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The carbon cycle and carbon dioxide over Phanerozoic time: the role of land plants

Robert A. Berner

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The carbon cycle and CO_2 over Phanerozoic time: the role of land plants

Robert A. Berner

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

A model (GEOCARB) of the long-term, or multimillion-year, carbon cycle has been constructed which includes quantitative treatment of (1) uptake of atmospheric CO_2 by the weathering of silicate and carbonate rocks on the continents, and the deposition of carbonate minerals and organic matter in oceanic sediments; and (2) the release of CO_2 to the atmosphere via the weathering of kerogen in sedimentary rocks and degassing resulting from the volcanic–metamorphic–diagenetic breakdown of carbonates and organic matter at depth.

Sensitivity analysis indicates that an important factor affecting CO_2 was the rise of vascular plants in the Palaeozoic. A large Devonian drop in CO_2 was brought about primarily by the acceleration of weathering of silicate rock by the development of deeply rooted plants in well-drained upland soils. The quantitative effect of this accelerated weathering has been crudely estimated by present-day field studies where all factors affecting weathering, other than the presence or absence of vascular plants, have been held relatively constant. An important additional factor, bringing about a further CO_2 drop into the Carboniferous and Permian, was enhanced burial of organic matter in sediments, due probably to the production of microbially resistant plant remains (e.g. lignin).

Phanerozoic palaeolevels of atmospheric CO_2 calculated from the GEOCARB model generally agree with independent estimates based on measurements of the carbon isotopic composition of palaeosols and the stomatal index for fossil plants. Correlation of CO_2 levels with estimates of palaeoclimate suggests that the atmospheric greenhouse effect has been a major factor in controlling global climate over the past 600 million years.

Keywords: carbon dioxide, land plants, weathering, phanerozoic, carbon cycle

1. INTRODUCTION: THE LONG-TERM CARBON CYCLE

The cycle of carbon that affects the level of atmospheric CO_2 over time can be divided into two different cycles. The first cycle involves the transfer of CO_2 between the atmosphere, oceans, soils, and the biosphere. These are the natural processes that control CO_2 on the time-scale of years to tens of thousands of years, and which constitute what is normally thought of as the 'carbon cycle'. However, this paper is concerned with many millions of years, and for this time-scale a completely different carbon cycle dominates. This is the long-term or geochemical carbon cycle (figure 1) that involves the transfer of carbon between rocks and the surficial reservoir consisting of the ocean, atmosphere, biosphere and soils. (For a detailed discussion of the geochemical carbon cycle consult Holland (1978) or Berner & Lasaga (1989).)

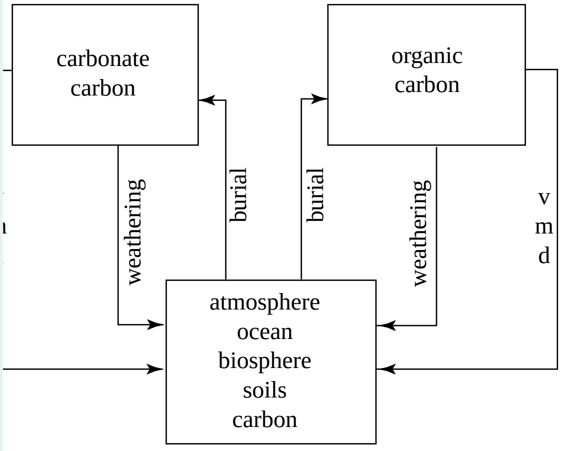
Demonstration of the quantitative dominance of the long-term cycle on a multimillion-year time-scale can be seen from table 1. The amount of carbon present in all life is about 0.6×10^{18} g of C. By comparison, the amount of organic carbon (kerogen, coal, hydrocarbons) stored in rocks is roughly $15\,000\times10^{18}$ g, and about 60×10^{18} g of this is weathered, or formed by burial in sediments, in 1 000 000 years. Thus, about 100 times as much C as exists in life (or in the atmosphere) is turned over every million years as part of the long-term carbon cycle.

The principal processes of the long-term cycle are as follows. (1) The uptake of CO_2 from the atmosphere and its transformation during the weathering of Ca and Mg silicate and carbonate minerals to dissolved HCO_3^-, which is transferred to the oceans by rivers and precipitated there as $CaCO_3$ and $MgCO_3$ minerals. (The overall result of Ca/Mg silicate weathering is the transfer of carbon from the surficial system to buried carbonate rocks, whereas there is negligible transfer of carbon resulting from $MgCO_3$ and $CaCO_3$ weathering because, on a million-year time-scale, carbonate weathering is rapidly followed by equivalent carbonate deposition.) (2) The weathering of ancient organic matter on the continents and the burial of new organic matter in marine sediments (the burning of fossil fuels by humans is a special case of greatly accelerated organic matter weathering). (3) The thermal breakdown at depth of carbonate minerals and organic matter via metamorphism, diagenesis and magmatism with the transfer of the resulting CO_2 (or organically derived reduced gases that subsequently become oxidized to CO_2 by O_2) back to the Earth's surface.

