Chapter 13

CHEMICAL WEATHERING AND ITS EFFECT ON ATMOSPHERIC CO_2 AND CLIMATE

Robert A. Berner

Department of Geology and Geophysics
Yale University
New Haven, CT 06520 U.S.A.

INTRODUCTION

It is well established that climate exerts an important influence on chemical weathering, but this statement can be inverted; it is also true that chemical weathering exerts an important influence on climate. Weathering affects climate by way of the atmospheric greenhouse effect. During the weathering of silicate and carbonate minerals atmospheric CO_2 is taken up and converted to dissolved HCO_3^- in natural waters. The HCO_3^-, after delivery to the oceans by rivers, can be stored there or removed from the oceans in the form of carbonate minerals or organic matter in sediments. Either way there is a net loss of atmospheric CO_2. Since CO_2 is a greenhouse gas, any change in its concentration, due to changes in its rate of uptake by weathering, affects its ability to absorb infrared radiation and warm the earth's surface. [For a summary discussion of CO_2 and the greenhouse effect consult IPCC, 1990.] It is the purpose of the present paper to document how CO_2 is converted to HCO_3^- by weathering, to show how various factors affect the rate of this process, and to show how atmospheric CO_2 levels could have changed during the geologic past as a result of changes in the rate of weathering.

Let us trace a carbon atom as it makes its way from the atmosphere to the oceans via the land (see Fig. 1). First of all the carbon is taken up via photosynthesis by terrestrial vegetation. The fixed carbon is then transferred to the soil as organic acids and CO_2 by roots and associated microflora, and by the decay of dead roots and litter (leaves, branches, dead trees, etc.). The carbon-containing acids attack silicate and carbonate minerals resulting in the formation of bicarbonate and organic anions in soil solution, with the organic anions soon thereafter oxidized to bicarbonate. These steps can be combined in terms of the overall weathering reactions:

For carbonates:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{++} + 2\,HCO_3^- \tag{1}$$

$$2\,CO_2 + 2\,H_2O + CaMg(CO_3)_2 \rightarrow Ca^{++} + Mg^{++} + 4\,HCO_3^- \tag{2}$$

For silicates (generalized and simplified as wollastonite and enstatite):

$$2\,CO_2 + 3\,H_2O + CaSiO_3 \rightarrow Ca^{++} + 2\,HCO_3^- + H_4SiO_4 \tag{3}$$

$$2\,CO_2 + 3\,H_2O + MgSiO_3 \rightarrow Mg^{++} + 2\,HCO_3^- + H_4SiO_4 \tag{4}$$

These reactions are accompanied by a separate weathering reaction involving the release of CO_2 via the oxidation of organic matter (kerogen, coal, oil) contained in old sedimentary rocks. The overall reaction, with organic matter simplified as CH_2O, can be represented as:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{5}$$

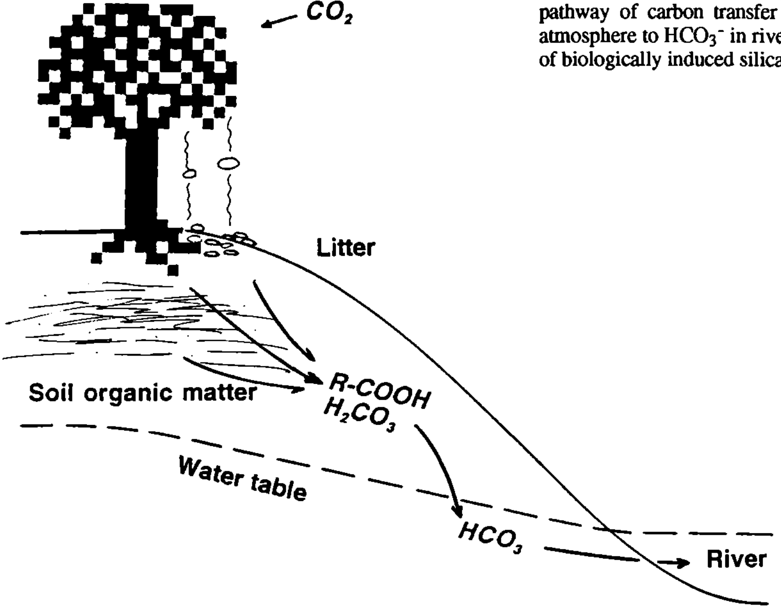


Figure 1. Generalized representation of the pathway of carbon transfer from CO_2 in the atmosphere to HCO_3^- in river water as a result of biologically induced silicate weathering.

This reaction shows that weathering can be a source, as well as a sink, for atmospheric CO_2. [An extreme example of Reaction (5) is the burning of fossil fuels which represents greatly accelerated weathering by humans.] Unfortunately the natural weathering of ancient organic matter is poorly understood (e.g. Hedges, 1993) and will not be discussed here. This is not too problematic because mass balance calculations (Berner, 1991) indicate that the release of CO_2 via kerogen oxidation is quantitatively less important than its uptake via silicate and carbonate weathering.

The HCO_3^- formed by silicate and carbonate weathering is transported from soil and ground waters to rivers and by rivers to the sea. Over time scales of 10^2 to 10^5 years this dissolved carbon can be stored in seawater, but over longer, multimillion year periods carbon storage cannot continue because seawater can hold just so much dissolved HCO_3^- (and accompanying CO_3^{-2}) before inorganic $CaCO_3$ precipitation occurs. [The same can be said about carbon storage in biota over millions of years since the earth can sustain just so much living matter.] Thus, oceanic storage of CO_2 in, and release from, the oceans is an important aspect of the carbon cycle on the hundred-to-thousand year time scale (e.g. Opdyke and Walker, 1992; Sarmiento, 1993) but not over many millions of years when oceanic inputs must be balanced by outputs (Berner, 1991). Here we distinguish the short term (10^3 to 10^5 year) carbon cycle where carbon storage and release involves transfers between the atmosphere, oceans, and the biosphere, from the much longer multimillion year *geochemical* carbon cycle where storage and release is only to and from rocks.

Since on a multimillion year time scale carbon cannot be stored in the oceans, we need to consider the means by which it is removed from seawater. Some carbon may be removed by CO_2 release during the formation of new silicates (reverse weathering—see Mackenzie and Garrels, 1966), but by far most is removed by the burial of $CaCO_3$ as skeletal remains and CH_2O as organic matter in bottom sediments (Berner and Berner, 1987). Extra Ca^{++}, beyond that contributed by rivers, is added to the oceans by exchange for Mg^{++} during basalt-seawater reaction (e.g. Holland, 1978) which enables the removal, as $CaCO_3$, of the additional HCO_3^- derived from the weathering of Mg silicates (Reaction 4). Representative reactions are:

For carbonate burial :

$$Ca^{++} + 2\,HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (6)$$

For organic matter burial:

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad (7)$$

Note that from Reaction (6) one mole of CO_2 is liberated for each mole of $CaCO_3$ buried and that Reaction (6) is the reverse of Reaction (1), which represents $CaCO_3$ weathering. As a result, if bicarbonate is not stored in the ocean, there is no net effect on atmospheric CO_2 of carbonate weathering combined with carbonate burial. This means that carbonate weathering is not an important factor in the control of atmospheric CO_2 on the multimillion year time scale. It is only on the thousand year time scale that HCO_3^- storage in the oceans can result from an excess of carbonate weathering over burial. Since we will only be discussing the long term geochemical carbon cycle here, we will ignore carbonate weathering as a factor affecting atmospheric CO_2 and climate.

The above reactions can be summarized in terms of succinct overall reactions, first elucidated by Högbom (1894) (see Berner, 1995) and later expressed explicitly by Urey (1952):

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2 \qquad (8)$$

$$CO_2 + MgSiO_3 \rightarrow MgCO_3 + SiO_2 \qquad (9)$$

Note that here, in contrast to the weathering of Ca- and Mg-carbonates, the weathering of Ca- and Mg-silicates results in the net removal of CO_2 from the atmosphere. It is the weathering of silicates, and not carbonates, that exerts a major long term control on atmospheric CO_2. Also, only the weathering of Ca- and Mg-silicates is important. This is because Na and K added to the oceans by silicate weathering on the continents are not removed as carbonates, by reactions analogous to (8) and (9) above, because of the great solubility of Na- and K-carbonate minerals. Most likely Na and K added by silicate weathering are removed by silicate formation (reverse weathering or basalt-seawater reaction) in the oceans with the return of CO_2, originally consumed by continental weathering, to the atmosphere.

