Degassing history and carbon cycle of the Earth: From an impact-induced steam atmosphere to the present atmosphere
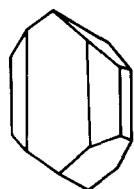
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ABSTRACT

The recent theoretical studies on the formation and evolution of the atmosphere and oceans of the Earth are reviewed. Impact degassing during accretion of the Earth would probably generate an impact-induced steam atmosphere on the proto-Earth. At the end of accretion, the steam atmosphere became unstable and condensed to form the proto-ocean with almost the present mass of ocean. The steam atmosphere would have thus evolved to the proto-CO_2 atmosphere during the earliest history of the Earth because CO in the proto-atmosphere may be photochemically converted to CO_2. However, CO_2 in the proto-atmosphere has decreased with time through the global carbon cycle which may have stabilized the terrestrial environment against an increase in the solar luminosity. The continental growth during Hadean and Archean would therefore have a significant influence on the carbon cycle and the surface temperature. It is also suggested that the continental growth is a necessary condition for the terrestrial environment to evolve to the present state. Both the impact degassing and the subsequent continuous degassing are suggested to have played a major role in the formation and evolution of the atmosphere and ocean. In particular, most of N_2 may have been produced by the impact degassing during accretion, and the contribution of the subsequent continuous degassing is at most 10% for N_2. As a consequence, after the CO_2 level decreased to less than 1 bar, the atmosphere may have been at about 1 bar and composed mainly of N_2 for most of the subsequent history of the Earth.

Introduction

According to recent studies on planetary formation, the Earth has been considered to be formed by accretion of planetesimals (e.g., Safronov, 1969). High-velocity impact generates high temperature and pressure in both impactor and target, which results in "impact degassing" (e.g., Lange and Ahrens, 1982a, b; Tyburczy et al., 1986). As a consequence, volatile components in planetesimals degas to form a proto-atmosphere surrounding the proto-Earth (Abe and Matsui, 1985, 1986, 1988; Matsui

and Abe, 1986a, b; Zahnle et al., 1988). This impact-induced proto-atmosphere was composed mainly of H_2O and CO or CO_2 (hence it has been called the "steam atmosphere"), which finally condensed to form the proto-ocean at the end of accretionary period (Matsui and Abe, 1986b; Abe and Matsui, 1988).

CO is finally oxidized to CO_2 by OH radicals produced from water vapor photolysis (e.g., Kasting et al., 1983, 1984). The atmosphere at the earliest history of the Earth was thus composed mainly of CO_2 (e.g., Abe, 1988a; Abe and Matsui, 1988). There were, of course, deficiencies in free oxygen and radiogenic argon which are both major components of the present atmosphere (Table 1). The proto-at-

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TABLE 1

Present surface environments of the terrestrial planets

	Venus	Earth	Mars
Atmospheric composition			
N_2	1.8%	78.1%	2.7%
O_2	–	20.9%	–
Ar	0.02%	0.93%	1.6%
CO_2	98.1%	0.035%*	95.3%
Effective temperature**	277 K	255 K	217 K
Surface temperature	750 K	288 K	240 K
Surface pressure	90 bar	1 bar	6 mbar
Existence of water	water vapor (1–1000 ppm)	sea water (270 bar)	ice cap permafrost

*CO_2 in the atmosphere of the Earth is $\sim 10^{-4}$ bar, but there exists $60 \sim 80$ bars equivalent CO_2 in the forms of carbonates and kerogen (old organic carbon) in the sedimentary and metamorphosed rocks at present.
**The effective temperature is defined so that the solar energy input may be balanced with the black body radiation from the planet at this temperature. The difference between the effective temperature and the surface temperature corresponds to the greenhouse effects of the atmosphere.

mosphere at this stage was quite different from the present terrestrial atmosphere, but resembling the present atmosphere of Venus (Table 1). The surface temperature of the proto-Earth would be higher than the freezing point of water in spite of the faint young sun at that time due to the greenhouse effect of dense-CO_2 atmosphere as shown for the present Venusian atmosphere. In this respect, it is thus important to understand the evolution of the terrestrial proto-CO_2 atmosphere (Tajika and Matsui, 1990, 1992a), as this will also enable an understanding of the difference in evolution between the Earth and Venus.

In this paper, we will review our recent theoretical studies on the origin and evolution of the Earth's atmosphere and oceans. We begin with the accretion stage and introduce the global geochemical cycle of carbon during the Earth's evolution, and then discuss the long-term stability of the terrestrial environment as a consequence of the atmospheric evolution.

Origins of the atmosphere and oceans

According to the classical theory of Rubey (1951), the atmosphere and ocean were formed by continuous degassing due to volcanic eruptions over the history of the Earth. However, an early cata-

strophic degassing, rather than continuous degassing, has been advocated although no concrete mechanism has been proposed (e.g., Fanale, 1971; Hamano and Ozima, 1978). Hamano and Ozima (1978) studied Ar isotope geochemistry and suggested that more than 80–90% of the volatile components which were originally contained in the solid-Earth, must have degassed to the surface within the first $\sim 5 \times 10^8$ years by some unknown catastrophic degassing event. Recently, impact degassing (Lange and Ahrens, 1982a) during accretion of the Earth has been recognized as a plausible mechanism for early catastrophic degassing (Matsui and Abe, 1986a).