The above description can be represented by succinct overall chemical reactions. These are:

$$CO_2 + CaSiO_3 \leftrightarrow CaCO_3 + SiO_2 \quad (1)$$

$$CO_2 + MgSiO_3 \leftrightarrow MgCO_3 + SiO_2 \quad (2)$$



:e 1. The long term or geochemical carbon cycle ıer 1991, 1994). Arrows indicate fluxes between voirs. v = volcanism; m = metamorphism; d = diagenesis; .l = burial in sediments. On a multimillion-year time-, the sum of inputs to the surficial reservoir osphere + ocean + biosphere + soils) must be very close to ım of outputs from it. Note that the important process of Ig silicate weathering is not shown separately because it ves the overall transfer of carbon from the surficial voir to the carbonate reservoir; in other words, atmo-ic CO_2 is converted to HCO_3^-, which is subsequently sited as Ca and Mg carbonates in marine sediments. text.)

le 1. *Masses of carbon in various reservoirs*

ion	mass (10^{18} g of C)
ınate in rocks	60 000
ıic C in rocks	15 000
ı $HCO_3^- + CO_3^{-2}$	42
arbon	4
spheric CO_2	0.7
here	0.6

$$O + O_2 \leftrightarrow CO_2 + H_2O \quad (3)$$

ıe first two reactions, which constitute the major rols on atmospheric CO_2 on geological time-scales, sometimes referred to as the Urey reactions (Urey), although the general principles had been enunciated before this (Ebelmen 1845). The formulae represent alcium and magnesium silicates and carbonates, e.g. mite, and do not refer to any specific mineral. The l reaction, going from right-to-left, should not be used with photosynthesis, which is written similarly. ıer it denotes *net* photosynthesis (photosynthesis ıs respiration) as represented by the burial of organic er, CH_2O. Likewise, going from left-to-right, this ion does not represent respiration but rather 'geore-tion', or oxidation occurring only after deep burial or t of the previously sedimented organic matter.

; stated above, the weathering of carbonate rocks has effect, over millions of years, on atmospheric CO_2 use the released carbon is quickly returned to the

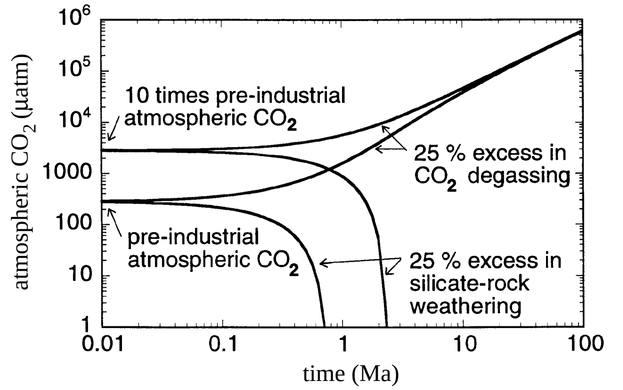


Figure 2. The effect on atmospheric CO_2 content of a 25% imbalance in CO_2 degassing and silicate rock-weathering rates, starting from two initial atmospheric CO_2 contents (280 μatm and 2800 μatm), assuming a balanced organic carbon subcycle. A 25% excess in CO_2 degassing would increase atmospheric CO_2 beyond reasonable Phanerozoic bounds within 10 Ma, and a 25% excess in silicate rock-weathering would deplete nearly all atmospheric CO_2 within a few Ma. This indicates that total CO_2 inputs and outputs to and from the atmosphere have been closely balanced throughout the Phanerozoic. (After Berner & Caldeira 1997.)

carbonate rock reservoir. In contrast, the weathering of silicate rocks removes carbon from the atmosphere–ocean system by fixing it as additional carbonate, (the Urey reactions above going from left-to-right), and the return of this carbon to the atmosphere–ocean–biosphere, via metamorphism, diagenesis, and volcanism (the Urey reactions going from right-to-left) may take tens of millions to hundreds of millions of years. This delay can result in an imbalance in exchanges of CO_2 between the atmosphere and the rock reservoirs.

Exchange imbalances, however, must be very small. There is extremely little CO_2 in the atmosphere compared to that in rocks (table 1), so that over a few million years if inputs and outputs were not closely balanced, the atmosphere would become overwhelmed with CO_2. This is shown in figure 2. Just a 25% sustained imbalance in the Urey reactions results in complete loss of CO_2 or extremely high values (note the logarithmic scale). If atmospheric CO_2 had varied this much over the past 550 million years, the Earth, because of the atmospheric greenhouse effect, would have been too hot or too cold to preserve life. But there is definite evidence for continual life over this period in the form of fossil plants and animals. The question then becomes: 'What has prevented a runaway greenhouse, or its opposite, a runaway icehouse, and what has preserved the necessary close balance between CO_2 input and CO_2 output? A number of studies (e.g. Walker *et al.* 1981; Berner *et al.* 1983; Caldeira 1995; Kump & Arthur 1997) have come to the conclusion that this balance is maintained primarily by a negative feedback response of rock-weathering to climate change. If more CO_2 comes into the atmosphere from increased volcanic activity, the global climate warms (due to the greenhouse effect), and this results in more CO_2 uptake via faster rock-weathering. The faster weathering is due to enhanced rock–water interaction by increased rainfall