WEATHERING AS A FEEDBACK CONTROL ON CO_2

The carbon dioxide level of the atmosphere on the million year time scale is affected by processes other than weathering. Both carbonates and organic matter are deeply buried and thermally decomposed at depth by diagenesis, metamorphism, and magmatism giving rise to degassing of CO_2 to the atmosphere. Additional CO_2 is supplied by the volcanic release of carbon stored for long periods in the mantle. Thus, atmospheric CO_2 is affected by changes in the rate of global degassing as well as by changes in the rate of weathering of Ca and Mg silicates. It is the balance between degassing and weathering that controls the level of CO_2 over geologic time (e.g. Walker et al., 1981; Berner et al., 1983). Note that the Högbom-Urey Reactions (8) and (9) above, can also be read from right-to-left, in which case they reflect carbonate decomposition and CO_2 degassing.

There is a need for a negative feedback control on atmospheric CO_2 level. If degassing became excessive it is possible that in the past there could have been a runaway greenhouse, resulting in very high temperatures as exist today on the planet Venus. However, such a situation (or its opposite a runaway icehouse due to a severe drop in degassing) has not existed on Earth for at least the past 3 billion years as attested to by a continuous record over this period of both life and an ocean consisting of liquid water. To prevent the development of a runaway greenhouse or icehouse a negative feedback mechanism must have existed. Furthermore, it is believed that the level of solar radiation 3 billion years ago was 20 to 30% less than that today and that it has been increasing linearly with time since then (Caldeira and Kasting, 1992). Calculations indicate that with such a reduced solar input, at the present level of atmospheric CO_2, the oceans would freeze over and there would be a *global* icehouse condition for much of geologic time (Kasting and Ackerman, 1986). Again this has not happened and there must have been a control mechanism that allowed for an enhanced greenhouse effect due (presumably) to higher CO_2 levels to compensate for lower solar input.

Chemical weathering is an ideal candidate for the needed negative feedback control mechanism. As CO_2 increases there is global warming due to the atmospheric greenhouse effect, but the rate of CO_2 uptake by silicate weathering also increases with increasing temperature, and this increased weathering rate provides negative feedback. Conversely, as CO_2 decreases, there is global cooling and the rate of CO_2 uptake by weathering decreases. Similar reasoning can be applied to solar radiation. As radiation increases with time, temperature and weathering rate increase so that CO_2 drops bringing about a counter-balancing effect. This temperature/weathering control mechanism first elucidated by Walker et al. (1981) is now accepted by most workers as the principal feedback control on global climate on the million year time scale.

Incorporation of the temperature feedback mechanism into global carbon cycle modeling (e.g. Berner, 1994) is presently done based on an empirical expression fitted to the results of general circulation models (GCMs) of the relation between global mean temperature and both CO_2 and solar radiation (e.g. Marshall et al., 1994; Manabe and Bryan, 1985).The expression employed (Berner, 1994) is:

$$T(t) - T(o) = \Gamma \, ln \, RCO_2 - W_S \, (t/570) \qquad (10)$$

where:
T = global mean surface temperature
RCO_2 = ratio of atmospheric CO_2 mass at time t to that at present
t = time before present in millions of years
o = present
Γ = empirical CO_2 greenhouse parameter
W_S = empirical solar radiation parameter

Use of this expression to calculate the feedback effect of temperature on weathering is discussed below under the subject of climate and weathering.

There are other possible feedback controls. Experiments indicate that plant growth, under conditions of abundant nutrients, water and light, accelerates with higher levels of CO_2 (for a summary consult Bazzaz, 1990). If enhanced growth involves enhanced silicate weathering in order to gain plant nutrients, then higher CO_2 could bring about accelerated weathering via a purely biological mechanism in addition to the temperature mechansim discussed above. This biological feedback mechanism was introduced by Volk (1989) and has been incorporated into the GEOCARB models (Berner, 1991; 1994). The GEOCARB formulation is:

$$f_B(CO_2)_{(plants)} = [\,(\Pi CO_2)_t/(\Pi CO_2)_o\,]^{0.4} \qquad (11)$$

$$\Pi(CO_2)_t/\Pi(CO_2)_o = 2\,RCO_2/(1 + RCO_2) \qquad (12)$$

where: $f_B(CO_2)$ = dimensionless feedback factor which is multiplied times the present weathering flux to obtain weathering fluxes for times in the past when RCO_2 was different from one. The subscript (plants) refers to the effect of plants alone which is multiplied by the temperature effect on weathering $f_B(CO_2)_{(temp)}$ to give the complete expression for $f_B(CO_2)$ (see below). $\Pi(CO_2)$ = land plant productivity

The expression for productivity (12) uses a standard Monod formulation and the exponent 0.4 is used to express the fact that not all plants respond to changes in atmospheric CO_2 due to limitation of growth by nutrients, water, or light.

Other feedbacks have been suggested, but they are less tenable. One is decreased CO_2 removal via less marine organic matter burial to accompany increased CO_2 removal via accelerated weathering due to mountain uplift (Raymo and Ruddiman, 1992), but there is no known reason why decreased organic burial should result from increased weathering. If anything, increased weathering should deliver more nutrients, such as phosphorus, to the oceans which should bring about increased biological production and, therefore, *increased* organic matter burial. Both Raymo and Ruddiman (1992) and Edmond (1993) have suggested that increased physical weathering accompanying colder climates should lead to increased CO_2 uptake via chemical weathering. Although this may help to trigger glaciations, this cannot persist for long because it constitutes positive feedback which would ultimately lead to a runaway icehouse. Others (Staudigel et al., 1989; Francois and Walker, 1992) have suggested submarine basalt weathering as a major feedback control on CO_2. However, there are both theoretical considerations (Caldeira, 1995) and experimental evidence (P. Brady, pers. comm.) for little or no CO_2 dependence of the low temperature reaction of basalt with CO_2 in seawater. Further, the field evidence for global CO_2 uptake via basalt weathering itself is limited to just two drill cores in buried Cretaceous seafloor rocks (Staudigel et al., 1989; Spivack and Staudigel, 1994).

FACTORS AFFECTING WEATHERING OVER GEOLOGIC TIME

In this section brief discussions of the major factors that affect weathering are presented, with emphasis on factors that are global in scope. They are: continental land area and lithology of exposed rocks, mountain uplift, global climate, and land vegetation. Each subject is discussed here in terms of how these factors may have varied over geologic time as incorporated into the Phanerozoic carbon cycle model (GEOCARB II) of the author (Berner, 1994). Because it is a subject of current active research by the author, special emphasis also will be on the role of land vegetation.

Continental land area and lithology

It has been amply demonstrated that over Phanerozoic time (past 600 million years) global sea level has risen and fallen on the scale of a few hundred meters giving rise to considerable variation in the land area of the continents. At first sight it would seem that the rate of uptake of CO_2 via silicate weathering might have varied over the same period in direct proportion to the area of land exposed to the atmosphere. However, those areas affected by hundred meter changes in sea level, i.e. coastal plains bordering the sea, often undergo little weathering because of the development there of thick covers of highly weathered, and therefore less reactive, material such as clay minerals (Stallard, 1992). By this reasoning covering of low-lying coastal lands by the sea, or their exposure by a drop in sea level, should not make much difference to the rate of global silicate weathering (Berner, 1994). This of course is true only where the lowlands are underlain by heavily weathered material. Coastal lowlands at the foot of high mountains undergoing glaciation and intense physical erosion may be underlain by a high proportion of unweathered primary silicates, such as feldspars, delivered rapidly to the lowlands. In this case exposure of the lowlands due to a drop in sea level could contribute appreciably to global weathering (Lasaga et al., 1994). Until lowlands of this type can be quantified for the geologic past, it will be assumed in the model of the present paper that silicate weathering is not appreciably affected by changes in sea level or land area.