The planets were probably formed by the accretion of planetesimals. High-velocity impacts of planetesimals result in release of volatile components, such as H_2O and CO_2, retained in the planetesimals. This "impact degassing", as suggested theoretically and experimentally (e.g., Lange and Ahrens, 1982a, b; Tyburczy et al., 1986), occurred as a consequence of the accretion of planetesimals, as the peak pressures and temperatures generated by planetesimal impacts are high enough to cause impact degassing. An impact-induced steam atmosphere was thus formed on the accreting Earth (Abe and Matsui, 1985, 1986; Matsui and Abe, 1986a). Because of the blanketing effect of the steam atmosphere, the surface temperature of the proto-Earth would have increased and exceeded the solidus temperature of surface rocks during accretion. The surface of the accreting Earth was thus covered with a magma ocean, and the amount of steam atmosphere was determined by the dissolution equilibrium between the atmosphere and the magma ocean (Abe and Matsui, 1986; Matsui and Abe, 1986a, b; Zahnle et al., 1988). This is of course depending on accretion rate and size distribution of planetesimals. If the accretion occurred as sporadic, rather than continuous, the situation would be different (Abe, 1988b; Rintoul and Stevenson, 1988). Details of the proto-atmosphere, such as H_2/H_2O and CO/CO_2, will be controlled by a redox state of the magma ocean (e.g., Holloway, 1988; Abe, 1992).

At the end of accretion, the steam atmosphere became unstable due to a decrease in impact energy flux and thus H_2O in the proto-atmosphere condensed to form the proto-oceans (Matsui and Abe, 1986b; Abe and Matsui, 1988). The mass of the proto-ocean is estimated to be on the order of 10^{21} kg

irrespective of the model parameters, which apparently coincides with the amount of the present ocean 1.4×10^{21} kg (Matsui and Abe, 1986b; Abe and Matsui, 1988).

The atmosphere just after the condensation of the steam atmosphere was composed mainly of CO or CO_2 (depending on a redox state of the magma ocean). This is because carbon would be the second most abundant volatile element in the accreting material judging from the composition of chondrite meteorites (e.g., Larimer, 1971). In fact, carbon is the second most abundant volatile element on the surface of the Earth at the present time (e.g., Holland, 1978). CO in the proto-atmosphere would have been converted to CO_2 by OH radicals produced from water vapor photolysis (e.g., Kasting et al., 1983, 1984), although continued production of CO by impacts during the heavy bombardment period could have maintained an atmospheric CO/CO_2 ratio at about unity (Kasting, 1990).

The maximum amount of CO_2 at that time was several hundred bars when it was determined only by the solubility equilibrium between the impact-induced atmosphere and the magma ocean. However, if metallic iron was present in the magma ocean, it would decrease to 100 bar (Abe, 1988a). It is noted that most of the carbon in the Earth's crust today is in the form of carbonates and kerogen (organic carbon in sedimentary rocks), and that the total amount of surface carbon is equivalent to 60–80 bar at present (Table 1). Before large continents were formed, atmospheric CO_2 would be controlled by the carbon cycle in the atmosphere–ocean–seafloor system. The partial pressure of CO_2 would not have decreased to a level lower than about 10 bar at this aquaplanet stage (Walker, 1985). This is considered to be the most plausible scenario proposed so far for the origin of the atmosphere and oceans of the Earth. According to this scenario, a CO_2-rich atmosphere and a sizable liquid ocean were formed during very early in the history of the Earth.

The faint young Sun paradox

The evolution of the proto-CO_2 atmosphere through the history of the Earth must have played a key role in the climatic evolution of the Earth. This is because the variation of CO_2 content in the atmosphere affects the surface temperature owing to its greenhouse effect (e.g., Owen et al., 1979; Kuhn and Kasting, 1983; Kasting and Ackerman, 1986; Kasting, 1987). Therefore, the evolution of the proto-CO_2 atmosphere has obviously been linked tightly with the evolution of the terrestrial environment (e.g., Tajika and Matsui, 1990, 1992a). This is especially important when we consider the so called faint young Sun paradox (Sagan and Mullen, 1972).

The luminosity of the sun has probably increased to its present level by an amount of 30% (e.g., Gilliland, 1989). If the atmospheric composition and its planetary albedo had been the same as those of today, the surface temperature of the Earth would have been much below $0 °C$ up until about 2 Ga ago as shown in Fig. 1 (Sagan and Mullen, 1972). However, there is no geological evidence for such a globally ice-covered Earth at that time. On the contrary, there is considerable geological evidence for the existence of a sizable liquid ocean and possibly even warmer climates in the past (e.g., Oskvarek and Perry, 1976). This has been called the "faint young Sun paradox", which was first pointed out by Sagan and Mullen (1972).