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Table 2. *Outline of processes in the GEOCARB II model (Berner 1994)*

weathering of silicates, carbonates and organic matter on the continents

1. Topographic relief as affected by mountain uplift (silicates and organic matter)
2. Global land area (carbonates)
3. Global river runoff and land temperature as affected by continental drift
4. Rise of vascular land plants
5. Rise of angiosperms
6. Enhancement of weathering flux by changes in global temperature due to (a) evolution of the sun; (b) changes in atmospheric CO_2 (greenhouse effect); (c) the effect on rate of mineral dissolution; and (d) the effect on river runoff
7. Enhancement of root activity due to fertilization by atmospheric CO_2

thermal degassing of CO_2 from the subsurface due to volcanism, metamorphism, and diagenesis

1. Changes in global sea-floor spreading rate
2. Transfer of $CaCO_3$ between platforms and the deep sea

burial of carbonates and organic matter in sediments

on the continents, and higher land temperatures accompanying global warming. This accelerated weathering results in a draw-down of CO_2 and a return to equilibrium. The opposite occurs if there is less volcanic activity, resulting in cooling and slower global weathering.

A computer model of the long-term carbon cycle over the Phanerozoic Eon (the past 550 Ma) has been constructed by the author (Berner 1991, 1994), and an outline of major model parameters is shown in table 2. Following table 2, the factors that are considered by the GEOCARB II model include changes in land area, changes in continental runoff and temperature due to changes in continent size and position accompanying continental drift, changes in ruggedness of the continents due to mountain uplift, and the evolution of vascular land plants, each of which affects weathering. In addition, special attention is paid to the role of atmospheric CO_2 as a negative feedback toward the weathering uptake of CO_2. This includes the effects of CO_2 on greenhouse warming and plant productivity, and how warming and productivity affect weathering rate. The evolution of the sun, with its effect on global mean temperature and rainfall (as they affect weathering rate), is especially emphasized (Berner 1994). Changes in the rates of carbonate and organic matter breakdown due to metamorphism, magmatism, and diagenesis are ascribed to changes in (i) the rates of sea-floor subduction and generation (spreading rate), and (ii) the amount of carbonate subjected to thermal decomposition (there being more decomposition when carbonate is present in deep-sea sediments). Finally, burial of carbonate and organic matter is calculated from mass-balance expressions, and data on the carbon isotopic composition of the oceans as recorded in fossils and limestones.

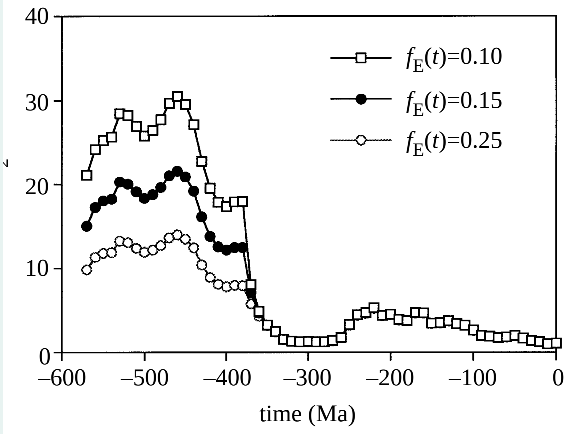
In keeping with the theme of this volume, this paper discusses the use of the GEOCARB model, in combination with field experiments on plants and weathering, to examine the role of plants in the long-term carbon cycle. Following the predictions of Lovelock & Watson (1982) and Lovelock & Whitfield (1982), I address the question of how the rise of vascular plants during the Palaeozoic might have affected the rates of silicate rock-weathering and organic matter burial in sediments, and how these could have brought about changes in the level of atmospheric CO_2 and, consequently, changes in climate. As I will show, the early evolution of vascular land plants had one of the most dramatic effects on CO_2 of any process occurring within the past 550 Ma.

2. LAND PLANTS AND ATMOSPHERIC CO_2

(a) *Plants and weathering*

In performing the GEOCARB modelling the value calculated for the palaeolevel of atmospheric CO_2 was found to be very sensitive to the quantitative role of plants in accelerating the rate of weathering. This is especially true of the Devonian, during which time vascular plants spread to upland areas where, because of deep rooting and good drainage, they could affect the chemical weathering of silicate rocks (Algeo *et al.* 1995; Retallack 1997; Driese & Mora 1997). To represent the effect of plants on weathering rate I have created the dimensionless plant-weathering parameter $f_E(t)$, which is defined as the rate of weathering at some time in the past to that today, where all factors affecting weathering other than biology (topography, atmospheric CO_2 level, etc.) are held constant. Low values of $f_E(t)$ prior to the rise of upland vascular land plants indicate large effects of plants on weathering and on the level of atmospheric CO_2. In other words, an increase in $f_E(t)$ accompanying the rise of land plants, indicates increased consumption of CO_2 due to accelerated weathering. An idea of the high sensitivity of palaeo-CO_2 to the value of $f_E(t)$ prior to the rise of upland vascular plants (before 400 Ma) is shown in figure 3. Here lower values of $f_E(t)$ are accompanied by dramatically higher levels of CO_2 and larger decreases in CO_2 during the Devonian.