Although carbonate weathering does not directly influence atmospheric CO_2, as discussed earlier, it is still must be included in mass balance expressions for carbon input to and output from the atmosphere/ocean system as part of overall carbon cycle modeling. The treatment of carbonate weathering in terms of land area is different from that for silicate weathering. The dissolution of carbonates occurs under both high relief and low relief conditions. For example, intense carbonate dissolution, with the formation of karst features, occurs beneath the state of Florida which is exceedingly flat and near sea level. Because of the non-dependence of carbonate weathering on relief or elevation, it is assumed to be directly proportional to the area of carbonates exposed on land. The area of land underlain by carbonate over Phanerozoic time has been calculated from paleolithologic maps by Bluth and Kump (1991) and their results are incorporated in the GEOCARB modeling via the dimensionless expression f_{LA} (t) (Berner, 1994):

$$f_{LA}(t) = \text{area of carbonates on land at time t / area of carbonates at present} \qquad (13)$$

Mountain uplift

The importance of mountain uplift to the weathering of silicates has been emphasized recently (Raymo, 1991; Francois and Walker, 1992; Raymo and Ruddiman, 1992). The idea is that uplift results in rugged relief, and cold temperatures at high elevations. The rugged relief enhances physical erosion and the removal of protective covers of highly weathered clay residues allowing greater exposure of primary silicates to chemical weathering. Cold temperatures result in greater physical weathering due both to freeze-thaw and to grinding where glaciers are present. The enhanced physical weathering, by granulation, exposes more surface area of the primary minerals to weathering solutions. In addition, mountains can bring about enhanced rainfall due to orographic effects resulting in greater flushing of rocks by water. All these factors should have brought about greater weathering of silicate minerals during geologic periods when the extent of high mountains was globally more important. An example is the late Cenozoic when the uplift of the Himalayan/Tibetan system occurred (Raymo and Ruddiman, 1992).

The author has no quarrel with the importance of mountain formation to silicate weathering and has in fact incorporated the effect into carbon cycle modeling. However, I do differ with the workers cited above in that I believe that other factors are also important in weathering and that mountain uplift is not always the primary cause of changes with time in Phanerozoic atmospheric CO_2. In the latest model, GEOCARB II (Berner, 1994), mountain uplift is parameterized in terms of the $^{87}Sr/^{86}Sr$ of seawater. It is assumed that more radiogenic ^{87}Sr is delivered to the oceans when there is greater exposure of deeply buried old highly radiogenic rocks, or rocks containing remobilized radiogenic Sr (Edmond, 1992), by mountain uplift into the zone of weathering. In the GEOCARB II model correction for changes in $^{87}Sr/^{86}Sr$ of the oceans with time due to basalt-seawater reaction is made and the expression used to represent the mountain uplift effect on weathering is:

$$f_R(t) = 1 - L\,[(R_{ocb}(t) - R_{ocm}(t)) / (R_{ocb}(t) - 0.7000)] \qquad (14)$$

where: f_R (t) = dimensionless weathering factor which is multiplied times the present weathering flux to obtain weathering fluxes for times in the past when the $^{87}Sr/^{86}Sr$ of the oceans was different from that at present.
$R_{ocm}(t)$ = $^{87}Sr/^{86}Sr$ of the oceans at a time t as recorded in the geologic record
$R_{ocb}(t)$ = $^{87}Sr/^{86}Sr$ calculated for the oceans if the only control on the isotope ratio was basalt-seawater reaction
L = multiplying factor for sensitivity analysis.

Unfortunately the interpretation of Sr isotopic data in terms of mountain uplift and weathering rate is equivocal (Richter et al., 1992; Edmond, 1992). An increase of the $^{87}Sr/^{86}Sr$ of the oceans can be due to either increased weathering of average continental rocks, to a constant rate of global weathering but of unusually radiogenic rocks, or to changes in the rate of exchange of Sr isotopes during basalt-seawater reaction not accounted for in Equation (14). In the future it is hoped that a new independent method of deducing paleotopography and its effect on silicate weathering rate will be developed. One approach might be the construction of paleogeographic maps where mountain chains and their relative height can be deduced from the collisional history of the continents.

Climate

Most workers agree that climate exerts an important influence on chemical weathering. That weathering is a function of climate is revealed by the incorporation of the word "weather" within it. Climate exerts its influence directly in terms of temperature and precipitation, and indirectly in terms of vegetation, runoff, and glacial/periglacial phenomena. Because the development of terrestrial vegetation is a product of biological evolution, in addition to climate, this topic is discussed separately in the present paper.

Temperature is important in weathering, first of all because minerals dissolve faster as temperature increases (cf. Lasaga et al., 1994). An average temperature coefficient (equivalent to an Arrhenius activation energy of 15 kcal/mol) for the dissolution of common silicate minerals (e.g. Brady, 1991; Lasaga et al., 1994) has been used in carbon cycle modeling (Berner, 1994) and is in agreement with results from natural watersheds (Velbel, 1994; White and Blum, 1995). White and Blum (1995) determined, for a large number of purely granitic watersheds, the rate of silica and sodium release via chemical weathering as a function of precipitation (rainfall) and temperature. A summary of their results is shown in Figure 2. General agreement with the formulation of the GEOCARB II model indicates that the use of laboratory derived temperature coefficients by this model is justified. This suggests that surface reaction controlled dissolution of primary minerals may be the rate limiting step in silicate weathering.

Temperature has another, indirect effect, because globally it correlates with precipitation. A warmer global climate in the past should have resulted in greater evaporation from the oceans and consequently greater precipitation on the continents. If greater precipitation leads to greater runoff, then there should have been enhanced weathering. The response of silicate weathering to increased runoff, however, is not linear because of dilution effects (Holland, 1978). Silicate dissolution does not keep pace with increased flushing of rocks so that the riverine concentration of dissolved ions liberated by weathering decreases as river runoff increases. A survey of recent field studies suggests that the silicate dissolution flux, because of dilution, should follow only the 0.65 power of runoff (Berner, 1994). The carbonate dissolution flux, by comparison, should undergo

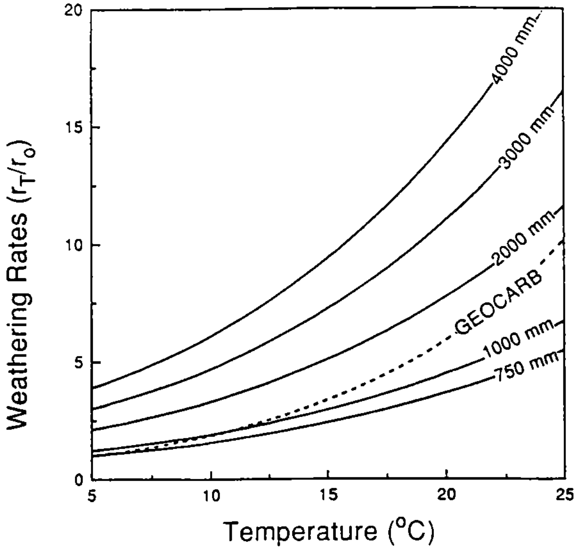


Figure 2. Observed dependence of silicate weathering rate as a function of mean annual temperature and precipitation. Curves summarize hydrochemical data on a large number of small watersheds underlain only by granite. The climate dependence used in GEOCARB modeling is shown for comparison (adapted from White and Blum, 1995).

less dilution with runoff because ground waters, due to rapid rates of dissolution, are generally fairly close to saturation with $CaCO_3$ (Langmuir, 1971; Harmon et al., 1975).

Based on the temperature effects on both the rate of mineral dissolution and runoff the temperature feedback expression $f_B(T)$ for silicate weathering is (Berner, 1994):

$$f_B(T) = [J(T) / J(T_o)] \times [R(T) / R(T_o)]^{0.65} \tag{15}$$

where:
$J(T)$ = the global weathering dissolution flux at some past time with global mean surface temperature T
$R(T)$ = global runoff at some past time with global mean surface temperature T
T_o = present global mean surface temperature and the subscript (o) refers to the present.