Among the solutions proposed so far for the faint young Sun paradox, the most reasonable and simplest one is that the atmosphere had more greenhouse gases in the past. A candidate gas is the reduced gas such as NH_3 (Sagan and Mullen, 1972). It has been shown, however, that NH_3 is photochemically unstable in the presence of water vapor, and that it is converted to N_2 within a geologically short period (Kuhn and Atreya, 1979; Kasting, 1982). A more likely candidate for the greenhouse gas is CO_2, because CO_2 is photochemically stable and also one of the most abundant components at the surface of the Earth. It has been demonstrated that 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 as shown in Fig. 1 (Owen et al., 1979; Kuhn and Kasting, 1983; Kasting and Ackerman, 1986; Kasting, 1987; Tajika and Matsui, 1990, 1992a). Recently Caldeira and Kasting (1992) questioned this suggestion by showing condensation of CO_2 under lower solar incidence. They suggest that clouds of CO_2 reflect solar radiation and that this effect could overwhelm the greenhouse effect. However, the evolutionary scenario from an impact-induced steam atmosphere to a proto-CO_2 atmosphere after the
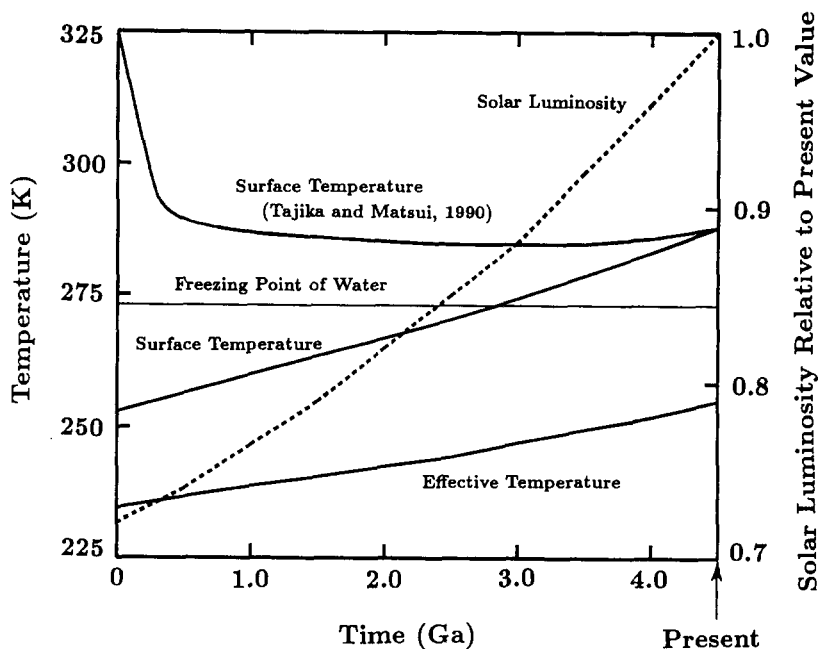
Fig. 1. The temporal variations of the solar luminosity, the effective temperature (see the note in Table 1), the surface temperature assuming constant atmospheric composition (from Kasting, 1989), and the surface temperature based on the global carbon cycle model (Tajika and Masui, 1990).

formation of proto-oceans seems to be consistent with the solution for the faint young Sun paradox (Matsui and Abe, 1986b). This is because the surface temperature 4.6 Ga ago was still higher than at present, resulting from the remnant of accumulated accretional energy. The problem is how such a CO_2-rich atmosphere became the present N_2-rich atmosphere, in which the CO_2 content is only 0.035%, while solar luminosity increased with time.

The global carbon cycle and the terrestrial environment

The amount of CO_2 in the atmosphere is regulated through the geochemical cycle of carbon (e.g., Holland, 1978, 1984; Walker et al., 1981; Berner et al., 1983; Tajika and Matsui, 1990, 1992a). It has been suggested that the climate on the Earth may have been stabilized by the carbon cycle system because of its negative feedback mechanism for the surface temperature (e.g., Walker et al., 1981; Kasting, 1989; Kasting and Toon, 1989; Tajika and Matsui, 1990, 1992a). This means that the carbon cycle probably plays a dominant role in evolutions

of the proto-CO_2 atmosphere and of the surface environment. We will consider the global carbon cycle and how the negative feedback mechanism controls the surface temperature.

The global carbon cycle

Carbon circulates through the surface reservoirs in various forms and on different time scales. The carbon cycle through the geologic time scale is outlined as follows: CO_2 in the atmosphere dissolves in raindrops or ground water, and produces carbonic acid, which weathers the silicate minerals on the land surface. Bicarbonate ions and cations produced by the weathering are carried to the oceans by rivers and will react there to form carbonates. The carbonates are deposited on the seafloor. They move with the motion of oceanic plates and eventually reach a subduction zone. Seafloor carbonates subducting with oceanic plates are metamorphosed at high temperatures and pressures. CO_2 is regenarated by this process and returns to the atmosphere via volcanoes. This is known as the "carbonate–silicate geochemical cycle" (e.g., Walker et al.,

1981; Berner et al., 1983; Lasaga et al., 1985; Kasting and Toon, 1989).

When we consider the entire history of the Earth, however, some other important processes should be taken into account. Because most carbonates precipitated in the ocean are now observed in the continental crusts (e.g., Ronov and Yaroshevsky, 1976), some process which brings carbonates into the continental crusts must have operated. For example, carbonates arriving at the subduction zones can be accreted to the continental crust in the form of accretionary prisms, or carbonates precipitate directly onto the continental crusts (Tajika and Matsui, 1990, 1992a). On the other hand, some carbonates subducted with the oceanic crust are reabsorbed into the mantle (e.g., Javoy et al., 1982; Abbott and Lyle, 1984; Des Marais, 1985; Koster van Groos, 1988; Walker, 1990; Eldridge et al., 1991). This process has been called the "regassing" of carbon. Moreover, it has been generally accepted that CO_2 degasses effectively from the mantle when new oceanic plates are formed at mid-ocean ridges (e.g., Javoy et al., 1982; Des Marais, 1985; Marty and Jambon, 1987).

In this way, carbon has been circulating among the surface reservoirs and the mantle during the history of Earth. Hereafter we call this circulation, including the carbon exchange between the surface and the mantle, the "global carbon cycle", which comprises all the geochemical and geophysical processes described above (Tajika and Matsui, 1990, 1992a). The carbonate–silicate geochemical cycle is considered to be a part of the global carbon cycle.

