THE EVOLUTION OF THE TERRESTRIAL ENVIRONMENT

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The evolution of the Earth's environment during its 4.6-b.y. history is investigated using a carbon cycle model in which the carbon is assumed to circulate among five reservoirs (the atmosphere, ocean, continents, seafloor, and mantle). In this model, we consider continental weathering, carbonate precipitation in the ocean, carbonate accretion to the continents, metamorphism of carbonates following CO_2 degassing through arc volcanism, carbon regassing into the mantle, and CO_2 degassing from the mantle. We also take into account changes in external conditions such as an increase in the solar luminosity, continental growth, and a decrease in tectonic activity with time, which obviously affect the carbon cycle. We numerically calculate the temporal variation of the carbon content of each reservoir under varying external conditions over the entire history of the Earth. We find that continental growth is required for the terrestrial environment to evolve to the present state, and that the carbon cycle has had an important role in stabilizing the surface temperature of the Earth throughout its entire history. The distribution of carbon at the surface is mainly controlled by one parameter, an accretion ratio, which represents the fraction of the seafloor carbonates accreted to the continents. When this value is equal to 0.7, correct values for the present distribution of carbon at the surface of the Earth can be obtained from the model.

INTRODUCTION

Recently Matsui and Abe (*Matsui and Abe,* 1986a; *Abe and Matsui,* 1985, 1986) have proposed that the surface of the accreting Earth was covered with a magma ocean due to the blanketing effect of an impact-induced steam atmosphere. This steam atmosphere became unstable with the decrease in the impact energy flux at the end of the accretionary period, and H_2O in the proto-atmosphere condensed to form the proto-ocean (*Matsui and Abe,* 1986b; *Abe and Matsui,* 1988). The composition of the atmosphere just after the formation of the ocean was thought to be mainly CO_2 because it is the second most abundant volatile on the surface of the Earth at the present time (*Holland,* 1978; *Kitano,* 1984). Before the continents formed, atmospheric CO_2 was controlled by the dissolution equilibrium between the atmosphere and the ocean. The partial pressure of CO_2 would not have decreased to a level lower than about 10 bar at this aquaplanet stage (*Walker,* 1985).

Because CO_2 gas has a greenhouse effect, the evolution of atmospheric CO_2 should have had a dominant effect on the evolution of the Earth's environment. This evolutionary scenario, from an impact-induced steam atmosphere to CO_2 atmosphere after oceanic formation, is consistent with the solution for the so-called "Faint Young Sun Paradox" (*Sagan and Mullen,* 1972). It has been known that the luminosity of the sun was initially about 30% lower than it is today (*Gough,* 1981) and that it has been increasing continually during the history of the Earth. So if the atmospheric composition had always been the

same as it is today, the surface temperature of the Earth would have been below 0°C up until 2 b.y. ago (*Sagan and Mullen,* 1972). However, there is no evidence indicating that the Earth was cold at that time, so this creates a paradox. If the atmosphere had more CO_2 in the past than it does today, the temperature could have been warmer even if the solar luminosity was lower (*Owen et al.,* 1979; *Walker,* 1982; *Matsui and Abe,* 1986b; *Kasting,* 1987).

Then the remaining problem is how such a CO_2-rich atmosphere has evolved to the present N_2-rich atmosphere. The changes in atmospheric CO_2 level are related to the carbon cycle among the various surface reservoirs and the interior of the Earth. The present carbonate-silicate geochemical cycle between the atmosphere, the ocean, and the continents has been studied by *Berner et al.* (1983) and *Lasaga et al.* (1985). Their results suggest that tectonic activity (such as the spreading rate of the seafloor) and the surface area of the land play an important role in surface temperature change. But these factors have changed a great deal throughout the entire history of the Earth. Also, the luminosity of the sun, which, as stated earlier, has increased by 30% of the present value, should have had an important effect on the surface temperature of the Earth.

Therefore, we will conduct a numerical simulation, starting from an impact-induced atmosphere model proposed by Matsui and Abe, and examine the response of the Earth's environment to change in external conditions such as the solar luminosity, continental growth, and tectonic activity, using the carbon cycle model.

MODEL

Present-Day Amount of Carbon

The amount of carbon at the surface of the Earth at the present time has been estimated by a number of geochemists (*Rubey,* 1951; *Poldervaart,* 1955; *Ronov and Yaroshevsky,* 1967, 1976; *Ronov,* 1968; *Hunt,* 1972; *Javoy et al.,* 1982; etc.). It is possible to estimate this amount by studying the chemical composition of the crust because almost all of the carbon exists as carbonate rocks on the continents and the seafloor. In addition to the amount, we need to know the distribution of the carbon in our study. Among these estimates, *Ronov and Yaroshevsky* (1976) studied the composition of three different types of crust (continental, subcontinental, and oceanic). Therefore, we will adopt their estimate of 9.27×10^{21} mol as the present-day amount of carbon at the surface.

The distribution of surface carbon estimated by Ronov and Yaroshevsky is shown in Table 1.

TABLE 1. *Distribution of carbon at the surface (in mol).*

Continental crust	6.07×10^{21}
Subcontinental crust	1.34×10^{21}
Oceanic crust	1.86×10^{21}
Atmosphere	5.75×10^{16}
Ocean	3.33×10^{18}

The amounts of carbon in the three types of crust are estimated by *Ronov and Yaroshevsky* (1976); the others are by *Holland* (1978).

The amounts of carbon in the atmosphere and ocean are also shown. As shown in this table, 65.5% of the total carbon is in the continental crust (land area), 14.5% is in the subcontinental crust (continental shelf), and 20.0% is in the oceanic crust.

The amount of carbon in the mantle is much more difficult to determine. *Javoy et al.* (1982) estimated it as 3.33×10^{22} mol by multiplying the concentration of carbon in peridotites by the total mass of the upper mantle. However, such a method is not yet accurate enough.

It should be noted that carbon in the crust exists in volcanic, granitic, metamorphic, and sedimentary rocks. According to *Hunt* (1972), three-fourths of it is in the form of carbonate and over half of the total carbon is in the form

of sedimentary carbonates. Organic carbon comprises only 20% of the total and it is mainly in the form of clays and shales. Living organic matter is 2.5×10^{16} mol, which is less than the amount of carbon in the atmosphere. For this reason we will not consider a cycle related to organic carbon in this model.

Carbon Cycle

We will consider five reservoirs of carbon in our model. They are the atmosphere, the ocean, the continents, the seafloor, and the mantle. In this case, the treatment of the continental shelf presents a small problem. The continental shelf should play a different role as a carbon reservoir than the continents or the seafloor. But here, for simplicity, we will assume it is a part of the continents, since the carbonates on both reservoirs never subduct into the interior.

The model is shown in Fig. 1. Each box represents a carbon reservoir and each arrow represents a flux produced by some process. These processes comprise the carbon cycle as follows: Atmospheric CO_2 dissolves in raindrops and becomes carbonic acid (H_2CO_3).

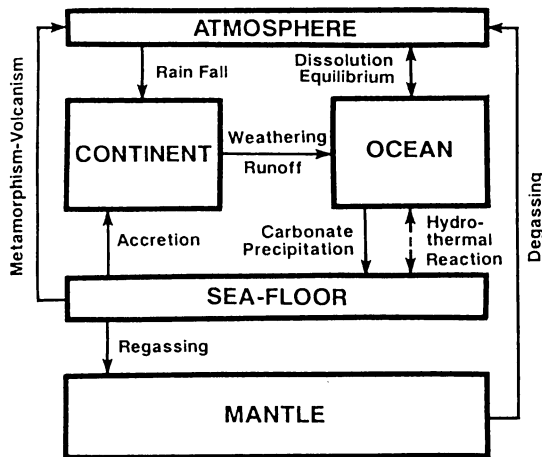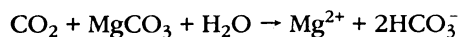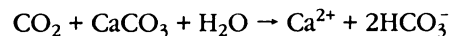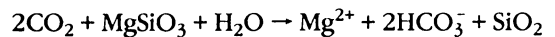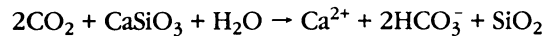**Fig. 1.** *Carbon cycle model in which each box represents a carbon reservoir and each arrow represents a carbon flux between reservoirs due to some process. The broken arrow relates to cation flux. See text for details about each process.*

When the rain falls to the surface, minerals such as silicates and carbonates are weathered. Cations and bicarbonate ions produced by this weathering are carried to the oceans by rivers. There, these ions react with each other to form carbonates. These carbonates are deposited on the seafloor where they move with the motion of the plates, and are eventually subducted under the continental crust. They are then metamorphosed under certain conditions of temperature and pressure, and CO_2 is reproduced. Finally, this CO_2 returns to the atmosphere by volcanism. This is known as "the Carbonate-Silicate Geochemical Cycle" (*Walker et al.,* 1981; *Berner et al.,* 1983; *Lasaga et al.,* 1985).

This cycle is affected by the evolution of the tectonic environment. The changes in flux due to tectonic evolution such as continental growth and tectonic activity will influence the flow of all components of the system. For example, sediments, including carbonates, that are accreted to the continental crust result in continental growth. On the other hand, sediments that are subducted under the continental crust may be reabsorbed into the mantle, which eventually allows CO_2 to be released from the mantle at the midocean ridge. Therefore, we must take into account all of these processes in our model.