Explicit expressions for J(T) and R(T) as a function of T are obtained by use of the GEOCARB II model. From the standard Arrhenius formulation of dissolution rate we have the relation:

$$J(T) / J(T_o) = \exp\{[\Delta E/R][(T - T_o) / T\,T_o]\} \tag{16}$$

where: ΔE = activation energy; R = the gas constant (1.99 cal deg^{-1} mol^{-1}); and T is in Kelvins. Substituting E = 15 kcal/mol and simplifying, we obtain approximately:

$$J(T) / J(T_o) = \exp[0.090\,(T - T_o)] \tag{17}$$

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

$$R(T_O)/R(T_O) = 1 + 0.038\,(T - T_O) \qquad (18)$$

Combining Equations (10), (15), (17) and (18), one obtains the CO_2-temperature feedback factor $f_B(CO_2)_{(temp)}$ for silicate weathering:

$$f_B(CO_2)_{(temp)} = \exp\,[-\,0.09\,W_S(t/570)] \times (RCO_2)^{0.09\Gamma}$$

$$\times\ [1 + 0.038\,\Gamma\,\mathit{ln}\,(RCO_2) - 0.038\,W_S\,(t/570)]^{0.65} \qquad (19)$$

This is the dimensionless factor which expresses the effect of CO_2, by way of the greenhouse effect, on weathering. When multiplied by Equation (11) for $f_B(CO_2)_{(plants)}$ one obtains the total feedback effect of CO_2 on weathering for periods of time since the advent of vascular land plants.

Global rainfall is a function of many factors besides global mean temperature. Both rainfall and runoff depend on the size, location, and topography of a given land mass (Crowley and North, 1991). Large continents located along subtropical latitudes can be very dry in their interiors and undergo intense monsoonal activity as was the case for the supercontinent of Pangea during the Permian and Triassic Periods (Kutzbach and Gallimore, 1989). Coastal mountain belts, if located facing into prevailing onshore winds, can experience extensive precipitation on their windward sides due to orography. Small equatorial land masses can be very wet. At any rate, it is obvious that greater rainfall should in general bring about greater weathering and for periods of time when continents were smaller and located at wetter latitudes weathering should have been enhanced (providing all other factors remained the same). The GEOCARB modeling currently employs the global runoff calculations of Otto-Bliesner (1995) for principal periods of the Phanerozoic in terms of the runoff factor $f_D(t)$:

$$f_D(t) = \text{global runoff at time t / global runoff at present (for constant } CO_2) \qquad (20)$$

For silicate weathering $f_D(t)$ is raised to the 0.65 power to express the effects of dilution as discussed above. Note that $f_D(t)$ is calculated only for the effects on runoff of changing geography, and not for changes in atmospheric CO_2 or global temperature which is covered separately by Equation (18).

Large scale glacial and peri-glacial activity associated with times of global cooling (e.g. the Pleistocene Epoch) should bring about enhanced grinding of rocks to produce more surface area for contact with weathering solutions. This has led some workers (e.g. Raymo and Ruddiman, 1992; Edmond, 1993) to suggest that global weathering is faster when the earth is colder. However, as stated above this situation cannot persist globally for a long time or it would lead eventually to a runaway ice house.

Edmond (1993) has cited the chemical composition of the Aldan River in Siberia as evidence that cold climates at high latitudes favor rapid silicate weathering due to freeze/thaw action. However, he did not find that high dissolved Ca^{++} and HCO_3^- concentrations were accompanied by appreciable dissolved silica or clay mineral weathering products as would be expected for silicate weathering. These observations suggest carbonate weathering rather than silicate weathering, which is in agreement with the presence of abundant limestones in the Aldan drainage basin (Gordeev and Siderov, 1993). Furthermore the idea that global cooling should lead to increased weathering at high latitudes is not in accord with climatological considerations. Model calculations indicate that greenhouse induced global warming should result in even greater warming at high latitudes with a concomitant increase in rainfall (Manabe and Stauffer, 1993). During the Cretaceous period when high latitudes were unusually warm, heavily vegetated, wet and frost-free in many areas, conditions must have favored greater weathering than at present where there is greater aridity and the ground is covered with snow most of the year and frozen at depth as permafrost. Finally, the observation that present day clay mineral formation by weathering is greater at lower latitudes (Biscaye, 1965) is a simple example that warmer, and not colder, climates lead to greater silicate weathering.

Vegetation

The role of vegetation in weathering is usually included under a discussion of climate and weathering. However, vascular land plants did not exist before about 400 million years ago and they have undergone evolution and many changes of habitat since that time. Prior to 400 million years the land surface may have been covered with primitive algae or lichens (Wright, 1985; Schwartzman and Volk, 1989), but the effectiveness of these organisms compared to higher plants in affecting the rate of weathering is debatable, as will be pointed out below. Because vascular plants exert a major influence on silicate weathering, their evolution must have had an effect on the level of atmospheric CO_2 and it is the purpose of this section to demonstrate this. [Parameterization of the effects of plants in the GEOCARB model is discussed in the following section.]

Vascular plants affect the rate of weathering in numerous ways. Some of the more important ones are:

1. Rootlets (+ symbiotic microflora) with high surface area secrete organic acids/ chelates which attack minerals in order to gain nutrients.
2. Organic litter decomposes to H_2CO_3 and organic acids providing additional acid for weathering.
3. On a regional scale plants recirculate water via transpiration followed by rainfall and thereby increase water/mineral contact time. There is greater rainfall in forested regions than there would be in the absence of the trees.
4. Plants anchor clay-rich soil against erosion allowing retention of water and continued weathering of primary minerals between rainfall events.

Plants accelerate weathering in order to obtain nutrient elements from rocks (Berner, 1992b). As part of this process the secretion of organic acids by plant roots and their associated mycorrhizae (micro-organisms attached to rootlets) is of special interest. A number of studies (e.g. Cromack et al., 1979; Koch and Matzner, 1993; Griffiths et al., 1994) have demonstrated enhanced concentrations of organic acids within short distances of mycorrhizae and plant roots (the rhizosphere) which can lead to localized weathering (April and Keller, 1990). This is due largely to the secretion by the mycorrhizae of various low molecular weight acids such as oxalic acid or citric acid. These acids, besides providing extra H^+ for the attack on minerals, also are able to complex and solubilize (chelate) otherwise insoluble elements such as Fe and Al. This helps to further break down those minerals containing Al and Fe. Because of an enhanced acid concentration within the microenvironment of the rhizosphere, one can be misled as to the chemical composition of the soil solutions that actually attack minerals. Laboratory experiments based on the use of organic chelators at concentrations found in average soil waters, as sampled by lysimeters, ignore the intense microenvironment of the rhizosphere, and as a result can come to erroneous conclusions regarding the importance of organic acids in weathering. This has been emphasized recently by Drever (1994).

An example of the effectiveness of rhizosphere solutions in attacking silicate minerals, based on the research of M.F. Cochran, is shown in Figure 3. Here plagioclase phenocrysts from a young Hawaiian basalt have been completely dissolved away by biological exudates, leaving molds of the phenocrysts in the immediate vicinity of plant

