uplift and Climate Change; New York, Plenum Press, p. 399–426.
Larson, R.L., 1991, Latest pulse of Earth: evidence for a mid-Creaceous superplume: Geology, v. 19, p. 547–550.
Louvat, P., 1997, Etude géochimique de l'érosion fluviale d'îles volcaniques à l'aide des éléments majeurs et traces: Ph.D. thesis, Université Paris 7, 322 p.
Lovelock, J.E., and Watson, A., 1982, The regulation of carbon dioxide and climate: Planetary and Space Science, v. 30, p. 795–802.
Manabe, S., and Bryan, K., 1985, CO_2-induced change in a coupled ocean-atmosphere model and its paleoclimatic implications: Journal of Geophysical Research, v. 90, p. 11,689–11,707.
Marshall, S., Oglesby, R.J., Larson, J.W., and Saltzman, B., 1994, A comparison of GCM sensitivity to changes in CO_2 and solar luminosity: Geophysical Research Letters, v. 21, p. 2487–2490.
McElwain, J.C., and Chaloner, W.G., 1995, Stomatal density and index of fossil plants track atmospheric carbon dioxide in the Paleozoic: Annals of Botany, v. 76, p. 389–395.
Moulton, K.L., West, J., and Berner, R.A., 2000, Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering: American Journal of Science, v. 300, p. 539–570.
Otto-Bliesner, B.L., 1995, Continental drift, runoff and weathering feedbacks: implications from climate model experiments: Journal of Geophysical Research, v. 100, p. 11537–11548.
Quade, J., Roe, L., DeCelles, P.G., and Ojha, T.P., 1997, The late Neogene $^{87}Sr/^{86}Sr$ record of lowland Himalayan rivers: Science, v. 276, p. 1828–1831.
Quideau, S.A., Chadwick, O.A., Graham, R.C., Wood, H.B., 1996, Base cation biogeochemistry and weathering under oak and pine: A controlled long-term experiment: Biogeochemistry, v. 35, p. 377–398.
Raymo, M.E., 1991, Geochemical evidence supporting TC Chamberlin's theory of glaciation: Geology, v. 19, p. 344–347.
Richter, F.M., Rowley, D.B., and DePaolo, D.J., 1992, Sr isotope evolution of seawater: the role of tectonics: Earth and Planetary Science Letters, v. 109, p. 11–23.
Robinson, J.M., 1991, Land plants and weathering: Science, v. 252, p. 860.
Ronov, A.B., 1993, Stratisfera—Ili Osadochnaya Obolochka Zemli (Kolichestvennoe Issledovanie).—Yaroshevskii, A.A., editor: Nauka, Moskva, 144 p. (in Russian).
——— 1994, Phanerozoic transgressions and regressions on the continents: a quantitative approach based on areas flooded by the sea and areas of marine and continental deposition: American Journal of Science, v. 294, p. 802–860.
Schwartzman, D.W., and Volk, T., 1989, Biotic enhancement of weathering and the habitability of earth: Nature, v. 340, p. 457–460.
Tajika, E., 1998, Climate change during the last 150 million years: reconstruction from a carbon cycle model: Earth and Planetary Science Letters, v. 160, p. 695–707.
Taylor, A.S., and Lasaga, A.C., 1999, The role of basalt weathering in the Sr isotope budget of the ocean: Chemical Geology, v. 161, p. 199–214.
Urey, H.C., 1952, The planets: their origin and development: New Haven, Connecticut, Yale University Press, 245 p.
Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebneth, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., and Strauss, H., 1999, $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater: Chemical Geology, v. 161, p. 59–88.
Volk, T., 1987, Feedbacks between weathering and atmospheric CO_2 over the last 100 million years: American Journal of Science, v. 287, p. 763–779.
——— 1989, Rise of angiosperms as a factor in long-term climatic cooling: Geology, v. 17, p. 107–110.
Wallmann, K., 2001, Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO_2 and climate: Geochiumica et Cosmochimica Acta (in press)
Wold, C.N., and Hay, W.W., 1990, Estimating ancient sediment fluxes: American Journal of Science, v. 290, p. 1069–1089.
Wright, V.P., 1985, The precursor environment for vascular plant colonization: Philosophical Transactions of the Royal Society, Series B, v. 30, p. 143–145.