Processes in the Carbon Cycle

Weathering. Silicates and carbonates are weathered by rainfall. We consider the weathering of $CaSiO_3$, $MgSiO_3$, $CaCO_3$, and $MgCO_3$. The reactions are

$$2CO_2 + CaSiO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$$
$$2CO_2 + MgSiO_3 + H_2O \rightarrow Mg^{2+} + 2HCO_3^- + SiO_2$$
$$CO_2 + CaCO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$
$$CO_2 + MgCO_3 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$$

These reactions are only symbolic for silicate weathering and, in fact, we will use the weathering function for feldspar. For carbonates, we will consider calcite and magnesite,

but not dolomite. The reason for this will be discussed later. The present-day fluxes of cations and bicarbonate ions due to weathering are estimated by multiplying the concentrations of these ions in world-average river water by the total amount of runoff in the world (*Berner et al.,* 1983).

$F_W^{cs \cdot} = 2.8 \times 10^{18}$ (mol/Ma):Ca^{2+} derived from Ca-silicate weathering

$F_W^{ms \cdot} = 3.1 \times 10^{18}$ (mol/Ma):Mg^{2+} derived from Mg-silicate weathering

$F_W^{calcite \cdot} = 8.3 \times 10^{18}$ (mol/Ma):Ca^{2+} derived from calcite weathering

$F_W^{dolomite \cdot} = 2.1 \times 10^{18}$ (mol/Ma):Ca^{2+} derived from dolomite weathering

$F_W^{dolomite \cdot} = 2.1 \times 10^{18}$ (mol/Ma):Mg^{2+} derived from dolomite weathering

where $\cdot$ represents the present value.

Instead of considering dolomite weathering here, we use the cation fluxes due to calcite and magnesite weathering. Then

$F_W^{cc \cdot} = 10.4 \times 10^{18}$ (mol/Ma):Ca^{2+} derived from Ca-carbonate weathering

$F_W^{mc \cdot} = 2.1 \times 10^{18}$ (mol/Ma):Mg^{2+} derived from Mg-carbonate weathering

We use the following weathering function

$$F_W = K_W \cdot g(T_s, P_{CO_2}) \cdot L$$

where K_W is a constant, L is the reservoir size (in mol), and g is

$$g(T_s, P_{CO_2}) =$$

$$\left(\frac{P_{CO_2}}{P_{CO_2}^{\cdot}}\right)^{0.3} \cdot \exp \left(\frac{T_s - 285}{13.7}\right) \cdot a \cdot b$$

which is derived from modification of the weathering function by *Walker et al.* (1981); a and b are correction factors determined from the condition that g → 0 (T_S → 273 K)

$$a =$$

$$\begin{cases} 1 & (T_s \geq 285K) \\ \ln\left(\frac{T_s}{273}\right) / \ln\left(\frac{285}{273}\right) & (273K \leq T_s \leq 285K) \\ 0 & (T_s \leq 273K) \end{cases}$$

and that g → 1 (T_S → 288 K)

$$b =$$

$$\exp\left\{(\frac{288 - 285}{13.7})\right\}^{-1} = 0.80$$

To estimate the constants, we assume that all carbon in the continental crust is in carbonate form and is divided into Ca-carbonate and Mg-carbonate by using the ratio $CaCO_3 : MgCO_3 = 8:2$ (*Berner et al.,* 1983). Then

$$K_W^{cc} = F_W^{cc \cdot}/g^{\cdot} \cdot L_{cc}^{\cdot} =$$
$$10.4 \times 10^{18}/(7.41 \times 10^{21} \times 0.8) =$$
$$1.75 \times 10^{-3} \text{ Ma}^{-1}$$

$$K_W^{mc} = F_W^{mc \cdot}/g^{\cdot} \cdot L_{mc}^{\cdot} =$$
$$2.1 \times 10^{18}/(7.41 \times 10^{21} \times 0.2) =$$
$$1.42 \times 10^{-3} \text{ Ma}^{-1}$$

where $g^{\cdot} = 1$.

For the constants in the equation for silicate weathering, we assume that the size of the silicate reservoirs are proportional to the continental surface area, i.e., $L \propto S_C \propto f_{S_C}$, where S_C is the continental area and f_{S_C} is the ratio of continental area at a given time to the present value ($=S_C/S_C^{\cdot}$). We define the silicate weathering function as follows

$$F_W = K_W \cdot g(T_s, P_{CO_2}) \cdot f_{S_C}$$

Then

$$K_W^{cs} = F_W^{cs\bullet}/g^\bullet \cdot f_{S_C}^\bullet = 2.8 \times 10^{18} \text{ mol/Ma}$$

$$K_W^{ms} = F_W^{ms\bullet}/g^\bullet \cdot f_{S_C}^\bullet = 3.1 \times 10^{18} \text{ mol/Ma}$$

where $g^\bullet = f_{S_C}^\bullet = 1$.

It is noted that this function includes the effects of an increase in rainfall and runoff due to an increase in surface temperature (see *Walker et al.*, 1981).

Carbonate precipitation. Cations and bicarbonate ions are brought to the oceans through rivers. In the oceans, they react with each other and form carbonates. The reactions are

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$$

$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \rightarrow CaMg(CO_3)_2$$
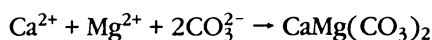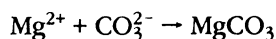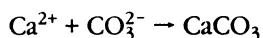
At the present day, about 40% of carbonates are dolomites. It is known from several experiments that dolomites are hard to produce by direct precipitation even under supersaturation conditions. They can be produced through secondary metamorphism by substituting magnesium ions for calcium ions in calcite at high temperature ($\geq 150°C$) (see *Kitano*, 1984; *Holland*, 1978). Magnesite has an even larger solubility product than dolomite as is shown by the lack of evidence for magnesite formation in the present oceans. Because of this, the production of magnesite gives us an upper limit to the concentration of magnesium ions in the oceans. Therefore, we will consider magnesite as the only product of magnesium precipitation and calcite as the only product of calcium precipitation.

Almost all of the present carbonates are produced by organisms. Inorganic carbonates such as oolite are hardly seen. However, in the absence of organic processes, carbonates would be produced inorganically if the ion activity product of carbonate in the ocean exceeds some critical value. The difference

TABLE 2. *Equilibrium constants and activity coefficients.*

K_0	3.48×10^{-2}	α_{H_2O}	0.967
K_1	4.45×10^{-7}	$\gamma_{H_2CO_3}$	1.130
K_2	4.69×10^{-11}	$\gamma_{HCO_3^-}$	0.550
K_{sp}^{cc}	3.60×10^{-9}	$\gamma_{CO_3^{2-}}$	0.021
K_{sp}^{mc}	1.00×10^{-5}	$\gamma_{Ca^{2+}}$	0.203
		$\gamma_{Mg^{2+}}$	0.260

between the organic and inorganic processes is mainly the level for the equilibrium and possibly the place where the carbonates are precipitated. For simplicity, we will only consider the inorganic production of carbonates. This flux F_P is estimated so as to maintain chemical equilibrium between the atmosphere and the oceans; carbonates are precipitated when the ion activity product of carbonate exceeds the thermodynamic solubility product (see Table 2; details will be shown in the next section).

Accretion. Some fraction of the carbonates deposited on the seafloor are considered to accrete onto the continental crust at the subduction zones. This idea is based on the accretion model in which an accretionary prism is formed by the accretion of seafloor sediments onto the continental crust (*Sleely et al.*, 1974; *Karig and Sharman*, 1975). Seamounts also accrete onto the continents. Examples of this are the west coast of North America and East Asia. To take into account this process, we define the accretion ratio as a parameter describing the amount of carbonates that accrete onto the continents (Fig. 2).

This flux is equal to the ratio of the accreting carbonates multiplied by the flux of the subducting carbonates and is expressed as

$$F_A = A \cdot t_r^{-1} \cdot P$$

where A is the accretion ratio, t_r is the residence time of carbon on the seafloor, and P is the amount of carbon in the seafloor reservoir (in mol).
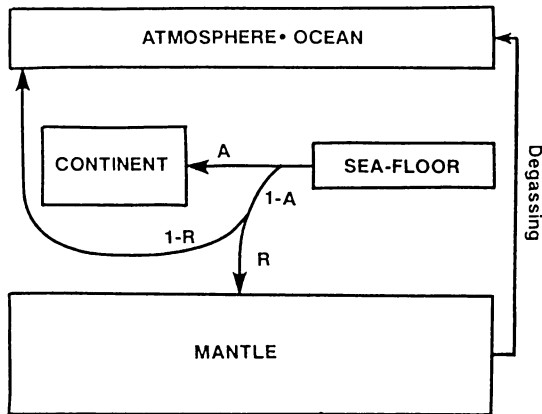
Fig. 2. *Definition of parameters A (accretion ratio) and R (regassing ratio). Parameter A represents the ratio of seafloor carbonates that accrete onto the continents to the total amount of precipitated seafloor carbonates; R represents the ratio of seafloor carbonates that regas into the mantle to the subducted carbonates. Note that the actual fraction of carbon regassed into the mantle is (1-A) · R.*

Regassing. Some fraction of carbonates subducted under the continental crust may be reabsorbed into the mantle. Actually, we do not know how much carbon is regassed into the mantle, but it should be related to the geotherm and the carbonate metamorphism conditions. According to *DesMarais* (1985), carbonates could not subduct into the mantle in the Archean because of the higher geotherm then. But at present-day values, 3-50% of the carbonates reaching subduction zones should be able to subduct into the mantle (*DesMarais,* 1985).

Here we define the regassing ratio as a second parameter (Fig. 2). The flux of regassing is expressed as

$$F_R = (1 - A) \cdot R \cdot t_r^{-1} \cdot P$$

where R is the regassing ratio.