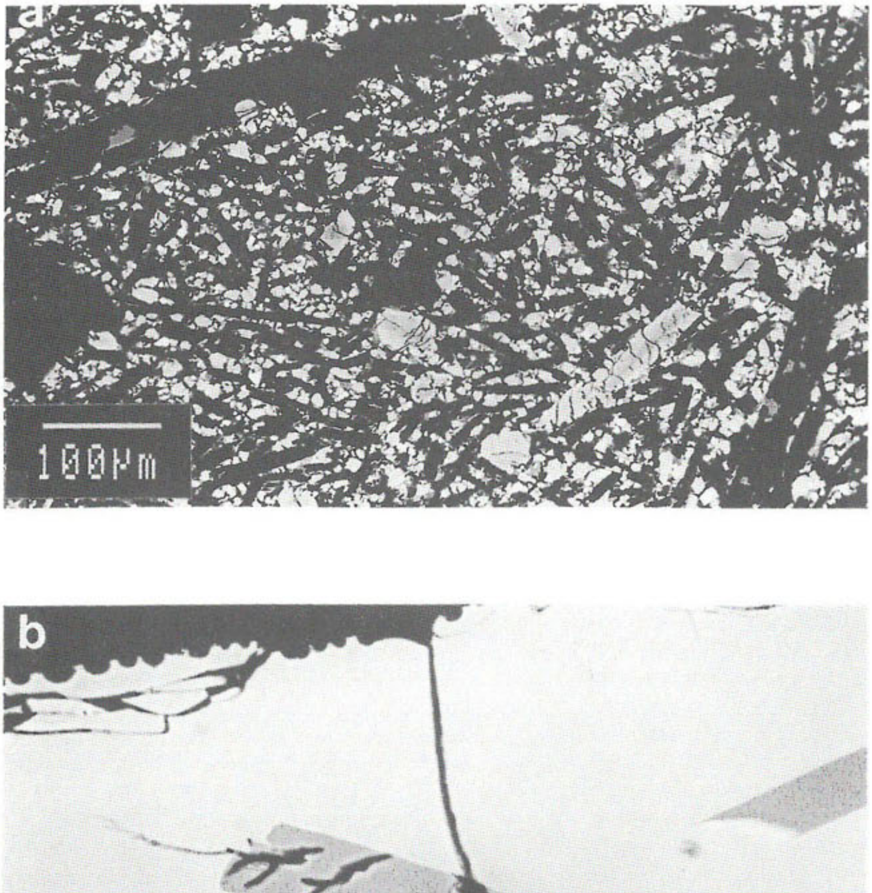


Figure 3. Evidence of plant induced weathering. (a) Molds of pre-existing plagioclase phenocrysts from a young Hawaiian basalt that have been dissolved away by the action of adjacent plant rootlets of the Ohia tree *Metrosideros*. (b) Plagioclase phenocryst from a young Hawaiian basalt showing etching from the activity of adjacent plant rootlets—note the access "tunnel" for aggressive solutions leading to the phenocryst (after Cochran, 1995).

rootlets (Fig. 3A). By contrast, away from rootlets there is no evidence for such intense weathering. The plant in this case (the Ohia tree *Metrosideros*) has dissolved away anorthitic plagioclase in order to extract the important nutrient calcium. One can actually observe widening of minute cracks by biological fluids in order to gain access to the Ca-rich minerals (Fig. 3B). By measuring the degree of porosity, due to the removal of minerals and volcanic glass, Cochran has been able to quantify the rate of initial biochemically induced weathering of Hawaiian basalts ranging in age from 100 to 5000 years (Cochran, 1995).

In contrast to the dissolution found around the roots of higher plants, we have found little or no evidence of dissolution under the lichen *Stereocaulon vulcani* developed on the same young basalts (Cochran, 1995; Cochran and Berner, 1993), This is in conflict with the earlier work of Jackson and Keller (1970) who have maintained that this lichen weathers Hawaiian basalts rapidly, even over time spans as short as 50 years. The material described by Jackson as the alteration residue of the underlying basalt, we have shown is, instead, largely dust trapped by the sticky, lipid-rich lichen thalli and altered in situ. This finding of much less weathering by *S. vulcani* is important in that Schwartzman and Volk (1989) have stated that, based on Jackson's findings, the role of lichens in weathering is immense. They used Jackson and Keller's results to calculate that silicate weathering during the Precambrian was greatly accelerated by lichens and that this helped to bring atmospheric CO_2 levels down to the point where earth surface temperatures became low enough to support higher forms of life. We believe this conclusion is based on insufficient evidence.

It is still possible that other lichens or primitive micro-organism could have been effective weathering agents prior to the rise of vascular land plants as has been maintained by others (e.g. Retallack, 1990; Schwartzman and Volk, 1989; Jackson, 1993; Horodyski and Knauth, 1994). However, we suggest that such weathering could not have been as important as that which accompanied the rise of vascular plants. There is definite evidence of limited leaching immediately underneath lichens (e.g. Wilson and Jones, 1983; Thorseth et al., 1992) but because of the very slow growth of these organisms (Ahmadjian, 1993) their effect over time becomes negligible compared to that of higher plants. The reason that higher plants are more effective is simple. Underneath even small crop plants the interfacial area between minerals and roots, rootlets, and root hairs is immense with values of 1000 m^2 per square meter of land surface (Wild, 1993). For lichens, on the other hand, the area of rock/biota interface is only about 1 m^2 per square meter of rock (land). Combined with the much slower growth rate (and, therefore, slower nutrient storage) by lichens compared to higher plants, this difference in interfacial area must mean that rooted higher plants are much more effective in attacking rocks and weathering them than are lichens.

A knowledge of the quantitative effect of plants on the rate of silicate weathering is necessary if one is to obtain any estimate of how the rise and spread of vascular plants on land could have affected levels of atmospheric CO_2 by altering rates of global weathering. Before the Devonian Period there were some vascular plants but they were small and confined to the vicinity of watercourses (Stewart, 1983). It was only during the Devonian that plants developed deep roots and spread to upland areas where they could be effective in altering rates of weathering (Algeo et al., 1995). If major vascular plants (e.g. trees) are much more important in affecting weathering than what may have existed earlier (e.g. algae and lichens), then their population of the continents during the Devonian could have had a major impact, not only on atmospheric CO_2, but also on geochemical cycles in general and even on marine ecology (Algeo et al., 1995).

It is difficult to estimate the quantitative effect of plants on the rate of weathering. However, some initial estimates have been made. Drever and Zobrist (1992) have shown that the stream flux of dissolved HCO_3^-, resulting from CO_2 uptake during silicate weathering in the southern Swiss Alps, is a strong function of elevation. The weathering flux at 300 m elevation is about 25 times higher than it is at 2400 meters. The two elevations differ in both mean annual temperature and in vegetation, but not in bedrock lithology. The low area is heavily forested by deciduous trees whereas the high area is above tree line and is essentially barren with lichen-encrusted rocks. If correction is made for the effect of temperature difference on the rate of mineral dissolution, which is a factor of about three based on the adiabatic lapse rate plus an activation energy of 15 kcal/mole, then the residual effect is a factor of about eight. If this difference is due mainly to the presence of the trees at the low elevation, then this data suggests a large effect (8×) of vascular plants on the rate of silicate weathering. This conclusion, however, is tentative because of the possibility that differences in hydrology and/or microclimatology between the two elevations could explain the results.

Another study whose results can be applied to the problem of the effect of plants on weathering was conducted by Arthur and Fahey (1993) at the Loch Vale Watershed of the Rocky Mountain National Park located at an elevation of between 3100 and 4000 meters. Here a small forest of Engelmann spruce is located in the lower elevations of the watershed which otherwise consists of bare bedrock, talus, and permanent snowfields. They found that the cationic denudation rate per unit area of the forested area was 3.5 times higher than that for the surrounding barren area.

A better estimate of the quantitative role of plants in weathering could be gained by performing controlled experiments where, climate, hydrology etc. were held constant. Fortunately such an experiment exists and is currently underway at the Hubbard Brook Experimental Forest Station in New Hampshire (Bormann et al., 1987). In 1983 three small equisized plots were constructed by filling 1.5-meter depressions with the same feldspathic glacial sand and lining the bottom of each with impermeable plastic sheeting to allow flow of all water passing through each plot to an exit pipe located below ground where the water could be sampled. One plot was planted with red pine trees, the second with two species of grass, and the third left fallow. [The fallow field has unavoidably developed a cover of lichens and other primitive plants which is an advantage in that this makes it a reasonable stand-in for the ancient land surface.] For the past 12 years the exit waters have been sampled, and chemical analyses for all major elements have been performed recently by our laboratory. Other workers in the meantime have been measuring the uptake of major elements by exchangeable phases and by the growing biota.