Biological processes certainly play important roles in the carbon cycle (e.g., Holland, 1978; Lasaga et al., 1985; Schwartzman and Volk, 1989). Organisms promote continental weathering and precipitation of carbonates today (e.g., Holland, 1978). However, the biological carbon cycle (photosynthesis and respiration) has usually been ignored in studies of the carbon cycle on a geologic time scale (10^8 yr). This is because the biomass is very small compared to that of the other carbon reservoirs, and the time scale of turnover for the biosphere is very short ($< 10^2$–10^3 yr). Although the mass of the sedimentary organic carbon (kerogen) is comparable to that of the inorganic carbon (carbonates), it is at most 20% of the amount of the total crustal carbon (e.g., Ronov and Yaroshevsky, 1976). Therefore the global carbon cycle may be represented by the in-

organic carbon cycle alone as a first approximation (e.g., Berner et al., 1983; Berner and Barron, 1984; Kasting, 1984; Volk, 19871; Tajika and Matsui, 1990, 1992a; Berner, 1991). However, in order to study the variations of oxygen in the atmosphere, we need to fully take into account the biogeochemical cycle of carbon because it is tightly coupled with the geochemical cycles of oxygen, sulfur and iron (e.g., Garrels and Perry, 1974; Holland, 1978, 1984; Berner and Raiswell, 1983; Garrels and Lerman, 1984; Lasaga et al., 1985; Kump and Garrels, 1986; Berner, 1987, 1989; Lasaga, 1989).

The carbon cycle and the climate

The surface temperature of the Earth is suggested to have been stabilized against the external perturbations with time such as an increase in solar luminosity and decrease in the CO_2 degassing rate. This is because the carbon cycle system may provide a negative feedback mechanism for the surface temperature (e.g., Walker et al., 1981; Kasting, 1989; Kasting and Toon, 1989; Tajika and Matsui, 1990, 1992a). Here, the negative feedback mechanism is usually described as follows (Walker et al., 1981): when the surface temperature increases, chemical weathering becomes more efficient owing to its strong temperature dependence. High surface temperature also results in an increase in evaporation of H_2O from the ocean. The rainfall on the continents therefore increases, which also promotes the weathering reactions. An increase in the rate of precipitation of carbonates in the ocean then follows. If the supply of CO_2 through volcanism remains the same, CO_2 in the atmosphere decreases. Hence the surface temperature tends to decrease because of the decrease in the greenhouse effect of CO_2. On the other hand, once the surface temperature decreases, weathering becomes less efficient and CO_2 begins to accumulate in the atmosphere. Then the surface temperature tends to increase. Such a negative feedback mechanism has the effect of stabilizing the surface temperature of the Earth (Walker et al., 1981).

The residence time of CO_2 in the combined atmosphere–ocean system ($=$ reservoir size/weathering rate) is about 0.5 Ma (Berner et al., 1983). Therefore the amount of CO_2 in the atmosphere, and so the surface temperature, will achieve a stationary state on a geologically short time scale. The

stationary solutions for the surface temperature as functions of the CO_2 degassing rate and the continental area can be obtained from the numerical modeling of the global carbon cycle. It is summarized in Fig. 2. Biotic enhancement of weathering rate is not considered in these calcul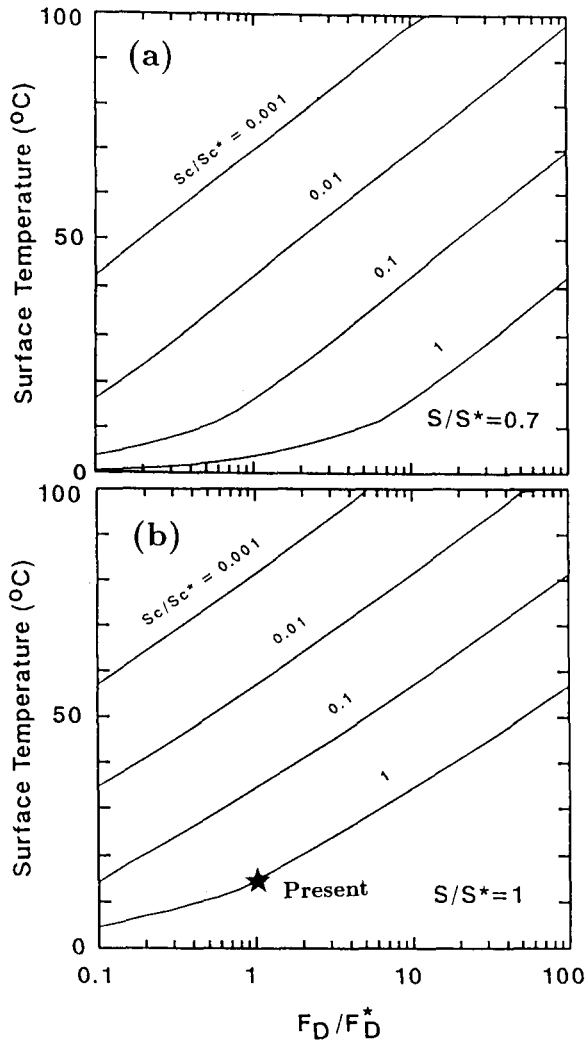ations, although it might have affected the carbon cycle system greatly (e.g., Schwartzman and Volk, 1989, 1991). However, this issue seems to be somewhat controversial at present (e.g., Walker 1990).