Metamorphism-volcanism. CO_2 is produced by metamorphism of carbonates subducted under the continental crust. This CO_2 can be released back into the atmosphere by volcanic activity.

The metamorphic reactions are as follows:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$
$$MgCO_3 + SiO_2 \rightarrow MgSiO_3 + CO_2$$
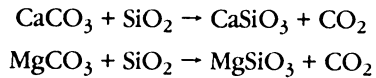
This flux is also difficult to estimate. *Berner et al.* (1983) estimated it at 5.9×10^{18} mol/Ma by explaining the present CO_2 budget. Here we express this flux as

$$F_M = (1 - A) \cdot (1 - R) \cdot t_r^{-1} \cdot P$$

Degassing. CO_2 is also degassed from midocean ridges and hot spots. It should be distinguished from the degassing of CO_2 as a volcanic gas at island arcs because the former comes from the mantle but the latter is considered to be a recycled gas.

This flux is estimated by measuring the C/^{3}He or $^{13}C/^{12}C$ in the hydrothermal fluid and in the basaltic glasses at the midocean ridge. Some recent estimates are $10-20 \times 10^{18}$ mol/Ma (*Javoy et al.,* 1982), $1-8 \times 10^{18}$ mol/Ma (*DesMarais,* 1985), or 2.2×10^{18} mol/Ma (*Marty and Jambon,* 1987). Among these, the value of Javoy et al. is considered to be too large when compared with more recent estimates. Therefore, we will use a flux of 4×10^{18}, which is the average of the latter two estimates.

Primordial degassing of CO_2 from the mantle is thought to have been small. This is because the solubility of CO_2 in a magma ocean is very low, so most of the CO_2 produced by impact degassing during accretion (e.g., *Matsui and Abe,* 1986a) would have existed in the proto-atmosphere. We assume as an extreme case that the initial content of CO_2 in the mantle was nearly zero, and if regassing of CO_2 into the mantle had not occurred, CO_2 degassing would be zero. But if regassing has occurred, the current degassing would be higher. We also assume that the amount of degassing is proportional to the carbon content in the mantle and the degassing rate is proportional to the seafloor production rate, which is, in turn, proportional

to heat flow. The expression of this flux is

$$F_D = K_D \cdot f_Q \cdot C_{mantle}$$

where K_D is a constant, f_Q is the ratio of the heat production rate at a given time to the present value, and C_{mantle} is the carbon content in the mantle. K_D is determined by giving the initial amount of carbon, C_{total}, which is taken as a parameter, then

$$K_D = \frac{F_D^\bullet}{f_Q^\bullet \cdot C_{mantle}^\bullet} = \frac{F_D^\bullet}{C_{total}^0 - C_{surface}^\bullet}$$

where

$$f_Q^\bullet = 1.0$$
$$C_{total}^0 = C_{surface}(t) + C_{mantle}(t)$$

Volcanic-seawater reaction (hydrothermal reaction). Magnesium ions in the ocean react with seafloor basalts and are exchanged for stoichiometrically equivalent calcium ions (*Holland*, 1978; *Wolery and Sleep*, 1976). This occurs mainly at the midocean ridges, but it also occurs at other lower temperature regions of the seafloor.

The reaction is

$$Mg^{2+} + CaSiO_3 \rightarrow MgSiO_3 + Ca^{2+}$$
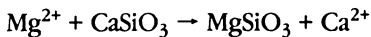
where $CaSiO_3$ represents, for example, volcanic glasses, plagioclases, pyroxenes, and olivines, and $MgSiO_3$ represents smectites, amphiboles, chlorites, and other hydrous phases.

We will assume that this flux is proportional to the amount of magnesium in the ocean and to the spreading rate of the seafloor, which is, in turn, proportional to the heat flow. The flux is

$$F_V = K_V \cdot f_Q \cdot M_{Mg}$$

where K_V is a constant and M_{Mg} is the amount of magnesium ions in the ocean (in mol).

This reaction controls the amount of both the magnesium and calcium ions in the ocean. Their present values are $M_{Ca}^\bullet = 1.37 \times 10^{19}$ mol and $M_{Mg}^\bullet = 7.26 \times 10^{19}$ mol (*Broecker*, 1974).

To estimate the constant K_V, we assume that magnesium ions added to the ocean by weathering are taken up by this reaction today (see *Berner et al.*, 1983). Then

$$K_V = \frac{F_V^\bullet}{f_Q^\bullet \cdot M_{Mg}^\bullet} = \frac{F_W^{ms\bullet} + F_W^{mc\bullet}}{M_{Mg}^\bullet} = 0.0716$$

Other processes. All carbon-related species in the atmosphere, oceans, and seafloor are in chemical equilibrium. This equilibrium depends on the pH, temperature, pressure, and salinity of the ocean. Among these, pH is set as a free parameter, but our simple box model cannot take into account the other factors. Therefore, for all equilibrium values, we will use constants, as will be shown in the next section.

Of course, the seafloor is weathered by seawater. At the present time, however, this process is very limited compared to continental weathering because of its low temperature, so we do not treat this process here. It might be of more importance, however, in the cases where the bottom of the ocean is rather hot or the pH in the ocean is very low.

External Conditions

There are some factors that have a strong influence on the Earth's environment. These are solar luminosity, continental surface area, and tectonic activity such as plate motion. These factors have been changing throughout the entire history of the Earth. We will attempt to analyze the response of the box model to variations in these external conditions. ("External" means that they are not constrained by the system of the carbonate-silicate geochemical cycle.)

Increase in solar luminosity. According to the theory of stellar evolution, the luminosity of the sun has been increasing since the Earth's formation. There are several evolutional models, but here we adopt the model proposed by *Gough* (1981). According to his model, the luminosity of the sun at 4.6×10^9 years ago was about 30% less than that of today. The luminosity change given by him is

$$L(t) = \left[1 + \frac{2}{5} \left(1 - \frac{t}{t^*} \right) \right]^{-1} \cdot L^*$$

where L is the luminosity of the sun, L^* is its present value, and t^* is the present age of the sun ($=4.6 \times 10^9$ yr). The solar constant at the Earth's orbit is

$$S(t) = \frac{L(t)}{4\pi D_E^2}$$

where D_E is the distance of the Earth from the sun. So we have

$$S(t) = \left[1 + \frac{2}{5} \left(1 - \frac{t}{t^*} \right) \right]^{-1} \cdot S^*$$

where S^* is the present value of the solar constant.

This change (shown in Fig. 3) affects the surface temperature of the Earth, as suggested by *Sagan and Mullen* (1972).
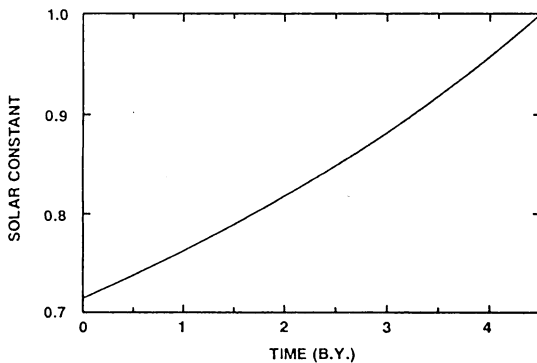
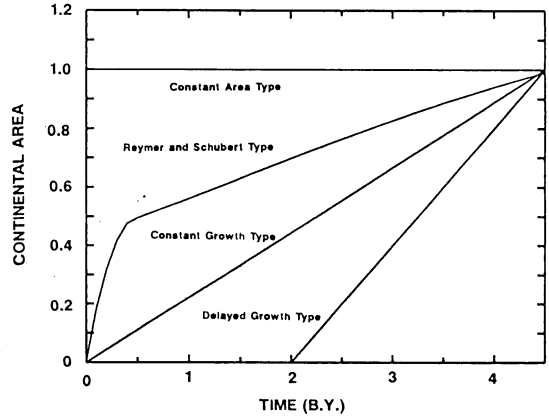**Fig. 3.** *Temporal variation of the solar constant (Gough, 1981).*

Fig. 4. *Continental growth models used in our simulation. The vertical axis represents the ratio of the continental area at a given time to that at the present time.*

Continental growth. Although many continental growth models have been proposed, we still have very little understanding of the process, especially in the Hadean and early Archean periods. For the present purpose, we do not need a detailed model. We will use several specific models: no continent model ($S_C = 0$), constant area model ($S_C = S_C^*$), constant growth model ($S_C \propto t$), delayed growth model ($S_C = 0$ for $t \leq t_C$ and $S_C \propto t$ for $t \geq t_C$), and the growth model proposed by *Reymer and Schubert* (1984). These models are shown in Fig. 4. (We should note here that, since we do not consider the continental shelves separately in this study, S_C means the area of the entire continental crust, not just the actual land area.)