It should be kept in mind that the Devonian drop in CO_2 was not due simply to an increase in the *rate* of plant-enhanced weathering. As is often misunderstood, the actual rate of CO_2 removal from the atmosphere by weathering, on a multimillion-year time-scale, is not an independent parameter and must be essentially equal to the supply of CO_2 from degassing (Berner & Caldeira 1997). Thus, an acceleration of weathering, in this instance by the rise of vascular land plants, must have been matched by some decelerating process, since there is no evidence of any equivalently large changes in degassing rate at this time. (Mathematically, this means that a rise in $f_E(t)$ must have been countered by a lowering of some other parameter affecting weathering rate.) The decelerating process was the drop in atmospheric CO_2. Lower CO_2, via the atmospheric greenhouse effect, brought about lower global temperatures and less river runoff, which had a decelerating effect on global weathering rates, which in turn helped to balance the accelerating effect of the plants. In this way plants brought about an increase in the *weatherability* of rocks, but not necessarily an overall increase in weathering *rate*. (Of course, there must have been a continuing series of transient increases



re 3. Plot of atmospheric CO_2 versus time calculated by GEOCARB II model. RCO_2 represents the ratio of mass of on in the atmosphere at some past time to that at present. rent curves represent results for different values of $f_E(t)$ ned prior to the rise of upland vascular land plants in the nian. A lower $f_E(t)$ value represents a greater effect of s on weathering.

Table 3. *Comparison of fluxes of dissolved ions in drainage waters (corrected for precipitation input), plus storage in vegetation and solid weathering products where available, for forested and minimally vegetated portions of different areas*

('Vegetated' refers to forested or grassland and 'bare' refers to adjacent land minimally vegetated with primitive organisms (mosses, lichens, etc.). All ratios are for fluxes, except for the Swiss Alps where only concentrations in stream waters are listed.)

area	ion[a]	ratio of ions (vegetated/bare)
southern Swiss Alps* Drever & Zobrist (1992)	Ca^{++}	8
Western Iceland** (Moulton & Berner: new data)	Ca^{++} Mg^{++}	4, 5, 6 6, 8, 10
Colorado Rocky Mountains (Arthur & Fahey 1993)	Ca + Mg + Na + K	4
Hubbard Brook, New Hampshire** (Bormann *et al.* 1997)	Ca^{++}	10

*Corrected for temperature difference between high and low elevations.

**Data include storage in trees (and in solid weathering products for Hubbard Brook) in addition to loss in drainage.

eathering rate which were matched soon thereafter by eases in rate due to falling CO_2.)

here is no simple way to calculate $f_E(t)$ on an *a priori* . However, estimates can be made by studying the ts of plants on weathering in the modern world. ular plants appear to have a major effect on the iical weathering of rocks. This results from the alter- ı by plants of both the chemistry and the odynamics of the soil. Plant rootlets (plus symbiotic oflora) have a very high surface area, and across this they secrete organic acids and chelates, which attack ary minerals, in order to gain nutrients. In addition, ts produce organic litter which decomposes to H_2CO_3 organic acids, providing additional acid for mineral lution. Hydrodynamically, plants anchor clay-rich against erosion, thereby allowing retention of water ıe soil and continued contact of primary minerals water between rainfall events. Furthermore, on a onal basis, vascular plants recirculate water via tran- tion, leading to enhanced rainfall and thereby eased flushing of rocks.

accelerating weathering, plants may also provide a tive feedback mechanism against atmospheric CO_2 ation (Volk 1987). Higher CO_2 levels in the past ıt have led to faster plant growth, which led to ter weathering by roots and associated microflora to in nutrients. However, this would have applied only e plant growth was not limited by water, nutrients, ght; thus, the global significance of a possible plant– weathering feedback needs further study. (A preli- ary quantitative treatment of this feedback ıanism is included in GEOCARB II modelling.)

ıe question arises as to how weathering took place e the land surface was populated by vascular plants ner 1992). There is some evidence that the early land ce was covered by a carpet of primitive organisms as lichens and algae (e.g. Wright 1985). Did these nisms also accelerate chemical weathering? Some studies have emphasized that they were very important (e.g. Schwartzman & Volk 1989). However, a simple argument militates against lichens and similar organisms being as effective as higher plants in rock-weathering. The interfacial area between plant and soil of a mat of lichens is simply equal to the area of the land covered by the lichens. In contrast, the interfacial area between soil and the large mass of rootlets associated with higher plants is very much larger for the same area of land. Moreover, higher plants grow much faster than lichens (e.g. Algeo & Scheckler, this volume) and, therefore, must extract nutrients from rocks (via weathering) much faster.

Some recent work has given an idea of the quantitative effect of vascular plants on the rate of chemical weathering of silicate rocks. These studies, the results of which are summarized in table 3, have attempted to hold constant all factors affecting weathering (e.g. slope, microclimate, lithology, aspect) other than variations in vegetation. Because this is not easily done, there are only a few such studies. Drever & Zobrist (1992) found that the riverine flux of dissolved species from a small granitic terrain in the southern Swiss Alps is a strong function of elevation. Correlated with elevation was a change from deciduous forest at the lowest elevation (200 m) through coniferous forests at higher elevations to alpine meadow and bare rocks above the tree line (2000 m). The stream flux of Ca^{++} plus Mg^{++} at the highest elevation was about 25 times lower than that at 200 m in the deciduous forest. If one subtracts the effect of temperature due to the differences in elevation, which is about a factor of 3, then the

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residual effect is a factor of about 8 between weathering by deciduous trees and that by pure rock–water interaction or by mosses and lichens.