As shown in Fig. 2, the surface temperature increases with the degassing rate. This is because, in a stationary state, the CO_2 supply and its consumption are balanced. Therefore, larger degassing rate balances with larger weathering rate which is accomplished by an increase in surface temperature. Because the weathering reaction has a strong temperature dependence (e.g., Walker et al., 1981), the surface temperature does not vary so much from the present value even when the degassing rate varies greatly. However, these variations in the surface temperature would be large enough to affect most of the present biosphere. It is also noted that sea-surface temperature during the height of the most recent glaciation are thought to have been only about $2°C$ colder than that of today (Schneider and Londer, 1984). Therefore the variation of the CO_2 degassing rate, which will be controlled by variations of seafloor spreading rate, is important for the evolution of the terrestrial environment (Tajika and Matsui, 1992a). The degassing rate in the past is recently suggested to have been nearly the same as that of today: in order to explain the present amount of ^{40}Ar, the degassing rate in the past is required to have been larger than that of today at most by a factor of 2–3 (Tajika and Matsui, 1993).

The surface temperature also increases with decrease in the continental area. This is a because smaller land area results in a smaller weathering rate, which means smaller consumption of atmospheric CO_2. Then a balance with CO_2 supply from the interior is accomplished by an increase in surface temperature. It is suggested that the surface temperature is low enough for the Earth to be glaciated when the present-sized continents were formed just after the Earth's formation with the present degassing rate (Fig. 2a). On the other hand, many authors seem to suggest that about 70–80% of the present continents would have formed before 2.0 Ga B.P., although the continental growth curve in the Hadean and Archean remains unknown (e.g., Condie, 1989). The oxygen isotope data indicate surface temperatures as high as $80°C$ during early in the Archean (e.g., Knauth and Epstein, 1976; Oskvarek and Perry, 1976; Karhu and Epstein, 1986). This might suggest that the continents were very small at that time, although we should note that the oxygen

Fig. 2. Summary of the stationary solutions for the surface temperature as a function of CO_2 degassing rate from the mantle, F_D, and the continental surface area, Sc, for (a) the solar constant S 30% lower than present value and for (b) the present solar constant. * represents the present value. We used a modified weathering expression by Walker et al. (1981) as functions of the surface temperature and CO_2 partial pressure (Tajika and Matsui, 1990). We also used the results of Kasting and Ackerman (1986) to estimate the surface temperature as functions of CO_2 partial pressure and the solar constant at given conditions.

isotopic composition could be altered during deposition, diagenesis and metamorphism. There is some other evidence that surface temperatures were below 57°C during the last 3.5 Ga (e.g., Holland, 1984). As shown in the stationary solutions (Fig. 2), the surface temperature becomes very high if the continents were very small. Therefore, we suggest that the terrestrial environment would never have evolved to the present state without the formation of continental crust on the Earth.

Evolution of the proto-CO_2 atmosphere

The evolution of the proto-CO_2 atmosphere can be numerically simulated by modeling the global carbon cycle under various boundary conditions such as an increase in solar luminosity, continental growth and a decrease in tectonic activity (Tajika and Matsui, 1990, 1992a). Figure 3 shows the result of such numerical calculations representing the temporal variations of the partial pressure of CO_2 and the surface temperature. The continental crusts were assumed to grow at a constant rate in this model. Although CO_2 was a major component of the proto-atmosphere, the amount of CO_2 in the atmosphere has decreased with time. This gives a profound influence on the surface temperature of the Earth: if the amount of CO_2 in the atmosphere does

not decrease with time, the surface temperature increases owing to an increase in the solar luminosity. However, a growth of continents results in a decrease in the atmospheric CO_2 and stabilizes the surface temperature against an increase in the solar luminosity. This is because once continents were formed on the Earth, they supply a large quantity of cations to the oceans by their weathering. This causes an increase in precipitation of carbonates on the seafloor, which results in net consumption of atmospheric CO_2. Carbonate precipitation and accretion of the seafloor carbonate to the continents result in a decrease in CO_2 in the atmosphere–ocean system, and thus the surface temperature decreases. This means that a negative feedback effect of the global carbon cycle on the surface temperature requires the existence of large continents on the Earth to maintain mild climates similar to the present ones (Tajika and Matsui, 1990, 1992a; see also Fig. 2).

Partial pressure of atmospheric CO_2 in Archean would be about 100–1000 times the present value to maintain the surface temperature above the freezing point of water at that time. The time scale for adjustment of the partial pressure of CO_2 is 0.5 Ma today and at most 10 Ma in the Archean. Hence the surface temperature and the partial pressure of CO_2 would be around the stationary solutions at given boundary conditions. It is noted that CO_2 in the atmosphere may have varied by four orders of
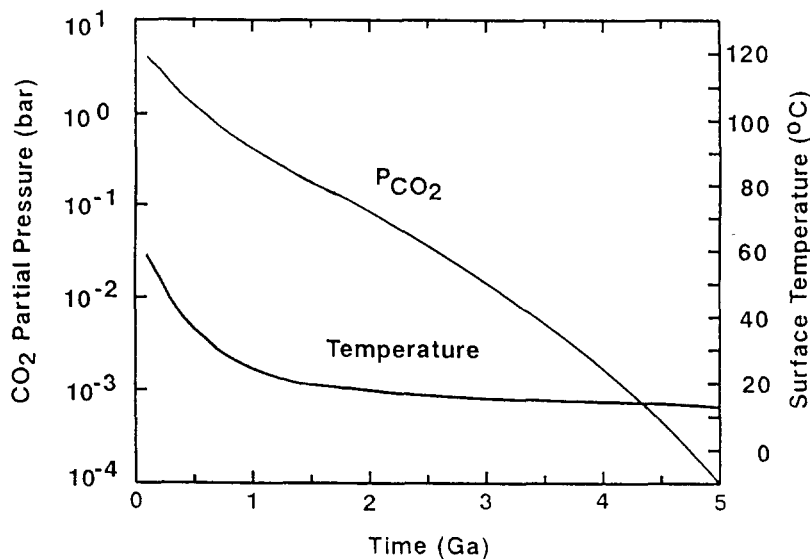

Fig. 3. Temporal variations of the partial pressure of CO_2 and the surface temperature of the Earth estimated from the global carbon cycle model (Tajika and Matsui, 1990, 1992a). The continental crusts are assumed to grow at a constant rate.

magnitude during the history of the Earth (Fig. 3).