We define the ratio of continental area at a given time to that at the present as

$$f_{S_C}(t) = \frac{S_C(t)}{S_C^*}$$

Decrease in tectonic activity. Tectonic activity is thought to be proportional to the heat flow from the interior of the Earth. To know its true temporal variation, we need to calculate the thermal history of the Earth,
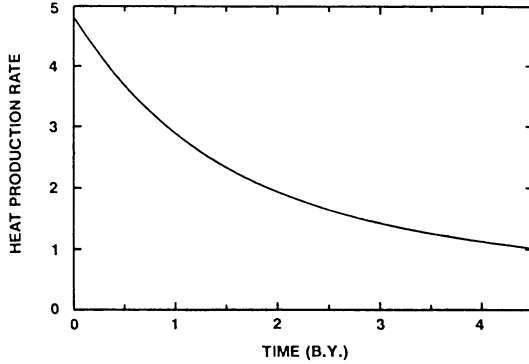
Fig. 5. *Temporal variation of the radiogenic heat production rate that is representative of tectonic activity. The vertical axis represents the ratio of the heat production rate at a given time to that at the present time.*

taking into account the energy of accretion and differentiation, and radiogenic heat production. However, for simplicity, we assume that the heat flow is proportional only to the radiogenic heat production rate (*Turcotte and Schubert*, 1982) as shown in Fig. 5. We define the ratio of the heat production rate at a given time to the present one as

$$f_Q(t) = \frac{Q(t)}{Q^*}$$

Then, the residence time of the seafloor is defined by using this heat production rate

$$t_r(t) = \frac{Q^*}{Q(t)} \frac{\sqrt{S_O}}{\sqrt{S_O^*}} \cdot tr^*$$

where t_r^* is the present seafloor residence time, equal to 60 Ma (*Sclater and Parsons,* 1981; *Sprague and Pollack,* 1980).

Surface Temperature

We need to calculate the surface temperature of the Earth for a given atmospheric CO_2 level and solar constant. For this purpose, we will use the results of a numerical calculation by *Kasting and Ackerman* (1986). They calcu-

lated the greenhouse effect of various CO_2 levels for two different solar constants ($S/S^* = 0.7, 1.0$) using a radiative-convective equilibrium model. In their calculation, the tropospheric lapse rate was set equal to its moist adiabatic value and the effect of clouds was not included explicitly. As a consequence of their relative humidity parameterization, a sharp increase in the surface temperature is seen in the present-day Earth model. However, this feature has only a small influence on our simulation, as will be seen later.

Their results are given for only two values of the solar constant. Therefore, we interpolate their results to calculate the surface temperature for the intermediate values of the solar constant.

METHOD

Basic Equations

In order to determine the evolution of each reservoir, we solve the following mass balance equations

$$\frac{dL_{cc}}{dt} = F_A^{cc} - F_W^{cc}$$

$$\frac{dL_{mc}}{dt} = F_A^{mc} - F_W^{mc}$$

$$\frac{dP_{cc}}{dt} = F_P^{cc} - F_A^{cc} - F_M^{cc} - F_R^{cc}$$

$$\frac{dP_{mc}}{dt} = F_P^{mc} - F_A^{mc} - F_M^{mc} - F_R^{mc}$$

$$\frac{dC_{mantle}}{dt} = F_R^{cc} + F_R^{mc} - F_D$$

$$\frac{dM_{Ca}}{dt} = F_W^{cc} + F_W^{cs} + F_V - F_P^{cc}$$

$$\frac{dM_{Mg}}{dt} = F_W^{mc} + F_W^{ms} - F_V - F_P^{mc}$$

where cc = calcium carbonate, mc = magnesium carbonate, cs = calcium silicate, and ms = magnesium silicate. L represents the

continental reservoir, P represents the seafloor reservoir, and M represents the oceanic reservoir. F_W, F_P, F_A, F_R, F_M, F_D, and F_V are the fluxes already explained in the previous section.

In the above equations, F_P^{cc} and F_P^{mc} are the carbonate precipitation fluxes. They are determined so as to sustain a chemical equilibrium among the atmosphere, the oceans, and the carbonate on the seafloor. To estimate these fluxes, we need to know the concentrations of the cations in the ocean. Therefore, we consider two equations for the concentrations of the two species of cations Ca^{2+} and Mg^{2+}.

We solve the mass balance equations under the constraints of the mass conservation of carbon and the condition of chemical equilibrium between the carbon-related species in the atmosphere, the ocean, and the seafloor reservoir. Under these constraints and by varying the external conditions described in the previous section, we can solve the mass balance equations.

Mass conservation of carbon. We set the total amount of carbon in the system (surface + mantle) as a free parameter. This amount is assumed to be conserved throughout the entire history of the Earth.

$$C_{total} = C_{surface} + C_{mantle}$$

In this equation

$$C_{surface} = L_C + P_C + A_C + M_C$$

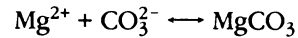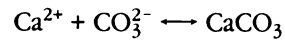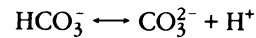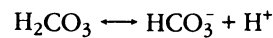where A_C is the atmospheric carbon content in mol, and
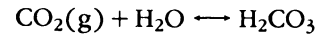
$$M_C = M_{H_2CO_3} + M_{HCO_3} + M_{CO_3}$$
$$L_C = L_{cc} + L_{mc}$$
$$P_C = P_{cc} + P_{mc}$$

Chemical equilibrium. As stated earlier, we assume that chemical equilibrium is always maintained between the carbon-related species in the atmosphere, the oceans, and the

seafloor reservoir. These are expressed as

$$CO_2(g) + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 \longrightarrow HCO_3^- + H^+$$
$$HCO_3^- \longrightarrow CO_3^{2-} + H^+$$
$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$
$$Mg^{2+} + CO_3^{2-} \longrightarrow MgCO_3$$

We can rewrite these relations by using the law of mass action

$$K_0 = \frac{a_{H_2CO_3}}{P_{CO_2} \cdot a_{H_2O}}$$

$$K_1 = \frac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}}$$

$$K_2 = \frac{a_{CO_3^{2-}} \cdot a_{H^+}}{a_{HCO_3^-}}$$

$$K_{sp}^{cc} = a_{Ca^{2+}} \cdot a_{CO_3^-}$$

$$K_{sp}^{mc} = a_{Mg^{2+}} \cdot a_{CO_3^-}$$

where the K_i are the equilibrium constants and the a_i are the activities. The activities are defined by

$$a_i = \gamma_i \cdot m_i$$

where γ_i is an activity coefficient and m_i is the concentration of ions of the i-th component in the seawater in mol/l. The equilibrium constants and the activity coefficients depend on the pH, temperature, pressure, and salinity of the ocean. However, as stated earlier, we use the constant values for them at 25°C and 1 atm total pressure as shown in Table 2 (*Kramer*, 1965; *Berner*, 1965; *Kitano*, 1984).

We use four parameters in our simulation. They are C_{total}, pH, A, and R. C_{total} is assumed to be equal to the initial amount of carbon at the surface, $C_{surface}^0$, for the reason we stated earlier. There are lower and upper limits to this value. The lower limit is the present-day amount of carbon at the surface, and the upper

limit is determined by the conditions required for liquidization of the impact-induced steam atmosphere. According to *Abe* (1988a), the latter corresponds to 1 kbar of CO_2 partial pressure. Then

$$9.27 \times 10^{21} \text{ mol} \leq C_{total} \leq 1.2 \times 10^{23} \text{ mol}$$

Numerical Scheme

We use the finite difference scheme to solve the mass balance equations numerically. In the mass balance equations, however, we do not know the carbonate precipitation fluxes (F_p^{cc}, F_p^{mc}). Therefore, we cannot solve them by using a simple forward difference scheme.

In this study, we consider that calcite precipitates in the ocean when the seawater is supersaturated with respect to calcite, which means that the ion activity product of calcite (IAP = $a_{Ca^{2+}} \cdot a_{CO_3^-}$) exceeds the thermodynamic solubility product (= K_{sp}^{cc}; shown in Table 2). On the other hand, calcite does not precipitate when the seawater is undersaturated with calcite (IAP $\leq K_{sp}^{cc}$). We consider a similar condition for magnesite precipitation. To calculate the ion activity products, however, we first need to know the amounts of the cations and carbonate ions carried to the oceans in each time step. Then we can estimate the carbonate precipitation fluxes by comparing IAP with K_{sp}.

For this purpose, we use the Euler-backward scheme. This is one of the difference schemes that is expressed as

$$\begin{cases} X^{n+1'} = X^n + \Delta t \cdot f^n \\ X^{n+1} = X^n + \Delta t \cdot f^{n+1'} \end{cases}$$

where $f^{n+1'} = f(X^{n+1'},(n+1)\Delta t)$. The first approximation $X^{n+1'}$ is determined from the Euler scheme and X^{n+1} is derived from the backward scheme (but in this case is not the implicit scheme). However, our scheme is different from this in the sense that $X^{n+1'}$ is not

just an approximation but has a physical meaning: It is the amount of cations carried into the ocean during one time step.

The carbonates on the seafloor will dissolve in the seawater when the ocean is undersaturated with the carbonates. It is therefore noted that the carbonate precipitation fluxes can even have a negative value until the carbonates on the seafloor have been exhausted.

The time step is initially taken to be 1.0 Ma as the standard. We choose a different, appropriate time step if the numerical calculation becomes unstable.

Initial Conditions

As described before, we assume that all the carbon initially existed in the atmosphere because of the low solubility of CO_2 in a magma ocean during planetary accretion. Therefore, as an initial condition for the amount of carbon

$$C_{surface}^0 = C_{total}$$
$$C_{mantle}^0 = 0$$

The distribution of carbon in each reservoir is determined by the initial amount of the cations. When the initial amount of the cations was nearly zero, the carbon distributed between the atmosphere and the ocean depends on the value of the pH.

In the proto-atmosphere, about 340×10^{17} kg of HCl and 48×10^{17} kg of SO_2 are considered to have existed. Because these gases can easily dissolve into water, the proto-ocean just after formation should have been a strong acid solution with a molality ≈ 0.5 mol/l (*Kitano*, 1984). This solution immediately eroded the seafloor basalts, and cations were supplied. Then the ocean would have been neutralized. Dissolving experiments of basalts in 0.5 mol/l HCl solution and also measurements of the composition of HCl acid hot springs give us information on the composition of such a proto-ocean. One of these estimates is shown in Table 3 (*Ronov*, 1964).