A study of the effect of plants on weathering rate has been underway for the past 14 years at the Hubbard Brook Experimental Forest Station in New Hampshire, USA (Bormann *et al.* 1987, 1998; Cochran & Berner 1993). Three 60 m^2 adjacent plots were set up in 1983 with one plot planted with pine seedlings, one with grasses, and one left barren. The material underlying all three plots is feldspar-rich glacial sand. Each 1.5 m deep plot was lined at the bottom with an impermeable base so as to force the water draining through each soil to flow to an exit pipe where it could be sampled. Over the past 14 years the trees have grown to a height of about 5 m, and the barren plot has been occupied sporadically by mosses, lichens, etc., but by no higher plants. In 1988 and 1989, trees were sampled for cation analysis as were various solid weathering products (clays, iron oxides, and organic matter). In addition, water chemical analyses were conducted on drainage water and rainwater over the 1983–1989 period. Results for the first five-to-six years indicate that the combination of cation uptake by vegetation, loss in drainage and addition to solid weathering products, caused an increase in the weathering release rate of Ca by a factor of about 10 for the tree-covered plot relative to the barren plot (table 3). In addition, our own (unpublished) work at Yale has found that the concentration of dissolved Na draining from the tree-populated plot was about 1.5–3.5 times higher than in water draining from the fallow plot over the same time period. Dissolved Na is a good indicator of the breakdown of silicate minerals due to dissolution because it is not taken up by trees to any extent and is less likely to be trapped in solid weathering products. Work at Hubbard Brook is continuing, including weekly chemical analyses of drainage waters over the past four years, and a second tree sampling is planned for late 1998.

Preliminary results are available for a study of the effects of plants on weathering in Iceland (Moulton & Berner 1996). Iceland has an advantage over Hubbard Brook, because of the absence in Iceland of anthropogenically produced acid rain. (At Hubbard Brook, rock dissolution under all plots may be accelerated by excess rain acidity.) In the Skorradalur valley of western Iceland we have been determining the water chemistry of streams draining the same basaltic bedrock underlying adjacent small areas that are populated by evergreens, birches, and grasses, and others which are essentially barren (sporadic moss cover). In addition, the Icelandic Forest Sevice has determined the cationic composition of the evergreen and birch trees. From the rate of flow of the streams and the rate of growth of the trees, one can calculate weathering rates for this area as a function of vegetation. The results shown in table 3 indicate an acceleration of the weathering release of Ca^{++} and Mg^{++} for vegetated ground versus barren ground, of a factor of about 5–10.

These results, along with those from a study by Arthur & Fahey (1993) in the Rocky Mountains of Colorado (table 3), indicate that the effect of higher plants on weathering is probably somewhere in the range of a fourfold-to-tenfold enhancement, and the preferred value of $f_E(t)$, prior

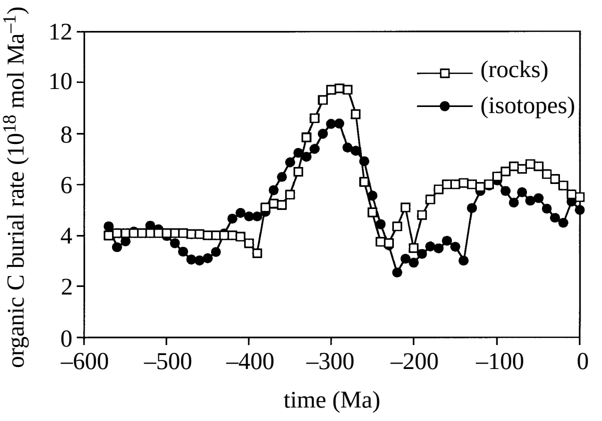


Figure 4. Rate of burial of organic carbon calculated from $^{13}C/^{12}C$ marine carbonate isotope data and the GEOCARB II model (Berner 1994) compared to burial rate derived independently from the abundance of organic carbon in different types of sedimentary rocks (Berner & Canfield 1989).