The situation was probably very different when there were no large continents during the early history of the Earth. The carbon cycle on such an aquaplanet was discussed by Walker (1985) assuming that there was no volatile exchange between the surface and the mantle. He considered the carbon cycle between the atmosphere, the ocean and the seafloor at this stage, assuming a continuous supply of cations from the mid-ocean ridges. Then, cations precipitate as carbonates onto the seafloor and are carried back into the mantle by plate motions, whereas CO_2 is returned to the atmosphere. Based on the comparison of the time scale of seawater circulation through the hydrothermal system 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 10 bar for lower ocean pH.

Tajika and Matsui (1990) performed numerical simulations for the evolution of the terrestrial environment based on the global carbon cycle. According to their results, the amount of CO_2 in the atmosphere did not decrease until continental crust was formed. If there were no land surface on the Earth, a negative feedback mechanism of the carbon cycle system for the surface temperature no longer works. Moreover, if there was an additional CO_2 degassing from the mantle, the amount of CO_2 increases and the surface temperature increases owing to increases in not only CO_2 but also the solar luminosity with time.

Even when there were no continents, there might have been some volcanic islands or island arcs, which can supply a small amount of cations to the oceans. This is not unreasonable, because Venus and Mars, which may have no continental crusts, are covered with many volcanos and/or uplifted topographies. The areas of typical volcanic island and typical island arc on the Earth are 10^{10} m^2 (10^{-4} of the whole surface area) and 10^{11} m^2 (10^{-3} of the whole surface area), respectively. Hence the Earth, even when the continental formation has never occurred, might have covered with small land surface area (10^{-3}–10^{-2} of the whole surface area).

Figure 4 shows the numerical result of the evolution of the carbon cycle system for such a case. The rapid growth of continents during 3.0–2.5 Ga ago has been suggested from the geochemistry of sedimentary rocks (e.g., Condie, 1989). Therefore, in this model, continents are assumed to have covered $\sim 10^{-2}$ of the whole surface area for the first 1.6 Ga ($=$ 3.0 Ga ago), and to have rapidly grown thereafter. As expected from the stationary solutions, higher surface temperature (about 70–80°C) is achieved during the aquaplanet stage as shown for the first 1.6 Ga. This is because consumption of CO_2 by weathering is very small in this period. Carbonates are formed and deposited on the seafloor, hence the seafloor becomes the largest carbon reservoir in this stage (Fig. 4). It is shown that the surface temperature never decreases in such a situation. In other words, we may say that the terrestrial environment would never have evolved to the present state if the continents had not formed on the Earth. It is, however, noted that there might be another mechanism to supply cations to the ocean even in such a case. Such mechanisms are the hydrothermal reactions (e.g., Wolery and Sleep, 1976; Edmond et al., 1979; Walker, 1985) and seafloor weathering at low temperature (e.g., Drever, 1982; Staudigel and Hart, 1983; Walker, 1990). Seafloor weathering may be effective when the water at the bottom of the ocean is hot and/or when the ocean pH is low. Hydrothermal reactions supply comparable or even much more quantities of cations to the oceans than low temperature weathering of the seafloor when the mantle was hotter and the crust was thinner during the Hadean (Abe, 1993, in this volume). However, once the continents begin to form, the flux of cations supplied to the ocean by continental weathering is much larger. Much more carbonates precipitate on the seafloor and some of them accrete to the continental crust. The surface temperature is stabilized around the present value after the formation of continents (Fig. 4). It should be noted that this model cannot represent any short-term fluctuations such as ice ages because we just try to model the long-term trend of atmospheric evolution.

Carbon that initially existed in the proto-atmosphere and oceans seems finally to be transported to the seafloor and the continental reservoirs (Fig. 4). This is because these reservoirs have longer residence time for carbon than those of the atmosphere and ocean reservoirs: the residence time of the seafloor reservoir is 100 Ma, compared to 0.5 Ma for carbon in the atmosphere–ocean system. In particular, the continents are very stable carbon reservoirs and provide a longer residence time for carbonates (500 Ma) than any other surface reservoirs
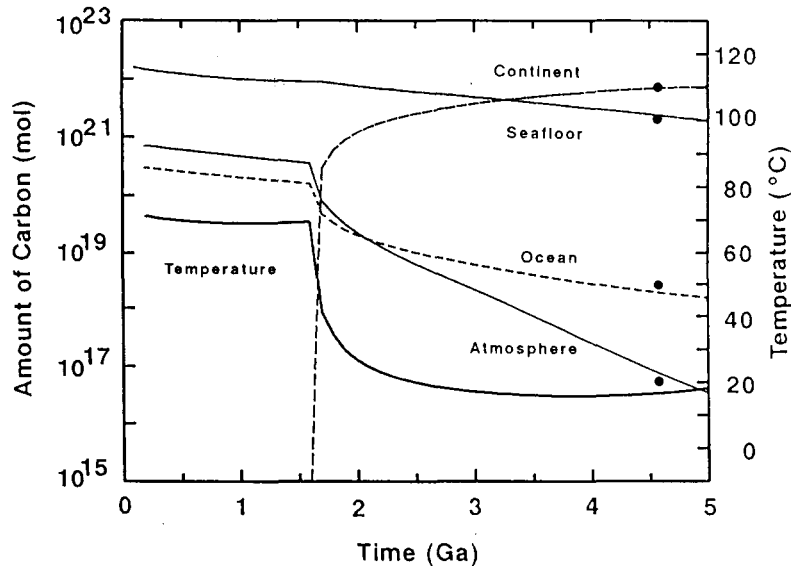
Fig. 4. Temporal variations of the amount of carbon in each surface reservoir (in mol) and the surface temperature (in °C; represented by the bold solid line) of the Earth. Continents are assumed to have constant surface area, 10^{-2} of the whole surface area of the Earth until $t = 1.6$ Ga ($= 3.0$ Ga B.P.), and begin to grow after $t = 1.6$ Ga. The dots represent the present values of each reservoir.