TABLE 3. *The composition of proto- and present ocean (%) (Ronov, 1964).*

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Total
Proto-ocean	29	24	30	17	100
Present ocean	3.2	10.7	83.1	3.0	100

We will use this estimate as an initial condition for the cations. We assume that the total charge of the cations in the ocean has never changed. (This is the same as assuming the amounts of Cl^- and SO_4^{2-} have not changed.) Then we can determine the concentration of cations in the proto-ocean as shown in Table 4.

We can estimate the initial amount of cations by multiplying the concentration by the volume of the ocean V_o ($= 1.36 \times 10^{18} \, m^3$)

$$M_{Ca}^{0'} = 115 \times V_o = 1.56 \times 10^{20} \, mol$$

$$M_{Mg}^{0'} = 95 \times V_o = 1.29 \times 10^{20} \, mol$$

Therefore, we can determine A_C^0, M_C^0, L_C^0, P_C^0, M_{Ca}^0, and M_{Mg}^0 by using the method described in the previous section.

Actually, the later evolution of each reservoir is not very sensitive to the initial amount of the cations except for the case in which too many cations exist compared to carbon ($\approx 10^{22} \, mol$).
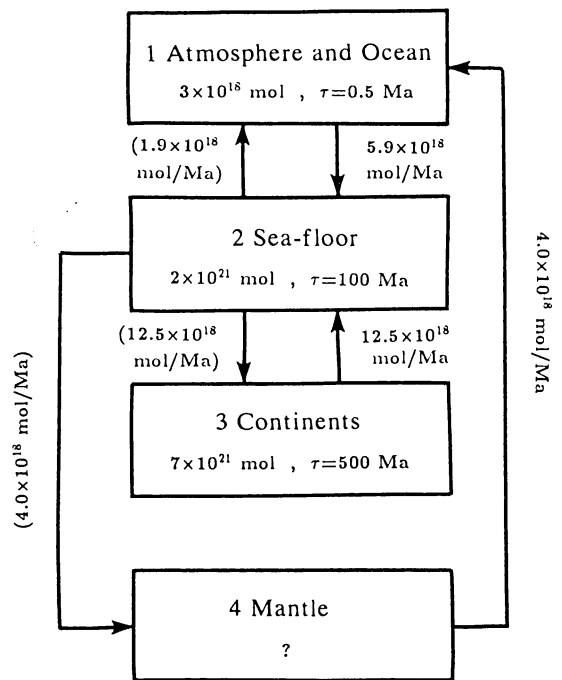
TABLE 4. *The concentration (upper row) and charge (lower row) of cations (mol/m³).*

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Total
Proto-ocean	115	95	119	67	—
	230	190	119	67	606
Present ocean	10	53	470	10	—
	20	106	470	10	606

STATIONARY SOLUTIONS

Present-Day Values of A and R

At the present time, the carbon cycle system may be in a stationary state. If so, we may be able to estimate A and R based on the present

Fig. 6. *Present-day stationary model for the carbon cycle. Each of the values represents the carbon fluxes between the reservoirs in mol/Ma. (Those in parentheses are the adjusted values for the stationary state of this sytem; the others are observed values.) The reservoir sizes (in mol) and the residence times (in Ma) are also shown in each reservoir.*

fluxes between each reservoir as shown in Fig. 6. In this figure, we number each reservoir (1 = the atmosphere and the ocean, 2 = the seafloor, 3 = the continents, and 4 = the mantle), and represent a flux from reservoir i to j as F_{ij}. In a stationary state, the flux of carbonate precipitation in the ocean will be equivalent to that of the weathering from the continents to the oceans to adjust the oceanic cation budget. Therefore

$$F_{41}^* = F_D^* = 4.0 \times 10^{18} \, mol/Ma$$

$$F_{12}^* = F_W^{cs*} + F_W^{ms*} = 5.9 \times 10^{18} \, mol/Ma$$

$$F_{32}^* = F_W^{cc*} + F_W^{mc*} = 12.5 \times 10^{18} \, mol/Ma$$

To adjust the other fluxes to the above observed values so as to satisfy a stationary state

$$F_{21}^{\bullet} = F_{12}^{\bullet} - F_{41}^{\bullet} = 1.9 \times 10^{18} \text{ mol/Ma}$$

$$F_{23}^{\bullet} = F_{32}^{\bullet} = 12.5 \times 10^{18} \text{ mol/Ma}$$

$$F_{24}^{\bullet} = F_{41}^{\bullet} = 4.0 \times 10^{18} \text{ mol/Ma}$$

Using these fluxes, we can calculate the values of A and R as

$$A = \frac{F_{23}^{\bullet}}{F_{21}^{\bullet} + F_{23}^{\bullet} + F_{24}^{\bullet}} = 0.68 \simeq 0.7$$

$$R = \frac{F_{24}^{\bullet}}{F_{21}^{\bullet} + F_{24}^{\bullet}} = 0.68 \simeq 0.7$$

These values are required for the present-day stationary state.

The ratio of the carbonates that subduct into the mantle to the total subducted carbonates is

$$(1 - A) \cdot R = 0.21$$

which is in the range of the recent estimate of 3-50% (*DesMarais*, 1985).

Present-Day Amount of Surface Carbon

We can derive the stationary solutions for the given system by setting the left sides of the mass balance equations equal to zero. The amount of carbon at the surface is written as

$$\begin{aligned}
C_{\text{surface}} &= L_C + P_C + A_C + M_C \\
&\approx L_C + P_C \\
&= \frac{A}{1 - A} \frac{K_W^{cs} + K_W^{ms}}{K_W^{cc}} \cdot f_{S_C} + \frac{t_r}{(1 - A) \cdot R} \cdot F_D
\end{aligned}$$

It is shown from this solution that the amount of carbon at the surface is a function of the tectonic parameters that characterize the model. The existence of this stationary solution suggests that the stable amounts of carbon on the continents and the seafloor are determined by a given tectonic condition.

To examine a controlling factor that determines the present-day amount of carbon at the surface, we investigate the effect of A and R

on the stationary solution by using the present observed values for other parameters ($f_{S_C}^{\bullet} = 1.0$, $t_r^{\bullet} = 60$ Ma, and $F_D^{\bullet} = 4.0 \times 10^{18}$ mol/Ma). The result is shown in Fig. 7. It is shown that the amount of carbon at the surface does not depend greatly on the value of the regassing ratio R, but does depend on the value of the accretion ratio A. The recent estimate for the amount of carbon at the surface by *Ronov and Yaroshevsky* (1976) can be explained when the accretion ratio is equal to 0.7.

This is consistent with the value obtained by the previous section on the present-day stationary flux. On the other hand, the value of the regassing ratio cannot be obtained from the above discussion.

The values of A and R would have been changed through the Earth's history. (For example, the regassing ratio depends on the geotherm, which should have been changed with time.) However, we will use the values A = 0.7 and R = 0.7, which are required for
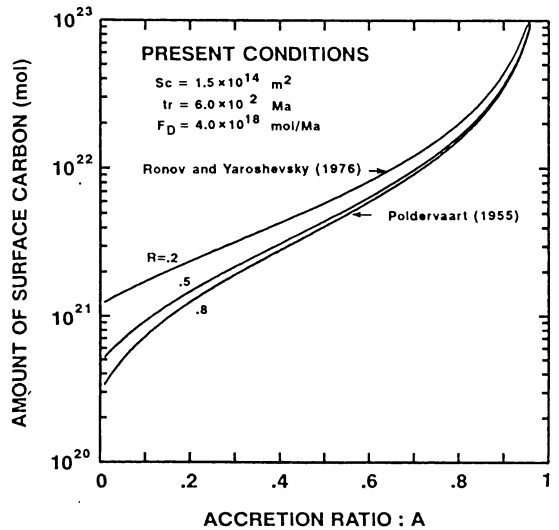

Fig. 7. *Amount of surface carbon under the present conditions as a function of the accretion ratio and the regassing ratio. The arrows show the estimates for the amount of surface carbon by Poldarvaart (1955) and Ronov and Yaroshevsky (1976), respectively.*

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the present-day stationary state, as the standard in our calculations. The geophysical meaning of parameter A will be discussed later.

RESULTS

Evolution of Carbon Reservoirs

We consider the case in which the carbonates on the seafloor subduct into the mantle (regassing ratio $\neq 0$). In this case, the amount of CO_2 degassing from the mantle will be proportional to the increase in the carbon content of the mantle. At first the total amount of carbon is assumed to be 1×10^{22} mol, which is nearly equal to the present surface value ($C_{total} = 1 \times 10^{22}$ mol $\approx C^{\bullet}_{surface}$), and the pH is taken to be equal to 8 (the present value).