Results for dissolved HCO_3^- as a function of time for the Hubbard Brook experiment, taken from the work of Cochran (1995), are shown in Figure 4. Here measured HCO_3^- concentrations are normalized to measured Cl^- concentrations in order to correct for changes in the concentration of all ions and in outflow rate due to evapotranspiration. As can be seen there are large seasonal variations. The release of bicarbonate from the tree-lined plot, as compared to the barren plot, is very large during periods of active growth and intense snowmelt, as occurs in the spring. Also, the accelaration of weathering by the pine trees is much greater than that by the grasses (not shown). A mean value for the total period of the relative bicarbonate flux for the trees relative to the barren plot is about a factor of four. This must be a minimum value because of the storage of nutrients in the actively growing trees. In a natural forest, trees eventually die, due to drought, fires, windstorms, landslides, etc., and release nutrient cations (Bormann and Likens, 1981), such as K^+ or Ca^{++}, which can be accompanied by additional HCO_3^-. It is the sum of HCO_3^- loss by

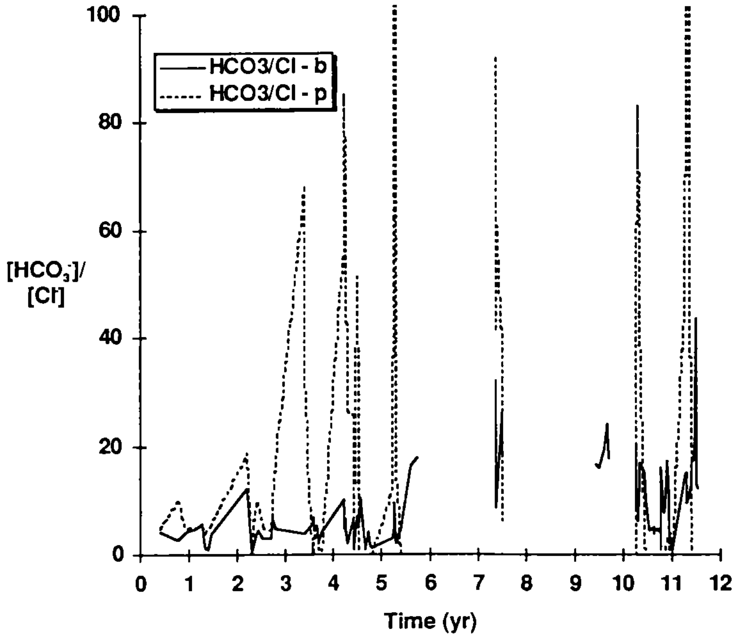


Figure 4. Plots of dissolved HCO_3^- vs. time for waters draining each of two small experimental weathering plots ("sandboxes') at Hubbard Brook, New Hampshire. All HCO_3^- concentrations have been normalized to dissolved Cl^- to correct for differences in evapotranspiration. p = plot with pine trees; b = "bare" plot populated by algae and lichens (after Cochran, 1995).

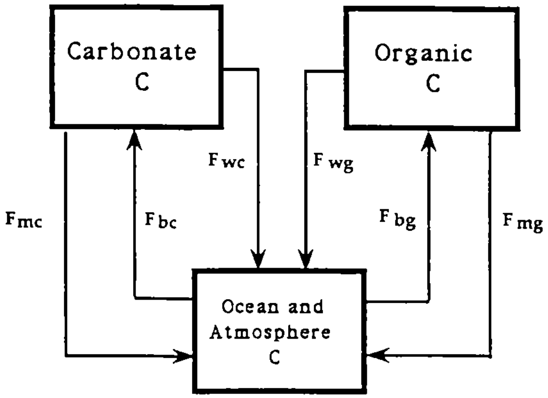
streams, plus that released with cation nutrients that were previously stored in growing plants, that constitutes the total time-integrated effect of plants on weathering rate (e.g. Taylor and Velbel, 1991). Once data on nutrient storage in the pine trees at Hubbard Brook is obtained, we will be able to derive a more accurate idea of the total effect of plants on the rate of uptake of CO_2 and its conversion to HCO_3^- during the weathering of silicate minerals.

SENSITIVITY OF THE GEOCARB CARBON CYCLE MODEL TO SOME WEATHERING PARAMETERS

In this section results, in terms of plots of carbon dioxide concentration vs. time, for different values for critical weathering parameters are presented based on the latest version of the GEOCARB geochemical carbon cycle model for Phanerozoic time (Berner, 1994 modified to introduce the rise of vascular land plants between 380 and 350 my BP—see Algeo et al., 1995). This model is explained in detail in previous publications (Berner, 1991; 1994) and the parameterization of weathering in the model is discussed above, so that only its essence will be summarized here.

The GEOCARB modeling assumes that, at each million year time step, the rate of input of carbon dioxide to the earth surface (the atmosphere/ocean/biosphere reservoir), by thermal degassing and the weathering of old carbonates and organic matter, is equal to its removal by weathering and the burial of new carbonates and organic matter in sediments. In other words, as input and output rates change over time it is assumed that a new steady state is re-established during each million year period. From the dynamics of the long term carbon cycle this is justified (Kump, 1989; Lasaga, 1989). A diagrammatic representation

Figure 5. Diagrammatic representation of the geochemical carbon cycle as treated by the GEOCARB modeling (Berner, 1991; 1994). F_{wc} = weathering of carbonates; F_{mc} = degassing from thermal carbonate decomposition; F_{wg} = weathering of organic matter; F_{mg} = degassing from thermal organic matter decomposition; F_{bc} = burial of carbonates in sediments; F_{bg} = burial of organic matter in sediments. On a multimillion year time scale carbon cannot be stored in the ocean/atmosphere reservoir, so that at each time in the past the total inputs to the ocean + atmosphere (+ biosphere) must be very close to that for total outputs. [In other words, $F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg}$.]



of the model is shown in Figure 5. Mass balance expressions are constructed for both total carbon and ^{13}C using the ^{13}C values for limestones over the Phanerozoic. The weathering flux terms for carbonates and silicates take into consideration changes with time by multiplying present weathering rates by time-dependent dimensionless weathering parameters such as those shown in Equations (11) through (20). The factors consider continental land area, surface lithology of rocks undergoing weathering, continental relief due to mountain uplift, global river runoff, the rise and evolution of land plants, slow constant increase in solar radiation, and changes in atmospheric CO_2 as they act as a negative feedback and affect global mean surface temperature and the rate of growth (weathering) by land plants. Degassing changes with time are parameterized by variations in the rate of seafloor spreading via plate tectonics and by fluctuations in the amounts of carbonates (deep sea vs. shallow water) available for thermal decomposition upon burial. Paleolevels of CO_2 are computed, using an inversion procedure, from values obtained for the feedback expression $f_B(CO_2)$ for silicate weathering at each million year time step.

To illustrate the effects of changing the values of input parameters for weathering, two sensitivity runs are presented here. [Many additional sensitivity runs can be found in the original paper—Berner, 1994.] The first, Figure 6, shows the effects on the rate of weathering of varying the quantitative importance of the rise of vascular land plants during the Devonian. The dimensionless parameter RCO_2 represents the ratio of the mass of CO_2 in the atmosphere at some time t to that at present. The dimensionless parameter $f_E(t)$ represents the ratio of the rate of weathering under existing biota at a time t to that under present day plants (with all other factors held constatnt). Values of $f_E(t)$ attached to the curves represent those assumed for the pre-vascular plant situation, and the range chosen is based on our Hubbard Brook experiments and the study of Drever and Zobrist (1992). Note that a knowledge of the quantitative effect of plants on weathering is critical in calculating values of CO_2. This is a principal reason why we are presently concentrating our research on this subject.

In Figure 7 is shown the sensitivity of CO_2 to the GCM climate model used for converting atmospheric CO_2 concentration and solar radiation level to global mean temperature. The empirical expression fitted to the results of general circulation modeling used for this purpose (Berner, 1994) is stated above as Equation (10). Three formulations are used to obtain values of Γ and W_s in Equation (10). One is based on the results of Marshall et al. (1994), another on those of Manabe and Bryan (1985) and S. Manabe (pers.