(Tajika and Matsui, 1990). This is because the continents are tectonically stable and also because the residence time of carbon in the continental reservoir is governed only by the chemical weathering, which is known as a fairly slow process.

The above results suggest important roles of the formation of continents on the terrestrial environment as a large cation source for the ocean and also as a stable carbon reservoir. A significant amount of continental crust is necessary for the terrestrial environment to evolve to the present state. If there were no large continents and only small volcanic islands on the Earth, the terrestrial environment would never have evolved to the present state. In this case, the terrestrial environment might have been too hot for organisms other than primitive microbes to survive.

Degassing history and the atmospheric evolution

The degassing history of the mantle may be constrained by using radiogenic ^{40}Ar as a tracer (e.g., Hamano and Ozima, 1978; Tajika and Matsui, 1993). This is because: (1) ^{40}Ar is a decay product of potassium, and so very little ^{40}Ar existed at the time of formation of the Earth. This means that ^{40}Ar

may not have experienced impact degassing. (2) The existence of ^{40}Ar in the present atmosphere suggests that the subsequent degassing of ^{40}Ar has occurred over the history of the Earth and (3) ^{40}Ar probably has not experienced any recycling into the mantle, and hence we can consider only the degassing process for the case of ^{40}Ar. In these respects, ^{40}Ar is considered to be an adequate indicator to constrain the degassing history of the Earth after its formation (Tajika and Matsui, 1993).

Tajika and Matsui (1992a, 1993) considered a degassing model coupled with the thermal evolution of the mantle. They take into account the effects of elemental partitioning and solubility during both melt generation and bubble formation processes, and also the effects of changes in seafloor spreading rate and melt generation depth in the mantle. The degassing flux is expressed as follows (Tajika and Matsui, 1992a, 1993):

$$F_D = K_D \cdot E_{mantle} \tag{1}$$

where K_D is the coefficient of degassing rate, and E_{mantle} is the amount of volatile element in the mantle. The coefficient of degassing rate is assumed to be

$$K_D(t) = f \cdot V_D(t) / V_{mantle}$$

$$= f \cdot Sr(t) d_m(t) / V_{mantle} \quad (2)$$

where V_D is the volume of the mantle from which degassing occurs in an unit time, and V_{mantle} is the volume of the mantle. Sr is the seafloor spreading rate and d_m is the melt generation depth in the mantle. We calculate these quantities from the thermal evolution of the mantle (Tajika and Matsui, 1992a, 1993). The factor f is the degassing fraction of volatile element, that is, the fraction of the amount of a certain element that degasses to the surface to the total amount originally included in V_D.

The average degassing efficiency over the history of the Earth may be approximated by the average degassing volume to the present one:

$$\alpha = \overline{V_D} / V_D^* = \frac{1}{t_p} \int_0^{t_p} \frac{V_D(t)}{V_D^*} dt \quad (3)$$

where $t_p = 4600$ Ma. The value for the most plausible argon degassing model is estimated to be 1.5 (Tajika and Matsui, 1993). Therefore we can obtain the total amounts of volatile elements degassed to the surface over the entire history of the Earth, T, as follows:

$$T = \int_0^{t_p} F_D(t) dt \sim \alpha \cdot F_D^* \cdot t_p \sim 6.900 \times F_D^* \text{ mol} \quad (4)$$

The results of estimates for the major volatile elements in the atmosphere and oceans at present are shown in Table 2.

We can classify these volatile elements into two categories: H_2O, Cl and N ($T/S < 100\%$), and C and

TABLE 2

Major volatiles supplied to the surface layers by continuous degassing

Element	F_D^* (mol/Ma)	S^{**} (mol)	T^{***} (mol)	T/S
H_2O	6.1×10^{18}	7.8×10^{22}	4.2×10^{22}	50%
C	2.2×10^{18}	8.0×10^{21}	1.5×10^{22}	200%
Cl	7.6×10^{16}	1.5×10^{21}	5.2×10^{20}	30%
N	3.0×10^{15}	4.3×10^{20}	2.1×10^{19}	10%
S	3.0×10^{17}	5.1×10^{20}	2.1×10^{21}	400%
^{40}Ar	2.5×10^{14}	1.7×10^{18}	1.7×10^{18}	100%

*The degassing rate from the mantle (Tajika, 1992).
**The surface amount at present (Holland, 1978; etc.).
***The total amount degassed to the surface through the history of the Earth.