No continental growth model. If there were no continents on the Earth, the level of the CO_2 in the atmosphere-ocean system would never decrease throughout the Earth's history in Fig. 8. The atmospheric CO_2 level

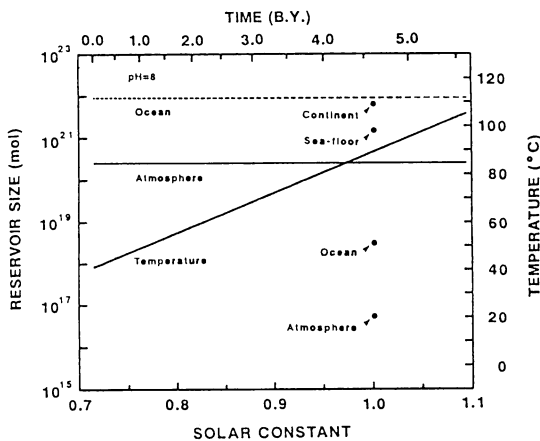**Fig. 8.** *No continental growth model (pH = 8, C_{total} = 1 × 10²² mol). Variation of carbon levels (in mol) in each reservoir and surface temperature (° C) of the Earth are shown as a function of the solar constant and time. The heavy solid line represents the surface temperature, the light solid line represents the atmospheric carbon reservoir, and the dashed line represents the oceanic carbon reservoir. The solid circles represent the present values of each reservoir. It is noted that surface temperature increases monotonically with an increase in the solar constant in this case.*

corresponds to about 2 bar in this model. This is because the lack of a supply of cations from the continents to the ocean prohibits precipitation of CO_2 in the ocean as carbonates, resulting in no regassing. The ratio of the amount of carbon in the atmosphere to that in the ocean is determined only by the value of the pH in the ocean. This is because we considered the initial amount of cations in the ocean to be equal to zero, as well as assuming that there was no supply of cations from the continents. Therefore, there is no carbonate in the seafloor reservoir. Even if we assume appropriate values for the initial amount of cations in the ocean (as stated in the previous section), the result is almost the same as in this model. A large amount of carbonates precipitate at first, but they soon subduct and return to the atmosphere through volcanism. After that, the situation becomes the same as mentioned above. It is noted here, however, that we neglect the effect of seafloor weathering that may also supply the cations to the oceans. Therefore, this estimate corresponds to the maximum limit for the atmospheric CO_2 level at a given ocean pH. However, as will be discussed later, even if we consider the effect of seafloor weathering, the partial pressure of atmospheric CO_2 would never decrease to a certain level. In any case, it is shown that the surface temperature of the Earth increases with an increase in the solar constant. In other words, the Earth's environment would not have evolved to the present state if the continents were not formed.

A continental growth model. There are continents on the Earth at present. Thus, we should turn our attention to the more realistic models that include continental growth. Here we study the delayed continental growth model in which the continents begin to grow 2 b.y. after the formation of the Earth (Fig. 9). Both the accretion and regassing ratios are 0.7. Before the formation of the continents, the situation is the same as mentioned in the first case. Once the continents begin to form, cations are supplied to the ocean and thus
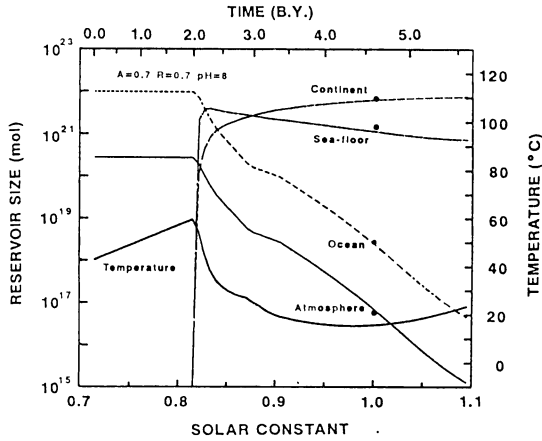
Fig. 9. *Delayed continental growth model (A = 0.7, R = 0.7, pH = 8, C_{total} = 1 × 10²² mol). Variation of carbon levels in each reservoir and surface temperature of the Earth as a function of the solar constant and time. The meaning of the curves and symbols are the same as in Fig. 8.*

carbonates can precipitate onto the seafloor. Some fraction of these carbonates subducts somewhere, but the rest accretes to the continents. Subducted carbonates are disintegrated into carbon dioxide and calcium silicate, and CO_2 returns to the atmosphere through volcanism. The accretion of seafloor carbonates onto continents results in a decrease of CO_2 in the atmosphere-ocean system. The surface temperature therefore decreases. This suggests that the surface temperature could be stabilized in spite of the increase in the solar constant. The sharp decreases in the temperature and the reduction rate of the atmospheric and oceanic reservoirs shown in Fig. 9 are due to the sharp increase in the temperature profile of *Kasting and Ackerman* (1986) that we used in this study.

The continents are a very stable carbon reservoir and provide a longer residence time for carbonates than the other reservoirs do. This is another important role of continental formation in addition to that of being a cation source for the ocean. As shown in Fig. 9, this model explains well the present distribution of carbon.

An alternative continental growth model. Various continental growth models have been proposed. Here we study the effect of, the continental growth curve on the numerical results. In this model, the continents are assumed to grow in a manner proposed by *Reymer and Schubert* (1984) (Fig. 10). The accretion and regassing ratios are the same as in the previous model. The evolution of each reservoir and the surface temperature are almost determined at the beginning of the Earth's history, since the continents grow rapidly. The basic features of the evolution are, however, almost the same as in the previous model. It is suggested that the evolution of each reservoir does not depend greatly on the continental growth model after the continents grow.

This model also explains well the present distribution of carbon in each surface reservoir. It is shown that the distribution of carbon depends mainly on the accretion ratio. In order to explain the present distribution, the accretion ratio A needs to be 0.7. For other values, the distribution of carbon is quite

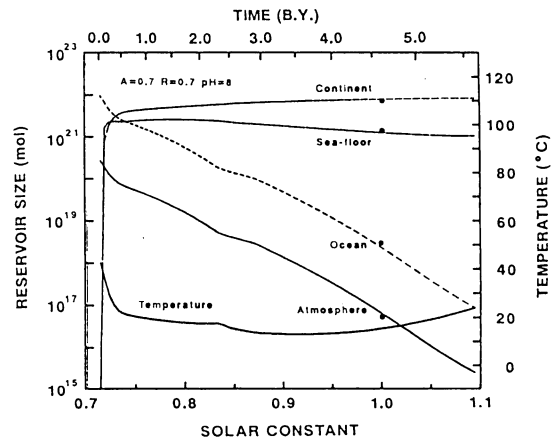**Fig. 10.** *Reymer and Schubert (1984) growth model (A = 0.7, R = 0.7, pH = 8, C_{total} = 1 × 10²² mol). Variation of carbon levels in each reservoir and surface temperature of the Earth as a function of the solar constant and time. The meaning of the curves and symbols are the same as in Fig. 8.*

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different from the present one. For example, a lower value of A will result in a lower carbon content on the continents than the seafloor.

The distribution of the carbon also depends on a regassing ratio that is equal to 0.7 in this model. The distribution changes when we assume other values for the regassing ratio. However, the effect of R on the distribution is much weaker than that of the accretion ratio, A. We can conclude that the distribution of carbon is mainly determined by A, and that the present distribution is well explained when A is equal to 0.7.

Effect of pH. Even when we use 7 as the value of the pH instead of 8, the result does not change significantly except for the ratio of carbon in the atmosphere to that in the ocean (Fig. 11). It is noted that the level of atmospheric CO_2 does not depend on the pH as long as the pH is larger than 6. Hence, the surface temperature stays at the same level as when the pH is equal to 8. We can conclude that the pH of the oceans does not greatly affect the surface temperature as long as the continents exist.
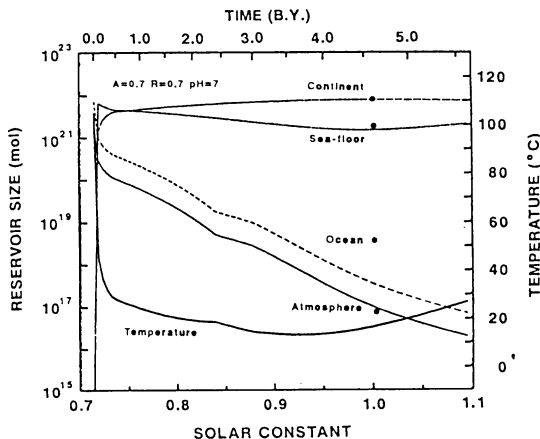

Fig. 11. *Reymer and Schubert (1984) growth model with different pH value (A = 0.7, R = 0.7, pH = 7, C_{total} = 1 × 10^{22} mol). Variation of carbon levels in each reservoir and surface temperature of the Earth as a function of the solar constant and time. The meaning of the curves and symbols are the same as in Fig. 8.*
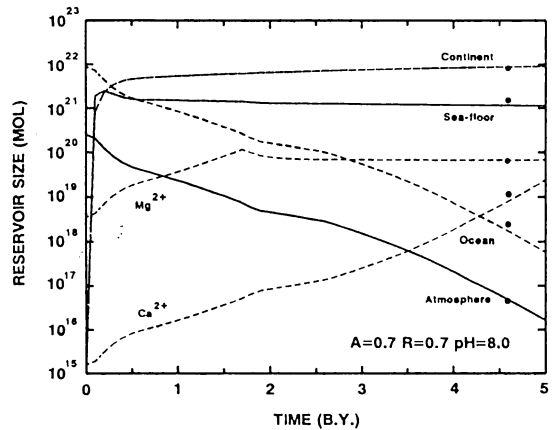

Fig. 12. *Temporal variation in the cation (Ca^{2+}, Mg^{2+}) reservoirs in addition to the carbon reservoirs for the Reymer and Schubert (1984) growth model (A = 0.7, R = 0.7, pH = 8, C_{total} = 1 × 10^{22} mol). The meaning of the curves and symbols are the same as in Fig. 8.*

Evolution of cation reservoirs. The evolution of the cation reservoirs is shown in Fig. 12. Basically, the cations (Ca^{2+}, Mg^{2+}) are in chemical equilibrium with the carbonate ions (CO_3^{2-}), so they are inversely proportional to the amount of carbon in the ocean. Calcium ions are shown to be in equilibrium with carbonate ions throughout the entire history of the Earth. This may be supported by the geological evidence that calcite has been produced continuously since the time of the oldest carbonate formation.