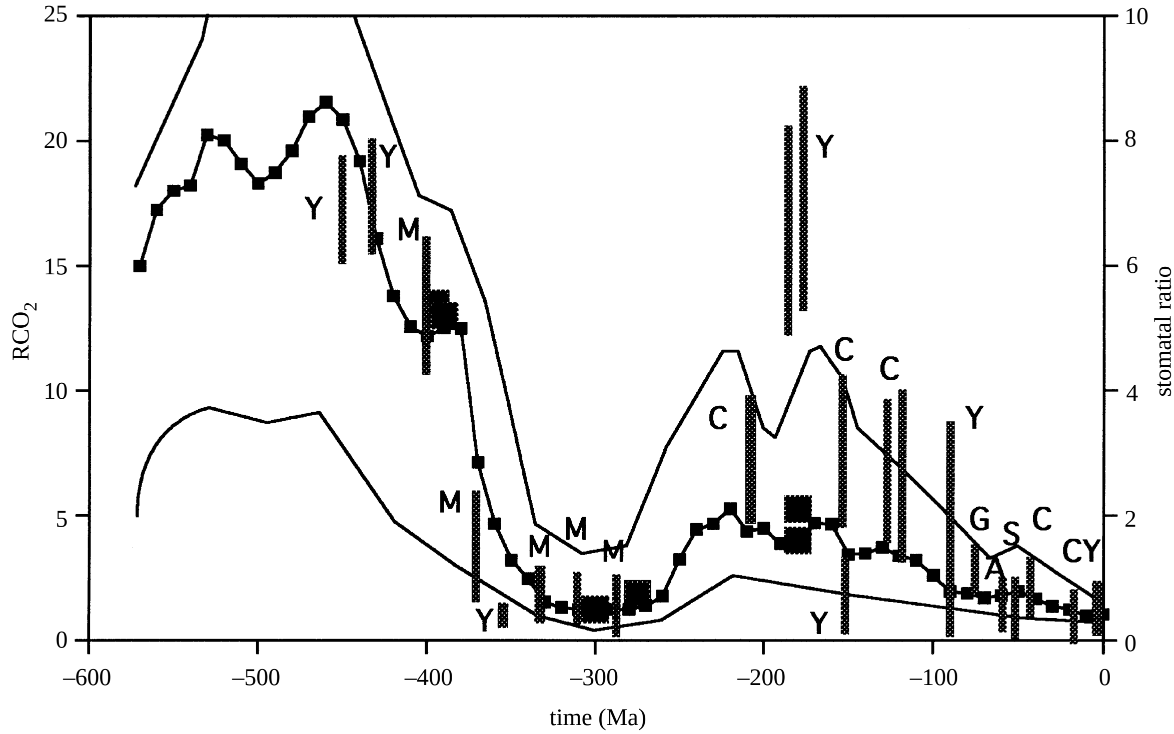
to the rise of vascular plants (before 350 Ma ago) is probably around 0.15 (sevenfold effect). This is the value that is used as a standard in GEOCARB modelling. However, much more work is needed before a more accurate number can be obtained. Also, it should be kept in mind that the larger scale or regional effect of plants on rainfall is not covered by studies of this sort.

(b) *Plants and the burial of organic carbon*

The rise of vascular land plants during the early Palaeozoic had another effect on atmospheric CO_2. It created a new source of microbially resistant organic matter, e.g. lignin, which could be buried in sediments. The burial of organic matter in sediments is another process for removing CO_2 from the atmosphere, as is shown by reaction (3) given earlier. Enhanced organic burial resulted from the rise of vascular plants, as witnessed by the vast coal swamps of the Carboniferous and early Permian periods (330–260 Ma ago) that followed closely on the heels of plant colonization. The rate of burial of organic carbon has been calculated by the GEOCARB model based on the carbon isotopic composition of limestones buried at that time (for the method of calculation see Garrels & Lerman (1984) or Berner (1991, 1994)), and results agree with independent estimates of the abundance of organic carbon in sediments of this age (Berner & Canfield 1989). This is shown in figure 4. Note that there is a large peak in inorganic carbon burial rate during the Permian and Carboniferous periods, due mainly to the presence of vast coal basins at this time. As for its effect on atmospheric CO_2, this increased carbon burial brought about a lowering of CO_2 concentration, but not as much as that caused by the increased silicate weathering that accompanied the Devonian rise of vascular plants (Berner 1994).

(c) *Climatological implications*

Figure 5 shows values of palaeo-CO_2 over Phanerozoic time based on best estimates of the various parameters that go into the GEOCARB II model (Berner 1994). The upper and lower lines represent rough error estimates based on



:e 5. Atmospheric CO_2 over Phanerozoic time. The central curve represents best estimates for various parameters according : GEOCARB II model (Berner 1994). Upper and lower lines represent crude error estimates based on modelling sensitivity /sis. Light vertical bars labelled with letters represent estimates of CO_2 based on the carbon isotopic analysis of palaeosols. ller dark squares represent results from the determination of stomatal index (McElwain & Chaloner 1995, 1996). RCO_2 is the of atmospheric CO_2 at time t divided by that 'at present' (= 300 ppmv). (Modified after Berner (1997).)

tivity analysis. The curve is based on a value for $f_E(t)$ 15 for times prior to the rise of upland plants in the onian, which is in keeping with the results of present- ield studies of weathering, as discussed above (see also : 3). Independent estimates of CO_2 based on measure- :s of the carbon isotopic composition of palaeosols and ·minations of stomatal index are also shown in the e, and the results are in generally good agreement the theoretical calculations. In other words, in all es higher values of CO_2 are found for the early eozoic (550–400 Ma ago) and during the Mesozoic –100 Ma ago) and lower values for the Permo-Carbo- ous (330–270 Ma ago) and the late Cenozoic (30– ı ago).

nsitivity analysis using the GEOCARB model ner 1994) shows that two factors were dominant in ting CO_2 during the Palaeozoic Era. One was the of vascular land plants. The large CO_2 drop extending the early Devonian to the early Permian (380– Ma before present (BP)) was due primarily to the and spread of vascular plants on the continents. ever, the very high values for the early Palaeozoic ılso attributable to the evolution of the sun. Sensitivity creasing solar radiation is shown in figure 6, and one see that calculated early Palaeozoic values of CO_2 are iderably lower when solar radiation is held constant. overall downward trend of the CO_2 curve for the e Phanerozoic represents the last portion of a much :r drop in CO_2 over billions of years due to the evolu- of the sun. In essence, over geological time, increasing radiation has been matched by decreasing CO_2, which, because of a resulting decrease in the atmospheric greenhouse effect, has counterbalanced solar heating and thereby provided an equitable climate for life (Caldeira & Kasting 1992).