S ($T/S > 100\%$). Among these volatile elements, Ar is considered to be a non-recycled volatile, which means that Ar will never regas into the mantle after degassing to the surface. Hence 100% of radiogenic ^{40}Ar accumulated into the atmosphere after the formation of the Earth. However, it has been suggested that more than 80% of primordial ^{36}Ar must have degassed by an early catastrophic degassing based on the study of evolution of ^{40}Ar/^{36}Ar in the atmosphere and the mantle (Hamano and Ozima, 1978). This suggests that all other volatile elements must have experienced impact degassing because the impact degassing, as a process of an early catastrophic degassing, is not a selective degassing mechanism.

The accumulation of H_2O, Cl and N by continuous degassing is very small, which constitute small fraction of the present surface amounts ($< 100\%$). This implies that the impact degassing at the time of formation of the Earth must have played a significant role in accumulation of theses elements. In particular, it is suggested that most of the N_2 ($> 90\%$) was degassed by impacts during accretion (Table 2). It is also shown that the continuous degassing contributes only 50% for the present water budget (Table 2). The ocean mass would have been influenced by the water exchange between the surface and the mantle through the global water cycle (i.e., the continuous degassing from the mantle and the subduction of hydrated oceanic crust) after condensation of steam atmosphere. Recently, Kasting and Holm (1992) have argued that the ocean mass has changed with time in such a way to keep the mid-ocean ridges submerged to their present depth. However, the small T/S value for H_2O suggests that the ocean mass may not have changed greatly over the history of the Earth. In fact, the numerical simulation of the global water cycle seems to support this view (Tajika and Matsui, 1992).

On the other hand, it is noted that the total amounts of degassed C and S are estimated to be much larger than the present surface amounts ($> 100\%$). This implies that preferential recycling has occurred for these volatile elements. Both carbon and sulfur are very reactive elements and are precipitated as constituents of carbonates, organic carbon and pyrite. Probably much of these sediments have been subducted into the mantle with the subduction of oceanic crusts and recycled several times over the history of the Earth. We should, however, note that the lower values of T/S for H_2O, Cl

and N than 100% do not mean that these volatiles are not recycled through subduction of the hydrated oceanic crusts, organic materials, pore water in the sediments and so on.

The degassing history of the Earth and the evolution of the atmosphere and ocean may be summarized as follows: (1) The initial catastrophic degassing (probably the impact degassing) must have occurred and almost all volatile elements degassed to the surface at the time of formation of the Earth. In particular, most of N_2 and ^{36}Ar in the present surface reservoirs would have degassed at this time. As a consequence, the proto-atmosphere and ocean probably formed during the earliest history of the Earth although their chemical compositions may be different from those of today. (2) The continuous degassing and, probably, continuous regassing has occurred. This means that the evolution of the atmosphere and ocean may have been promoted by the global cycles of volatile elements between the surface reservoirs and the mantle over the history of the Earth. Although the contribution due to the continuous degassing would be small for the budgets of N, Cl and H_2O in the atmosphere and ocean, it would be very large for C and S. (3) The amount of volatile elements at the surface reservoirs (atmosphere, oceans and sediments) may be determined not only by the earliest catastrophic degassing but also by the subsequent continuous degassing from and regassing into the mantle over the history of the Earth.

A proposed scenario for origin and evolution of the atmosphere and ocean

The formation and evolution of the terrestrial atmosphere and ocean reviewed above are summarized as follows: (1) An impact-induced atmosphere composed mainly of H_2O and CO_2 (and also H_2 and CO for reduced condition) is probably formed on the accreting Earth by impact degassing during accretion. (2) At the end of accretion, the steam atmosphere became unstable and condensed to form the proto-ocean with almost the present ocean mass. Although the ocean mass could have affected the water exchange process between the surface and the mantle thereafter, it may not have

changed greatly throughout the history of the Earth. (3) The proto-atmosphere (~ 100 bar of the CO_2-rich atmosphere) would have been formed after condensation of the steam atmosphere, because CO in the proto-atmosphere may be photochemically converted to CO_2. (4) The degassing rates and the present surface amounts of H_2O, C, N, S, Cl and Ar suggest that these volatiles were supplied by the impact degassing during accretion and followed the subsequent global cycle between the surface and mantle reservoirs (in other words, degassing from and regassing into the mantle). (5) CO_2 in the proto-atmosphere has decreased through the global carbon cycle against an increase in the solar luminosity with the continental growth during Hadean and Archean, which would have affected the carbon cycle itself and the surface temperature greatly at that period. Continental growth is required for the terrestrial environment to evolve to the present state. (6) Most of N_2 and ^{36}Ar has degassed by impacts during accretion. In particular for N_2, the subsequent continuous degassing contributes at most 10% of the present budget. Therefore the total pressure of terrestrial atmosphere would have been kept about 1 bar since N_2 dominant atmosphere formed. (7) Free oxygen is produced through photosynthesis by organisms. It is, however, difficult to constrain the evolution of oxygen by the geochemical cycle model because the production rate of oxygen today is very large compared to the amount of oxygen in the atmosphere (i.e., it takes $\sim 10^7$ yr for oxygen to reach the present amount). However, the composition of paleosols suggests that oxygen partial pressure increased dramatically from $\leqslant 0.01$ PAL (present atmospheric level) to > 0.15 PAL between 2.2 and 1.9 Ga ago (Holland et al., 1989; Holland and Beukes, 1990).

In order to study the evolution of the atmosphere and ocean as a whole quantitatively, we will need to construct an evolution model of the whole Earth system which includes chemical coupling among the geochemical cycles of all the major volatile elements at the same time (Tajika 1992; Tajika and Matsui, 1992b). The above scenario will provide a clear perspective for the evolution of the atmosphere and ocean tightly coupled with the evolution of the solid-Earth such as surface tectonics, volcanism and continental growth, and also with thermal evolution of the mantle.

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