# 1. The Rise of Trees and How They Changed Paleozoic Atmospheric CO<sub>2</sub>, Climate, and Geology

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## **1.1 Introduction**

Large vascular plants with deep, extensive root systems arose and spread over the continents starting about 380 million years ago during the Devonian Period. Previously there were only bryophytes, algae, and small vascular plants restricted to the edges of water courses (Gensel and Edwards 2001). Large plants are important because their vast root systems produce a larger interface between the geosphere and the biosphere than do the more primitive species, where the plant/mineral interface is greatly reduced. This large interface allows plants to take up nutrients more rapidly, to grow bigger and faster (Algeo and Scheckler 1998), and to accelerate mineral weathering (Berner 1998). In addition, the larger plants, upon death, supply a much greater mass of organic matter for burial in sediments. Because of these effects, the rise of large vascular plants brought about a dramatic change in the level of atmospheric  $CO_2$ , the climate, and the formation of carbon-rich deposits (coal) during the late Paleozoic.

## 1.2 Plants, Weathering, and CO<sub>2</sub>

The level of  $CO_2$  is controlled, on a long-term, multimillion-year timescale, by two carbon cycles: the silicate-carbonate cycle and the organic matter cycle. The

silicate-carbonate cycle can be represented succinctly by the following reactions (stated in words by Ebelmen 1845 but symbolized by Urey 1952):

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$$
 (1.1)

$$\text{CO}_2 + \text{Mg SiO}_3 \rightarrow \text{MgCO}_3 + \text{SiO}_2$$
 (1.2)

The arrows, from left to right, refer to all Ca-Mg silicate weathering (the silicate formulae are generalized) plus sedimentation of marine carbonates. These two weathering reactions summarize many intermediate steps, including photosynthetic fixation of  $CO_2$ , root/mycorrhizal respiration, organic litter decomposition in soils, the reaction of carbonic and organic acids with primary silicate minerals thereby liberating cations to solution, the conversion of  $CO_2$  to  $HCO_3^-$  in soil and ground water, the flow of riverine  $Ca^{++}$ ,  $Mg^{++}$ , and  $HCO_3^-$  to the sea, and the precipitation of Ca-Mg carbonates in bottom sediments. (The reactions, from right–to–left, represent thermal decomposition of carbonates at depth resulting in degassing of  $CO_2$  to the atmosphere and oceans by diagenesis, metamorphism, and volcanism.)

Plants accelerate the rate of weathering and liberation of  $Ca^{++}$ ,  $Mg^{++}$ , and  $HCO_3^-$  to solution in the following ways:

- 1. Rootlets (+ symbiotic microflora) with high surface area secrete organic acids/chelates, which attack primary minerals in order to gain nutrients (in this case Ca and Mg).
- 2. Organic litter decomposes to carbonic and organic acids providing additional acid for mineral dissolution.
- 3. Plants recirculate water via transpiration and thereby increase water/mineral contact time.
- 4. Plants anchor clay-rich soil against erosion allowing retention of water and continued dissolution of primary minerals between rainfall events.

Based on present-day field studies of the quantitative effects of plants on weathering rate (Drever and Zobrist 1992; Arthur and Fahey 1993; Bormann et al. 1998; Moulton, West, and Berner 2000), these effects combine to accelerate silicate weathering rates by a factor of approximately 2 to 10. When the field results are applied to global carbon cycle modeling, the calculated effect on atmospheric  $CO_2$ , due to the rise of trees during the Paleozoic Era, turns out to be dramatic (Fig. 1.1).

## 1.3 Plants, the Organic Cycle, and CO<sub>2</sub>

The organic cycle can be represented succinctly by the following reaction (stated in words by Ebelmen 1845):

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \to \mathrm{CH}_2\mathrm{O} + \mathrm{O}_2 \tag{1.3}$$



**Figure 1.1.** Plot of RCO<sub>2</sub> versus time based on GEOCARB III modeling (Berner and Kothavala 2001). The three curves illustrate sensitivity to the quantitative effect of the rise of large land plants on weathering rate.  $RCO_2$  is the ratio of mass of carbon dioxide in the atmosphere at a past time divided by the present preindustrial mass.

The reaction, from left to right, refers to the burial of organic matter in sediments. This represents a net excess of global photosynthesis over respiration and is a major sink for atmospheric  $CO_2$ . (From right to left, the reaction refers to weathering of old organic matter (kerogen) on the continents or thermal decomposition of organic matter upon deep burial combined with the oxidation of reduced gases emitted to the atmosphere and oceans.)

Enhanced burial of organic matter occurred after the rise of large land plants. This is because of the production of a new compound, lignin, which is relatively resistant to biodecomposition. The burial of lignin-derived humic material, and other plant-derived microbiallyresistant substances, in terrestrial and coastal swamps and in the oceans (after transport there via rivers) resulted in not only large increases in the global burial of organic matter (Holland 1978; Berner and Canfield 1989) but also the formation of vast coal deposits of the Carboniferous and Permian periods (Bestougeff 1980). In fact, production and preservation of terrestriallyderived organic debris was so large that it may have dominated over the burial of marine-derived organic matter at this time (Berner and Raiswell 1983; Broecker and Peacock 1999).

## 1.4 Carbon Cycle Modeling

A carbon cycle model, GEOCARB, has been constructed for calculating weathering rates, carbon burial rates, degassing rates, and levels of atmospheric  $CO_2$  over Phanerozoic time (Berner 1994; Berner and Kothavala 2001). The model quantifies the effects of changes in climate, tectonics, paleogeography, paleohydrology, solar evolution, and plant evolution on the rates of silicate weathering. Sensitivity analysis indicates that for the Paleozoic Era, the most important factor affecting  $CO_2$  was the rise of land plants. Feasible variations in tectonic, paleogeographic, and other factors result in  $CO_2$  variations that are far less divergent than those brought about by plant evolution. Sensitivity of atmospheric  $CO_2$  to the value used for the acceleration of Ca-Mg silicate weathering by plants, based on the results of modern plant-weathering studies mentioned above, is shown in Fig. 1.1. Use of a factor of 4, based on our own modern plant studies in Iceland (Moulton, West, and Berner 2000) results in the plot of  $CO_2$  versus time shown in Fig. 1.2.