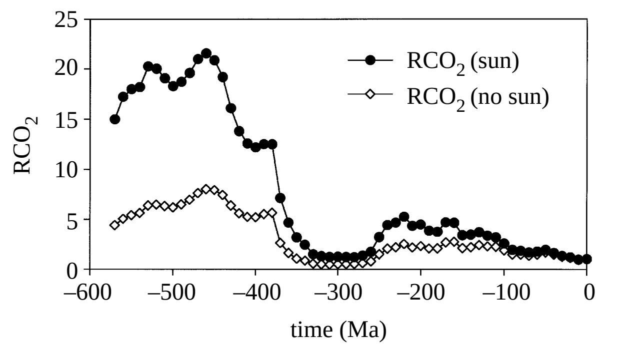


Figure 6. RCO_2 for constant solar flux over time (no sun) compared to that for the standard situation of increasing solar radiation with time (sun). RCO_2 = mass of atmospheric CO_2 at time t divided by that 'at present' (= 300 ppmv). (After Berner 1994.)

The atmospheric CO_2 results of figure 5 correlate with what is known about ancient climates (see Crowley & North 1991). The two most extensive and long-lived glaciations over the past 550 Ma occurred during the same times as the minima in CO_2 shown in the figure. Also, climates decidedly warmer than today's occurred during the Mesozoic and early Palaeozoic, when CO_2 is calculated to have been high. (The short glaciation that occurred at the end of the Ordovician period, about 440 Ma BP, during a time of apparently high CO_2, can be explained in terms of continental drift and lower solar radiation (Crowley & Baum 1995) combined with a short-term drop in CO_2 (Gibbs *et al.* 1997).) Thus, the results of long-term carbon cycle modelling support the hypothesis of the CO_2 atmospheric greenhouse effect as a principal control of climate over geological time.

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REFERENCES

Algeo, T. J., Berner, R. A., Maynard, J. B. & Scheckler, S. E. 1995 Late Devonian oceanic anoxic events and biotic crises: rooted in the evolution of vascular plants? *GSA Today* **5**, 45, 64–66.

Arthur, M. A. & Fahey, T. J. 1993 Controls on soil solution chemistry in a subalpine forest in North-Central Colorado. *Soil Sci. Soc. Am. J.* **57**, 1123–1130.

Berner, R. A. 1991 A model for atmospheric CO_2 over Phanerozoic time. *Am. J. Sci.* **291**, 339–376.

Berner, R. A. 1992 Weathering, plants, and the long-term carbon cycle. *Geochim. Cosmochim. Acta* **56**, 3225–3231.

Berner, R. A. 1994 GEOCARB II: a revised model of atmospheric CO_2 over Phanerozoic time. *Am. J. Sci.* **294**, 56–91.

Berner, R. A. 1997 The rise of plants and their effect on weathering and atmospheric CO_2. *Science* **276**, 544–546.

Berner, R. A. & Caldeira, K. 1997 The need for mass balance and feedback in the geochemical carbon cycle. *Geology* **25**, 955–956.

Berner, R. A. & Canfield, D. E. 1989 A new model of atmospheric oxygen over Phanerozoic time. *Am. J. Sci.* **289**, 333–361.

Berner, R. A. & Lasaga A. C. 1989 Modeling the geochemical carbon cycle. *Scient. Am.* **260**, 74–81.

Berner, R. A, Lasaga, A. C. & Garrels, R. M. 1983 The carbonate–silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* **283**, 641–683.

Bormann, F. H., Bowden, W. B., Pierce, R. S., Hamburg, S. P., Voigt, G. K., Ingersoll, R. C. & Likens, G. E. 1987 The Hubbard Brook sandbox experiment. In *Restoration ecology* (ed. W. R. Jordan, M. E. Gilpin & J. D. Aber), pp. 251–256. Cambridge University Press.

Bormann, B. T., Wang, D., Bormann, F. H., Benoit, G., April, R. & Snyder, R. 1998 Rapid plant induced weathering and soil development in an experimental pine system. *Biogeochemistry.* (Submitted.)

Caldeira, K. 1995 Long-term contol of atmospheric carbon dioxide: low-temperature seafloor alteration or terrestrial silicate-rock weathering. *Am. J. Sci.* **295**, 1077–1114.

Caldeira, K. & Kasting, J. F. 1992 The lifespan of the biosphere revisited. *Nature* **360**, 721–723.

Cochran, M. F. & Berner, R. A. 1993 Enhancement of silicate weathering rates by vascular land plants: quantifying the effect. *Chemical Geol.* **107**, 213–215.

Crowley, T. J. & Baum, S. K. 1995 Reconciling late Ordovician (440 Ma) glaciation with very high (14×) CO_2 levels. *J. Geophys. Res.* **100**, 1093–1101.