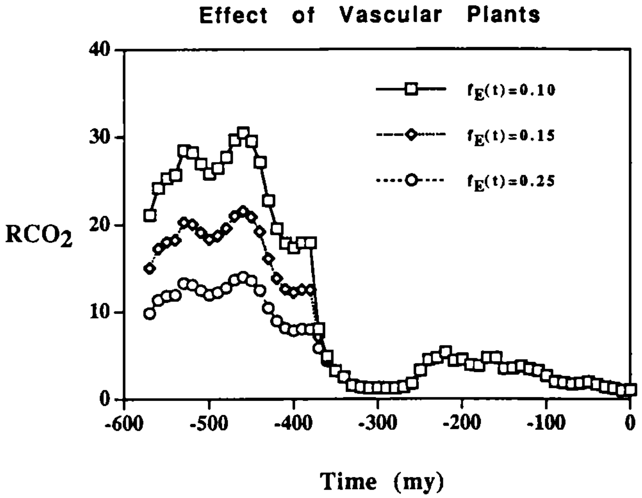


Figure 6. Plot of CO_2 vs. time, calculated according the GEOCARB II model, showing sensitivity to the parameter $f_E(t)$ for the period prior to the rise of deeply rooted vascular plants in upland areas. RCO_2 represents the mass of CO_2 in the atmosphere at some time t divided by that today. The parameter $f_E(t)$ is set equal to one at present; thus, a value of $f_E(t) = 0.10$ means that present day plants accelerate weathering by a factor of ten over that for the primitive vegetation of the early Paleozoic. Plot is for values of $\Gamma = 6$, $W_S = 12.9$ (see caption to Fig. 7).

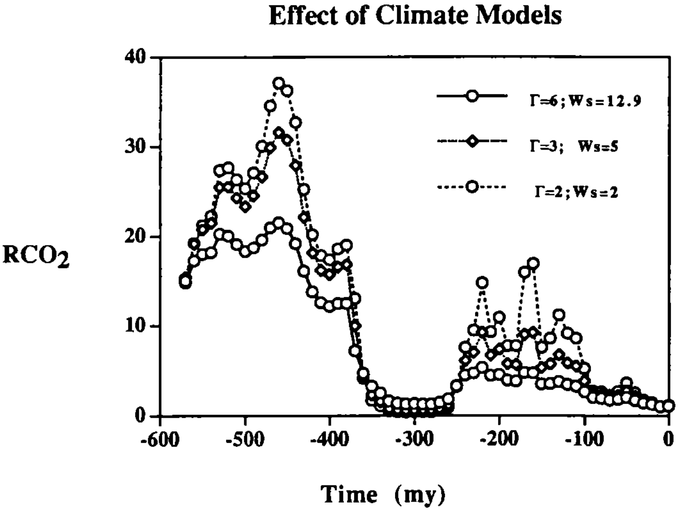


Figure 7. Plot of CO_2 vs. time, calculated according to the GEOCARB II model, showing sensitivity to the climate feedback parameters Γ and W_S. RCO_2 represents the mass of CO_2 in the atmosphere at some time t divided by that today. The parameters Γ and W_S represent the sensitivity of global mean temeperature to atmospheric CO_2 level and solar radiation respectively based on an empirical equation fitted to the results of general circulation modeling (see text). The highest values are based on the work of Marshall et al. (1994), intermediate values on that of Manabe and Bryan (1985) and Manabe (pers. comm.), and the lowest values are minima allowable for physically possible values of RCO_2.

comm.), and the third using the lowest values of Γ and W_S permissible without producing negative RCO_2 values. The amplitude of variations in CO_2 with time depends on which GCM formulation is used, but the general shape of the curve is not altered. Also, similar results are obtained if different formulation are used for the response of plant-induced weathering to CO_2 level. Thus, the *shape* of the CO_2 curve is robust relative to whichever feedback is employed; this is an important result. It is in agreement with earlier work (Berner, 1991; 1994) that has shown that variation of *all* modeling parameters within geologically reasonable limits, either those associated weathering or those reflecting degassing, results in the same general curve shape.

SUMMARY: WEATHERING, CLIMATE, AND CO_2

There is no doubt that atmospheric CO_2 has varied appreciably over Phanerozoic time and a large part of the variation has been due to changes in the rate of weathering. Variations with time in continental land area, elevation, and surface lithology and in global climate, vegetation, and the amount of solar radiation all have influenced weathering and consequently the level of atmospheric CO_2. The values of CO_2 vs. time calculated by the GEOCARB model and shown in Figures 6 and 7 are in rough agreement with independent estimates (see Berner, 1992a) in that all methods show at each time about the same value of RCO_2 (within a factor of two). Also, the modeling agrees with observed climates if the atmospheric greenhouse effect is a major control of climate (Crowley and Baum, 1992). High CO_2 levels occur during periods of global warming and low levels during glacial times. [The Ordovician glaciation is a special case—see Crowley and Baum, 1995.]

Modeling results show that the dramatic drop in CO_2 during the Devonian-Carboniferous was mainly the result of an increase in weathering intensity accompanying the rise and evolution of vascular land plants. The newly risen plants accelerated weathering, but to keep the CO_2 removal flux equal to the CO_2 degassing input flux, the level of CO_2 dropped, thus counterbalancing the plant accelerating effect and providing the necessary feedback to stabilize the system. [Additional CO_2 drop was provided by the enhanced burial of vascular-plant derived organic matter—see Berner, 1991.] The CO_2 drop led to global cooling and the onset of the Permo-Carboniferous glaciation, the longest and most extensive glacial period of the entire Phanerozoic. Since these results hinge on assumed values for the quantitative effects of plants on weathering, they show that it is imperative that a better knowledge of the role of plants in weathering be obtained. This is an outstanding example of how weathering may be important to global climate and shows why a better understanding of weathering, as discussed by the many papers in the present volume, has major application to other aspects of earth science.

ACKNOWLEDGMENTS

This work has been supported by grants from the National Science Foundation (EAR-9117099 and EAR-9417325). The writer thanks M. Ford Cochran for many helpful discussions.

REFERENCES

Ahmadjian V (1993) The lichen symbiosis. Wiley, New York, 250 p

Algeo TJ, Berner RA, Maynard JB, Scheckler SE (1995) Late Devonian oceanic anoxic events and biotic crises: "rooted" in the evolution of vascular land plants? GSA Today 5:45, 5:64-66

April R, Keller D (1990) Mineralogy of the rhizosphere in forest soils of the eastern United States. Biogeochemistry 9:1-18

Arthur MA, Fahey TJ (1993) Controls on soil solution chemistry in a subalpine forest in north-central Colorado. Soil Science Soc Am J 57:1122-1130

Bazzaz FA (1990) The response of natural ecosystems to the rising global CO_2 levels. Ann Rev Evolution and Systematics 21:167-196

Berner EK, Berner RA (1987) The Global Water Cycle:Geochemistry and Environment. Prentice-Hall, Engleood Cliffs, NJ, 397 p

Berner RA (1991) A model for atmospheric CO_2 over Phanerozoic time Am J Sci 291:339-376

Berner RA (1992a) Paleo-CO_2 and climate. Nature 358:114

Berner RA (1992b) Weathering, plants, and the long-term carbon cycle. Geochim Cosmochim Acta 56:3225-3231

Berner RA (1994) GEOCARB II: A revised model for atmospheric CO_2 over Phanerozoic time. Am J Sci 294: 56-91

Berner RA (1995) A.G. Hogbom and the development of the geochemical carbon cycle. Am J Sci 295:491-495

Berner RA, Lasaga AC, Garrels RM (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

Biscaye PE (1963) Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean. Geol Soc Am Bull 76:803-832

Bluth GJS, Kump, L R (1991) Phanerozoic paleogeology. Am J Sci 291:284-308

Bormann FH, Bowden WB, Pierce RS, Hamburg SP, Voigt GK, Ingersoll RC, Likens, GE (1987) The Hubbard Brook sandbox experiment. In: Restoration Ecology. Jordan R, Gilpin ME, Aber JD (eds) Cambridge Univ Press, p 251-256

Bormann FH, Likens GE (1981) Pattern and process in a forested ecosystem. Springer-Verlag, New York, 253 p

Brady PV (1991) The effect of silicate weathering on global temperature and atmospheric CO_2. J Geophys Res 96:18, 101-18, 106