On the other hand, magnesium ions are shown to be in equilibrium with carbonate ions only during the early Archean period, but not after that. This is because the equilibrium level of magnesium in the ocean increases with decreasing atmospheric CO_2 level. This means that the supply of magnesium ions from the continents becomes too low to sustain their consumption by hydrothermal reaction after the magnesite on the seafloor reservoir is exhausted. Once the equilibrium is broken, the concentration of the magnesium ions in the ocean is determined only by the balance of the supply of those ions from the continents and the consumption of them by the hydro-

thermal reaction. Because this estimate gives the upper limit for the concentration of magnesium ions, we can say that magnesites might have formed only in the early Archean period, but not after that. This is consistent with the lack of geological evidence that magnesite was formed recently.

When we consider chemical equilibrium and assume the ocean pH to be near the present value, the concentrations of calcium and magnesium ions in the oceans should be less in the past than today because of the higher atmospheric CO_2 level in the past. Also, judging from the values of the solubility products, we know that the concentration of magnesium ions should always be higher than that of calcium ions. We can also explain the present value of these ions by assuming an accretion ratio equal to 0.7.

Closed system model. Finally, we consider the case where the seafloor carbonates do not subduct into the mantle. In this case, CO_2 does not degas from the mantle because of the assumption that almost all of the carbon existed as CO_2 in the proto-atmosphere initially. Therefore, we name this case the closed system.

We set the total amount of carbon equal to the present-day amount at the surface ($C_{total} = C^*_{surface}$), the pH equal to 8 (the present value), and the regassing ratio equal to zero ($R = 0$).

As shown in Fig. 13 the result is almost the same as for that of the open system models (in the case of $R \neq 0$). Before the formation of the continents, CO_2 in the atmosphere-ocean system cannot decrease at all and hence the surface temperature increases with an increase in the solar constant. Once continental growth begins, however, CO_2 in the atmosphere-ocean system decreases and the surface temperature becomes stabilized. There seems to be no difference in the results between the closed and open system models. The distribution of carbon depends on an accretion ratio that, to explain the present distribution, again needs to be equal to 0.7.
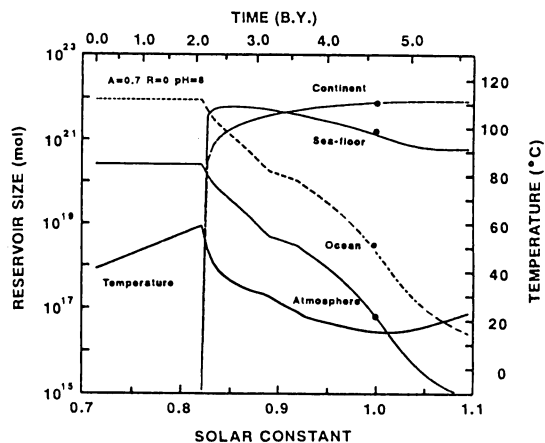

Fig. 13. *Delayed continental growth model (A = 0.7, R = 0, pH = 8, $C_{total} = C_{surface}^*$). Variation of carbon levels in each reservoir and surface temperature of the Earth as a function of the solar constant and time. The meaning of the curves and symbols are the same as in Fig. 8.*

Effect of total carbon amount. Because we do not know the present carbon content of the mantle, the total amount of carbon cannot be determined for the open system model. However, each reservoir evolves to the present-day environment irrespective of the assumed total amount of carbon. This might be because we used the CO_2 degassing function from the mantle that produces the present flux at the present condition irrespective of the carbon contents in the mantle. In every case, the amount of carbon at the surface reaches a stationary level, which is determined by some tectonic factors such as the CO_2 degassing flux (as stated in the section on stationary solutions).

One example of the result of regassing and degassing fluxes is shown in Fig. 14. The "extra" amount of carbon at the surface precipitates to the seafloor as carbonates that eventually subduct into the mantle, and thus the amount of carbon at the surface decreases. ("Extra" refers to the extra value above a stationary level.) However, once it decreases to a certain level, the fluxes of the CO_2 regassing into the mantle and the CO_2 degas-
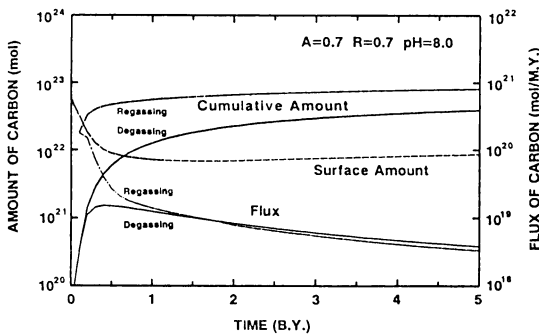
Fig. 14. *Variation in the fluxes of regassing carbon (the surface to the mantle) and degassing CO_2 (the mantle to the surface) in mol/m.y. The cumulative amount represents the integrated amount of the regassing and degassing carbon fluxes since the beginning of the Earth's history (mol). The variation in the surface amount of carbon is also shown. It is noted that since these two fluxes become almost balanced, the amount of surface carbon decreases to a certain level. [Reymer and Schubert (1984) growth model; A = 0.7, R = 0.7, pH = 8, C_{total} = 5×10^{22} mol.]*

sing from the mantle become balanced and reach a stationary state for the amount of carbon at the surface.

It is noted here that the timescale for establishing an equilibrium between surface and mantle carbon during the Archean was roughly 500 m.y., and that, whatever the amount of the carbon in the mantle at present, it is in a steady state with the surface.

A Mechanism to Stabilize Surface Temperature

The evolution of the surface temperature for various models is shown in Fig. 15. In spite of the large differences in the parameters A, R, and pH, surface temperatures stay within a fairly narrow range. This is because a decrease in atmospheric CO_2 results in a decreasing greenhouse effect, which compensates for the effect of the increase in solar luminosity. This means that the negative feedback mechanism proposed by *Walker et al.* (1981) plays a key role in stabilizing surface temperature even when continental growth and tectonic evolution are taken into account. Here, the negative

feedback mechanism is described as follows. When the surface temperature increases, weathering becomes more efficient because of the increase in evaporation of H_2O from the ocean, that is, the increase in rainfall. This results in a decrease of CO_2 in the atmosphere, if we assume that the supply of CO_2 through volcanism remains the same. Then the surface temperature will decrease because of the decrease in the greenhouse effect of CO_2. On the other hand, when the surface temperature decreases, weathering becomes less efficient, and CO_2 will accumulate in the atmosphere. Then the surface temperature will begin to increase. In this way, such a negative feedback mechanism will stabilize the surface temperature (*Walker et al.*, 1981, 1983; *Kasting and Toon*, 1988).

In modeling this mechanism, they estimated separately the effects of changes in the effective temperature (which relates to the solar constant) and the rate of CO_2 release through volcanism (which relates to tectonic activity) from the present values. However, all factors (solar constant, tectonic activity, and continental area) are greatly changed throughout the entire history of the Earth. The
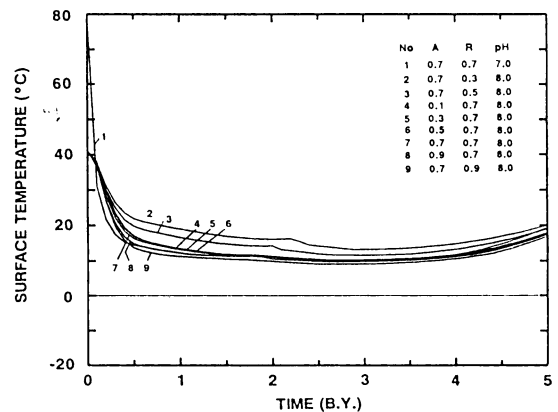

Fig. 15. *Temporal variation of the surface temperature of the Earth for various values of the parameters. It is noted that the surface temperature is stabilized over the entire history of the Earth except for the early stage where the continents had not yet grown large. [Reymer and Schubert (1984) growth model; C_{total} = 1×10^{22} mol.]*

coupled changes of all these factors would have affected the carbon cycle. As shown in the numerical results, the surface temperature is relatively high until the continents grow to a certain degree. But after that, the temperature becomes stabilized even if these conditions are greatly changed. The level at which the temperature is stabilized depends mainly on the tectonic factors such as f_{S_C}, tr, F_D, A, and R. Therefore, the negative feedback mechanism would have a stabilizing effect on the surface temperature of the Earth throughout most of its history.

This mechanism does not work when there are no continents and no tectonic activity (no plate motion and no CO_2 degassing from the mantle). Since the carbonate-silicate geochemical cycle does not work in these cases, the surface temperature cannot be stabilized.

DISCUSSION

Accretion Ratio

We showed that the accretion ratio plays an important role in our carbon cycle model. As shown in the section on stationary solutions, the accretion ratio is 0.7 at the present time. We also showed that this value results in the present distribution of carbon at the surface. Then we discussed what the physical meaning of the accretion ratio is.

There is some geological evidence that the carbonate sediments on seamounts accreted onto the continental crust in the past (*Ozawa,* 1986). At present, however, evidence of the accretion of seafloor sediments onto the continents has not yet been found. Although deep seafloor drilling experiments have not been widely done, all the experiments have revealed that not the accretion type but the tectonic erosion type has occurred (*Nagumo,* 1987).