The theoretical values of Fig. 1.2 agree well with those obtained for paleo- $CO_2$  by independent methods (Mora, Driese, and Colarusso 1996; McElwain and Chaloner 1995; Mora and Driese 1999; Cox, Railsback, and Gordon 2001). The figures show that tree-accelerated weathering brought about a large drop in atmospheric  $CO_2$ . However, the cause of this drop in  $CO_2$  is often misrepresented as resulting from simply an increased weathering carbon flux. Instead, the acceleration of weathering by plants was balanced by greenhouse-induced decel-



**Figure 1.2.** Plot of RCO<sub>2</sub> versus time based on GEOCARB III modeling for a fourfold effect (Moulton, West, and Berner 2000) of plants on weathering rate (line connecting dots). The superimposed vertical bars and larger squares represent independent estimates of paleo-CO<sub>2</sub> via the carbonate paleosol method (Mora, Driese, and Colarusso 1996; Mora and Driese 1999; Cox, Railsback, and Gordon 2001), and the stomatal ratio method (McElwain and Chaloner 1995), respectively.

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eration of weathering due to falling  $CO_2$ , and this resulted in the stabilization of  $CO_2$  at a series of lower levels.

Further drop of  $CO_2$  into the Carboniferous and Permian periods is due to the increased burial of organic matter accompanying the production of bioresistant organic matter by large woody land plants. This is shown in Fig. 1.3 for the result of maintaining the carbon isotopic composition of the oceans and atmosphere constant with time and comparing the result to that based on recorded carbon isotopic data (Berner 1994).

Organic burial rate in GEOCARB modeling is calculated mainly from the carbon isotopic record, with elevated oceanic  ${}^{13}C/{}^{12}C$  representing faster removal of  ${}^{13}C$ -impoverished carbon from seawater and the atmosphere due to greater photosynthesis and burial. The additional drop in CO<sub>2</sub> is due to a rise in oceanic  ${}^{13}C/{}^{12}C$  to high values between 400 and 250 million years ago. (Rapid isotopic equilibration of carbon isotopes between the oceans and the atmosphere is assumed so that burial of plant-derived organic matter on land can affect the  ${}^{13}C/{}^{12}C$  of the oceans via atmospheric and riverine transport.)

#### 1.5 Climatic and Geological Consequences

The large decrease in atmospheric  $CO_2$  beginning in the Devonian and continuing into the Carboniferous (see Fig. 1.2) correlates with the initiation of continental glaciation. The Parmo-Carboniferous glaciation was the longest and most extensive glaciation of the entire Phanerozoic (Crowley and North 1991),



**Figure 1.3.** Plot of RCO<sub>2</sub> versus time showing the effect of the variation of <sup>13</sup>C/<sup>12</sup>C during the Permian and Carboniferous. The lower curve is derived from GEOCARB II modeling (Berner 1994) based on published carbon isotope data. The upper curve represents the effect of holding the value of  $\delta^{13}C = 1\%$  for the entire period.

lasting about 80 million years and extending at times from the South Pole to as far north as 30°S. Coincidence of this glaciation with a drop in  $CO_2$  (Crowley and Berner 2001) strongly suggests that  $CO_2$ , by way of the atmospheric greenhouse effect, was a major factor in bringing about the glaciation. Although the waxing and waning of the glaciers during this period could have been caused by, for example, variations in Earth's orbit (Crowley and North 1991), the most reasonable explanation is that the lowering of  $CO_2$  to a level sufficient for the year-round accumulation of snow and ice at high latitudes allowed glaciation to be initiated and to occur on a continental scale. This lowering of  $CO_2$  resulted primarily from the rise of large vascular land plants.

The massive burial of plant-derived organic matter also led to the formation of vast coal deposits during the late Paleozoic Era. Permian and Carboniferous coals are much more abundant than coals from any other period (Bestougeff 1980), in spite of the fact that these coals are much older and have been subjected to loss by erosion for a much longer time. This must mean that original production and/or preservation for burial was unusually large. Perhaps preservation was enhanced by a lag in the evolution of lignin-decomposing microorganisms (Robinson 1991). However, the coal abundance also owes something to paleogeography. During the Permian and Carboniferous periods there was one large continent (Pangaea) with vast lowlands under wet climates that were topographically and geomorphically suitable for the growth of swamp plants and the preservation of their debris. Thus, the Permo-Carboniferous increase in organic burial probably was due to both biological and geological factors.

#### 1.6 Summary

The effect on atmospheric  $CO_2$  of the spread of large vascular plants beginning in the Devonian was twofold. First, the uptake of nutrients from rocks resulted in the enhanced weathering of Ca-Mg silicate minerals resulting in the transfer of  $CO_2$  from the atmosphere to marine Ca-Mg carbonates. Second, the rise of trees caused the production of large amounts of microbially resistant organic matter, in the form of lignin, which resulted in increased sedimentary organic burial and further  $CO_2$  removal. These changes in the carbon cycle led to a large drop in atmospheric  $CO_2$ , massive long-term glaciation, and the formation of vast coal deposits. Computer models of the long-term carbon cycle, based partly on field studies of the effects of plants on modern weathering, have been employed to calculate atmospheric  $CO_2$  levels over this time period; the resulting values agree with independent estimates.

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