Caldeira K (1995) Long-term contol of atmospheric carbon dioxide: low-temoerature seafloor alteration or terrestrial silicate-rock weathering. Am J Sci 295 (in press)

Caldeira K, Kasting JF (1992) The life span of the biosphere revisited. Nature 360:721-723

Cochran MF (1995) Weathering, plants and the geochemical carbon cycle. PhD Dissertation, Yale Univ, New Haven, CT

Cochran MF, Berner RA (1993) Reply to the comments on "Weathering, plants and the long-term carbon cycle. Geochim Cosmochim Acta 57:2147-2148

Cromack K, Sollins P, Graustein WC, Speidel K, Todd AW, Spycher G, Li CY, Todd RL (1979) Calcium oxalate accumulation and soil weathering in mats of the hypogeous fungus *Hysterangium Crassum* . Soil Biol and Biochem 11:463-468

Crowley TJ, Baum SK (1992) Modeling late Paleozoic glaciation. Geology 20:507-510

Crowley TJ, Baum SK(1995) Reconciling late Ordovician (440 Ma) glaciation with very high (14×) CO_2 levels. J Geophys Res 100:1093-1101

Crowley TJ, North GR (1991) Paleoclimatology. Oxford University Press, New York, 339 p

Drever JI (1994) The effect of land plants on weathering rates of silicate minerals. Geochim Cosmochim Acta 58:2325-2332

Drever JI, Zobrist J (1992) Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps. Geochim Cosmochim Acta 56:3209-3216

Edmond JM (1992) Himalayan tectonics, weathering processes and the strontium isotope record in marine limestones. Science 258:1594-1597

Edmond JM (1993) Weathering processes on hot and cold cratons: the Guyana and Aldan Shields. Geol Soc Am Ann Meeting Abstracts, 414-415

Francois LM, Walker JCG (1992) Modeling the Phanerozoic carbon cycle and climate: constraints from the $^{87}Sr/^{86}Sr$ isotopic ratio of seawater. Am J Sci 292:81-135

Gordeev VV, Siderov IS (1993). Concentrations of major elements and their outflow into the Laptev Sea by the Leana River. Marine Chem 43:33-45

Griffiths RP, Baham JE, Caldwell BA (1994) Soil solution chemistry of ectomycorrhizal mats in forest soil. Soil Biol and Biochem 26:331-337

Harmon RS, White WB, Drake JJ, Hess JW (1975) Regional hydrochemistry of North American carbonate terrains. Water Resources Res 11:963-967

Hedges J (1993) Global biogeochemical cycles: progess and problems. Marine Chem 39: 67-93

Högbom AG (1894) On the probability of secular variations of atmospheric carbon dioxide (in Swedish) Svensk Chemisk Tidsskrift 6:169-176

Holland HD (1978) The Chemistry of the Atmosphere and Oceans. Wiley, New York, 351 p

Horodyski RJ, Knauth LP (1994) Life on land in the Precambrian. Science 263, 494-498

IPCC (Intergovernmental Panel on Climate Change) (1990) The IPCC assessment. Cambridge Univ Press, 200 p

Jackson TA (1993) Comment on "Weathering, plants and the long-term carbon cycle". Geochim Cosmochim Acta 57,:2141-2144

Jackson TA, Keller WD (1970) A comparative study of the role of lichens and "inorganic" processes in the chemical weathering of recent Hawaiian lava flows. Am J Sci 269:446-466

Kasting JF, Ackerman TP (1986) Climatic consequences of very high carbon dioxide levels in the earth's early atmosphere. Science 234:1383-1385

Koch AS, Matzner E (1993) Heterogeneity of soil and soil solution chemistry under Norway spruce) and European beech as influenced by distance from the stem base. Plant and Soil 151:227-237

Kump LR (1989) Alternative modeling approaches to the geochemical cycles of carbon, sulfur and strontium isotopes. Am J Sci 289:390-410

Kutzbach JE, Gallimore RG (1989) Pangean climates: megamonsoons and megacontinents. J Geophys Res 94:3341-3357

Langmuir D (1971) The geochemiistry of some carbonate ground waters in central Pennsylvania. Geochim Cosmochim Acta 35:1023-1046

Lasaga AC (1989) A new approach to isotopic modelling of the variation of atmospheric oxygen theough the Phanerozoic. Am J Sci 289:411-435

Lasaga AC, Soler JM, Ganor J, Burch TE, Nagy K (1994) Chemical weathering rate laws and global geochemical cycles. Geochim Cosmochim Acta 58:2361-2386

Mackenzie, FT and Garrels, RM (1966) Chemical mass balance between rivers and oceans. Am J Sci 264:507-525

Manabe S, Bryan K (1985) CO_2-induced change in a coupled ocean-atmosphere model and its paleoclimatic implications. J Geophys Res 90:11,689-11,707

Manabe S, Stauffer RJ (1993) Century-scale effects of increased atmospheric CO_2 on the ocean-atmosphere system. Nature 364:215-218

Marshall S, Oglesby RJ, Larson, JW, Saltzman B (1994) A comparison of GCM sensitivity to changes in CO_2 and solar luminosity. Geophys Res Lett 21:2487-2490

Opdyke BN, Walker JCG (1992) Return of the coral reef hypothesis: basin to shelf partitioning of $CaCO_3$ and its effect on atmospheric CO_2. Geology 20:733-736

Otto-Bliesner B (1995) Continental drift, runoff and weathering feedbacks: implications from climate model experiments. J Geophys Res (in press)

Raymo ME (1991) Geochemical evidence supporting T.C. Chamberlin's theory of glaciation. Geology 19:344-347

Raymo ME, Ruddiman WF (1992) Tectonic forcing of late Cenozoic climate. Nature 359:117-122

Retallack GJ (1990) Soils of the Past. Unwin-Hyman, Boston, 520 p

Richter FM, Rowley DB, DePaolo DJ (1992) Sr isotope evolution of seawater: the role of tectonics. Earth Planet Sci Lett 109:11-23

Sarmiento JL (1993) Oceanic carbon cycle Chemical and Engineering News 71:30-43

Spivack AJ, Staudigel, H (1994) Low-temperature alteration of the upper oceanic crust and the alkalinity budget of seawater. Chem Geol 115:239-247

Stallard RF (1992) Tectonic processes, continental freeboard, and the rate-controlling step for continental denudation. In SS Butcher, RJ Charlson, GH Orians, GV Wolfe (eds) Global biogeochemical cycles. Academic Press, New York, p 93-121

Staudigel H, Hart SR, Schminke HU, Smith BM (1989) Cretaceous ocean crust at DSDP Sites 417 and 418: Carbon uptake from weathering vs. loss by outgassing. Geochim Cosmochim Acta 53:3091-3094

Stewart WN (1983) Paleobotany and the evolution of plants. Cambridge Univ Press, Cambridge, 405 p

Taylor AB, Velbel MA (1991) Geochemical mass balances and weathering rates in forested water-sheds of the southern Blue Ridge II Effects of botanical uptake terms. Geoderma 51:29-50

Thorseth H, Furnes H, Heldal M (1992) The importance of microbiological activity in the alteration of natural basaltic glass. Geochim Cosmochim Acta 56:845-850

Urey HC (1952) The Planets: Their Origin and Development. Yale Univ Press, New Haven, 245 p

Volk T (1987) Feedbacks between weathering and atmospheric CO_2 over the last 100 million years. Am J Sci 287:763-779

Volk T (1989) Rise of angiosperms as a factor in long-term climatic cooling. Geology 17:107-110

Walker JCG, Hays PB, Kasting JF (1981) A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. J Geophys Res 86:9776-9782

White AF, Blum AE (1995) Effects of climate on chemical weathering in watersheds. Geochim Cosmochim Acta 59:1729-1748

Wild A (1993) Soils and the Environment: An Introduction. Cambridge Univ Press, Cambridge, 287 p

Wilson MJ, Jones D (1983) Lichen weathering of minerals: implication for pedogenesis. In: RCL Wilson (ed) Residual deposits surface related weathering processes and materials. Blackwells, Oxford, p 5-12

Wright VP (1985) The precursor environment for vasacular plant colonization. Phil Trans Royal Soc London Ser B 309:143-145