It may be better, therefore, to define the present accretion ratio as the ratio of the amount of carbonates that will not subduct under the continents to the total precipitated carbonates. In this respect, we need to take
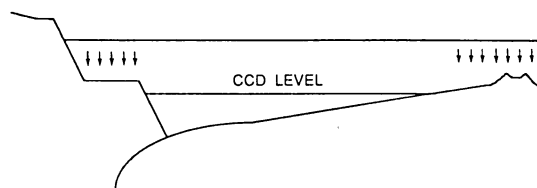

Fig. 16. *Schematic diagram of the carbonate precipitation in the present ocean. Because there exists a CCD (calcium carbonate compensation depth) level in the present ocean, carbonates can precipitate only in the shallower regions such as around the midocean ridges and the continental shelves.*

note of the carbonates deposited on the continental crust directly (Fig. 16). The present ocean has a CCD (calcium carbonate compensation depth), so carbonates can precipitate only at the continental shelves and the shallower depth regions around the midocean ridges. In fact, at present, very large amounts of carbonates are formed at coral reefs. Therefore, the present accretion ratio is estimated from the carbonate precipitation rate at the continental shelves and at the midocean ridges, and also the growth rate of the worldwide coral reefs.

In this study, we considered the continental shelves as a part of the continents. But the features of the continental shelves as carbon reservoirs are different from both the continents and the seafloor. It will be better to treat them as an independent reservoir in future studies.

Weathering of the Seafloor

The weathering of the seafloor is not as important as that of the continent today. However, when the water at the bottom of the ocean is hot, or the pH of the oceans is low, it becomes more effective. This suggests that the seafloor weathering effect may be important during the "aquaplanet" stage (no continent period).

The effect of the weathering of the seafloor was discussed by *Walker* (1985) for the case where R = 0. In his paper he considered the carbon cycle in the atmosphere, the ocean,

and the seafloor at the aquaplanet stage. He assumed a continuous supply of cations from the midocean ridges that precipitates as carbonates onto the seafloor and is carried back into the mantle with the plate motion. In this respect, this estimate corresponds to the upper limit for the effect of the seafloor weathering. Based on the comparison of the timescale of seawater circulation and the residence time of carbon on the seafloor, he concluded that the partial pressure of atmospheric CO_2 would never decrease to a level lower than about 0.2 bar when the pH is equal to 8. (However, in his paper he considered that the pH of the early ocean was much lower than today. When pH was lower than 6, the CO_2 partial pressure is about 10 bar.) Our results show that the CO_2 partial pressure would never decrease to a level lower than about 2 bar. This is because we do not take into account the weathering of the seafloor. In this respect, our treatment corresponds to the lower limit for the effect of seafloor weathering. For both cases, however, the partial pressure of atmospheric CO_2 is constant during the aquaplanet stage. Therefore, the surface temperature increases with an increase in the solar constant.

Even if we consider the effect of seafloor weathering, our main conclusions do not change. For the case of no continents, the Earth's environment would never evolve to the present state.

Depletion of Carbon at the Surface

It is well known that the amount of carbon at the Earth's surface is depleted ($1/10 \sim 1/100$) compared to other volatiles judging from the value inferred from $C/^{36}Ar$ and C/H for the various kinds of meteorites (*Otting and Zahringer,* 1967). If we assume that an impact degassing occurred during the formation of the Earth, almost all of the carbon-related gas species should have been degassed at that time and constituted a major atmospheric component. The upper limit of the initial amount of

CO_2 is given by the conditions necessary for the formation of the ocean. According to *Abe* (1988a), the upper limit is almost 1 kbar. If the Earth formed by the accretion of planetesimals with a chondritic C/H ratio, we need to consider a sink for the decrease of such a large amount of CO_2 to the present level. The only sink so far proposed is the core. CO_2 dissolves into the magma ocean and reacts with metallic iron, and is removed from the magma ocean by core formation (*Abe,* 1988b).

However, there is a possibility that the mantle becomes a sink for carbon through the carbon cycle between the surface reservoirs and mantle. Characteristic timescales for the carbon cycle may determine the distribution of carbon between the surface and the mantle. For example, the surface carbon would be determined by the residence time of carbon in the mantle, which is obviously related to the tectonic (and thermal) evolution of the Earth.

The amount of H_2O, which is the most abundant volatile at the surface, was determined basically at the time of the Earth's accretion by the dissolution equilibrium between a steam atmosphere and a magma ocean (*Matsui and Abe,* 1986a,b). On the other hand, the amount of surface CO_2, which is the second most abundant volatile at the surface, might have been determined during the tectonic evolution of the Earth after ocean formation by the carbon cycle between the surface reservoirs and the mantle.

Problem of Organic Carbon

At the present time carbonates are produced mainly by organisms such as *Coccolithophores* (algae), *Planktonic foraminifera, Pteropoda,* or coral as their hard material in the ocean (*Broecker,* 1974). Of course, through either organic or inorganic processes or both, carbonates are formed in the ocean as long as the seawater is saturated. The organic carbon (CH_2O) is also produced as the soft parts of such organisms, and it also precipitates to the seafloor.

The ratio of carbonate carbon to organic carbon may have been constant at 4:1 during the last 3.8 b.y. according to the isotopic record (*Schidlowski*, 1988; *Junge et al.*, 1975; *Broecker*, 1970). This constancy may be explained by using the carbon cycle model in which the ratio of the flux of organic carbon precipitation to the flux of carbonate precipitation ($= F_P^{C_{org}}/F_P^{C_{carb}}$, where C_{org} represents the organic carbon and C_{carb} represents the carbonate carbon) and the ratio of the weathering constant of organic carbon to that of carbonate ($= K_W^{C_{org}}/K_W^{C_{carb}}$) are assumed to be constant (*Junge et al.*, 1975). ·

In this study we did not take into account the organic carbon-related processes. However, judging from the ratio (4:1), we consider that our results are not affected significantly by taking into account the organic processes. However, the organic carbon-related processes play a key role in the evolution of oxygen in the atmosphere, because oxygen has been accumulated due to biogenic photosynthesis

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$
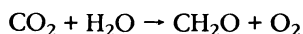
The incorporation of the organic processes into our model is a future problem.

Future of the Earth's Environment

In this paper we showed the change in surface temperature from the beginning of the Earth's history to a time in the near future. It is obvious from geological evidence that there were several glaciation periods in the past, but our results cannot predict them. This is because the Earth's environment is perturbed by many factors that we did not take into account in this study. Such factors may cause local and even global changes in surface temperature for very short periods compared to the Earth's history. Such factors are, for example, the distribution and topography of the continents (*Barron and Washington*, 1982, 1984), changes in the spreading rate of the seafloor (*Berner et al.*, 1983; *Owen and Rea*, 1985), changes in the orbital elements

(*Berger*, 1988), and, possibly, giant impacts (*Kasting et al.*, 1986). It is noted, however, that characteristic timescales related to these factors are very short in comparison with the age of the Earth. Therefore, we can consider that the basic trend of the evolution of the Earth's environment has been regulated mainly by the CO_2 cycle.

As seen in Fig. 15, however, the long-range variation of the surface temperature seems to be at a turning point at present, that is, from decreasing to increasing. This is because the present greenhouse effect of CO_2 is at its lowest level of the Earth's history. At present, the greenhouse effect due to H_2O is comparable with that due to CO_2 (*Walker*, 1982). Therefore, from now on, the Earth may not be able to maintain the surface temperature by decreasing the CO_2 partial pressure in response to increasing solar luminosity. In addition, as pointed out by *Lovelock and Whitfield* (1982), green plants may not be able to photosynthesize once the atmospheric CO_2 level drops below 150 ppm. From these points of view, the period in which the Earth's environment was regulated by the CO_2 cycle may have already ended. As a rough trend, a long-term increase in the surface temperature of the Earth would be expected. Someday the Earth will become like Venus, unless some unknown mechanism such as cloud feedback plays a role in reducing the surface temperature.

SUMMARY

The main results are summarized as follows:

1. Continental growth is required for the terrestrial environment to evolve to the present state.

a. If there were no continents on the Earth, the atmospheric CO_2 could not decrease to a certain level. This is because the cations that react to form carbonates would not be supplied much to the oceans. The partial pressure of CO_2 would therefore be

around 2 bar (when the pH is equal to 8), resulting in an increase in the surface temperature with an increase in the solar luminosity.

b. The formation of the continents makes possible the supply of various cations to the oceans, so carbonates can precipitate to the seafloor. If these carbonates accrete to the continents, the continents act as a sort of storage for carbon in the CO_2 cycle because the continents have a very long residence time for the carbon cycle. In this case, the Earth's environment will evolve to the present state.

c. Even if we take into account the effects of regassing into and degassing from the mantle, continental growth plays the key role in controlling the environment.

d. The distribution of carbon at the surface is determined by a parameter called the accretion ratio, and the present distribution can be explained when this value is equal to 0.7.

2. The carbon cycle, including the carbonate-silicate geochemical cycle, has an important role in controlling the Earth's environment. Throughout the entire history of the Earth, the surface temperature has been stabilized by this cycle against changes in external conditions such as the solar constant, continental growth, and tectonic activity. The surface temperature cannot be stabilized when this cycle cannot work (for example, no oceans, no continents, or no tectonic activity).

3. Cations in the oceans are basically in chemical equilibrium with carbonate ions. Calcium ions have been in equilibrium with carbonate ions throughout the history of the Earth. In the case of magnesium ions, however, the equilibrium has been broken ever since the supply of magnesium ions from the continents was less than enough to balance their consumption, perhaps since sometime during the Archean period.

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