Crowley, T. J. & North, G. R. 1991 *Paleoclimatology.* New York: Oxford University Press.

Drever, J. I. & Zobrist, J. 1992 Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps. *Geochim. Cosmochim. Acta* **56**, 3209–3216.

Driese, S. G. & Mora, C. I. 1997 Evolution and diversification of Siluro-Devonian root traces: influence on paleosol morphology and estimates of paleoatmospheric CO_2 level. In *Early land plants and their environments* (ed. P. G. Gensel & D. Edwards). (In the press.)

Ebelmen, J. J. 1845 Sur les produits de la décomposition des espèces minérales de la famille des silicates. *Ann. des Mines* **7**, 3–66.

Garrels R. M. & Lerman, A. 1984 Coupling of the sedimentary sulfur and carbon cycles—an improved model. *Am. J. Sci.* **284**, 989–1007.

Gibbs, M. T. , Barron, E. J. & Kump, L. R. 1997 An atmospheric PCO_2 threshold for glaciation in the late Ordovician. *Geology* **25**, 447–450.

Holland, H. D. 1978 *The chemistry of the atmosphere and oceans.* New York: Wiley Interscience.

Kump, L. R. & Arthur, M. A. 1997 Global chemical erosion during the Cenozoic: weatherability balances the budget. In *Tectonic uplift and climate change* (ed. W. F. Ruddiman). New York: Plenum Press. (In the press.)

Lovelock, J. E. & Watson, A. 1982 The regulation of carbon dioxide and climate. *Planet. Space Sci.* **30**, 795–802.

Lovelock, J. E. & Whitfield, M. 1982 Lifespan of the biosphere. *Nature* **296**, 561–563.

McElwain, J. C. & Chaloner, W. G. 1995 Stomatal density and index of fossil plants track atmospheric carbon dioxide in the Paleozoic. *Ann. Botany* **76**, 389–395.

McElwain, J. C. & Chaloner, W. G. 1996 The fossil cuticle as a skeletal record of environmental change. *Palaios* **11**, 376–388.

Moulton, K. L. & Berner, R. A. 1996 The effect of higher land plants on the weathering of calcium and magnesium silicates in Iceland. *1996 Geol. Soc. Am. Ann. Meet.*, **339** (abstract).

Retallack, G. J. 1997 Early forest soils and their role in Devonian global change. *Science* **278**, 583–585.

Schwartzman, D. W. & Volk, T. 1989 Biotic enhancement of weathering and the habitability of earth. *Nature* **340**, 457–460.

Urey, H. C. 1952 *The planets: their origin and development.* New Haven, CT: Yale University Press.

Volk, T. 1987 Feedbacks between weathering and atmospheric CO_2 over the last 100 million years. *Am. J. Sci.* **287**, 763–779.

Walker, J. C. G., Hays, P. B. & Kasting, J. F. 1981 A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *J. Geophys. Res.* **86**, 9776–9782.

Wright, V. P. 1985 The precursor environment for vascular plant colonization. *Phil. Trans. R. Soc. Lond.* B **309**, 143–145.

Discussion

T. Lenton (*School of Environmental Sciences, University of East Anglia, UK*). Would you expect land plants to also be accelerating the rate of phosphorus release from weathering? In doing so, would they (ultimately) increase the amount of new production in the ocean (and the total earth system)? This might have added to the draw-down of carbon dioxide as plants colonized the land and evolved deeper and more extensive root systems.

R. A. Berner. The effect of plant-accelerated weathering on the release of phosphate and enhanced marine production is discussed by Algeo & Scheckler (this volume).

M. Tester (*Department of Plant Sciences, University of Cambridge, UK*). In your talk, you compared erosion ath bare rock with that beneath vegetation. Do rent major plant taxa (e.g. ferns, gymnosperms, osperms) cause different rates of erosion?

. Berner. The effects of different flora on weathering has not been systematically studied to date. There has a suggestion that angiosperms attack rocks faster gymnosperms, but this needs to be investigated on a matic basis. Our own work at Hubbard Brook ests greater weathering of granitic sand by pine trees ompared with grasses.

. Beerling (*Department of Animal and Plant Sciences, ersity of Sheffield, UK*). I wonder if I could ask Professor er to play Devil's advocate regarding the construction s model, and to comment on which palaeorecord used e model introduces the greatest uncertainties in his ictions of Phanerozoic CO_2 reconstruction?

R. A. Berner. There are several weak points in the modelling. The use of strontium isotopes to express the effects of mountain uplift on weathering rate has been criticized recently by a number of studies. The rate laws for weathering before the advent of vascular land plants ignore any acceleration of weathering by a possible primitive terrestrial microflora. Variations in global CO_2 degassing with time before 150 Ma BP are based on rates of sea-floor spreading deduced indirectly from palaeo-sea level estimates. Estimates of the variation in the amount of carbonate being thermally decomposed, leading to degassing, are crude. One can list others. However, extreme, but physically possible, variation of the many parameters going into the modelling, as a part of sensitivity analysis, shows that *the general pattern of high and low CO_2 values versus time* does not change. (The error envelope of results shown in figure 5 represents the results of varying these parameters.)

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES