



The chemical composition of the early terrestrial atmosphere: Formation of a reducing atmosphere from CI-like material

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[1] The chemical composition of Earth's early atmosphere is likely to have played an important role in the origin of life. In particular, the redox state of Earth's early atmosphere may have controlled greatly the efficiency of abiotic synthesis of biologically important organic compounds. However, the chemical composition of the Earth's early atmosphere has not been studied extensively before. In this study, we theoretically estimate the chemical composition of an atmosphere near the end of the completion of planetesimal accretion of the Earth. Our calculation results show that the Earth's early atmosphere is very reducing, rich in H₂ and/or CH₄, regardless of which meteoritic materials accrete and regardless of which chemical reactions control the molecular abundance in the atmosphere. In other words, impact-degassed origin of Earth's atmosphere leads inevitably to a reducing chemical composition, which is very favorable to efficient prebiotic synthesis of organic matter on Earth.

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1. Introduction

[2] Standard theories for the planetary formation predict that the planets grow via accretion of planetesimals [e.g., Safronov, 1972; Hayashi *et al.*, 1985]. Accretion of planetesimals heats the protoplanets through the release of gravitational energy, and the magnitude of heating increases as the protoplanets grow. Once the protoplanets reached a critical size, protoatmospheres would begin to form due to impact degassing [e.g., Lange and Ahrens, 1982; Ahrens *et al.*, 1989].

[3] The very earliest terrestrial atmosphere during the main phase of its growth is estimated to be very reducing (i.e., rich in H₂) because its chemical composition is controlled by metallic iron constantly supplied by accreting planetesimals [e.g., Dreibus and Wänke, 1989; Abe *et al.*, 2000] and perhaps contributed by a gravitationally captured solar nebula gas [e.g., Porcelli and Pepin, 2000]. It is also likely that an extremely dense steam atmosphere was formed during this phase [e.g., Abe and Matsui, 1986; Matsui and Abe, 1986; Zahnle *et al.*, 1988].

[4] However, when the accretion of the Earth is almost completed, the accretional heat flux rapidly decreases and ceases to sustain the steam atmosphere, and a hot proto-ocean would be formed as a result of the condensation of water vapor in the hot protoatmosphere [e.g., Abe and

Matsui, 1986; Matsui and Abe, 1986]. Even after the formation of the first proto-ocean, proto-oceans would probably have been repeatedly vaporized by large impacts for several hundred million years [e.g., Sleep *et al.*, 1989]. About 3.8 billion years ago, when the heavy bombardment of planetesimals is almost ended, the surface of the Earth probably started to harbor the life continuously since then [e.g., Maher and Stevenson, 1988; Kasting, 1993 and references therein]. However, the composition of the atmosphere around this important period of Earth's history is uncertain because geologic evidence is very scarce. The composition of this stage of terrestrial atmosphere is the focus of this study.

[5] When most of H₂O in the steam atmosphere collapses to form the ocean, a large amount of H₂ will be left in the atmosphere. It is not evident whether H₂ is lost through hydrodynamic escape in a short time or not [e.g., Sekiya *et al.*, 1980, 1981; Tian *et al.*, 2005]. However, the atmospheric composition was probably not controlled by chemical reaction with metallic iron because the supply of metallic iron is greatly reduced and metallic core segregation is also likely to have finished by this time (i.e., probably 4.5 billion years ago) [e.g., Abe, 1993; Abe *et al.*, 2000]. Thus the dominant contributor to the atmosphere during the final stage of Earth's accretion is most likely volatile degassing upon meteoritic impacts.

[6] In the final stage of Earth's accretion, an accretion of oxidizing material is inferred from the abundance of highly siderophile elements (Pt, Pd, Rh, Ru, Os, Ir, Au, and Re) in the terrestrial mantle [e.g., Wänke *et al.*, 1984]. The observed abundance of highly siderophile elements is known to be much higher than that is equilibrated with metallic iron. This excess of highly siderophile elements in the mantle can be accounted for by accretion of oxidizing

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material, such as CI chondrite, after the end of core formation [e.g., *Kimura et al.*, 1974; *Chou et al.*, 1983]. Such a late-stage accretion of oxidizing material, so-called late veneer, is generally believed to generate an oxidizing atmosphere that is composed largely of H₂O and CO₂. An atmosphere dominated by CO₂-N₂-H₂O, which is often called a neutral atmosphere, is referred to as an oxidizing atmosphere in this paper in order to clarify the contrast to a reducing atmosphere. However, whether H₂O and CO₂ were the main components of gas phase degassed from CI chondrites is not examined yet.

[7] The composition of Earth's early atmosphere has been also considered rather oxidizing: CO₂-rich mixtures with only trace amount of H₂ and CH₄ [e.g., *Rubey*, 1955; *Kasting*, 1993]. This prevailing view is based on the fact that modern volcanic gas composition is relatively oxidizing [e.g., *Holland*, 1984]. Such oxidizing volcanic gases are consistent with the composition predicted for equilibrium with their mantle sources that have O₂ fugacities of the quartz-fayalite-magnetite (QFM) buffer [*Holland*, 1984]. After the removal of metallic iron from the Earth's mantle as a result of early core formation [e.g., *Stevenson*, 1990], the upper mantle has been near the QFM-buffered redox state [e.g., *Delano*, 2001]. Thus volcanic gases released from Earth's interior after iron segregation should have been relatively oxidizing [*Holland*, 1984].

[8] However, a reducing early atmosphere is favored by researchers studying the origin of life. Here we use the term "reducing atmosphere" to refer to an atmosphere containing H₂, CH₄, and CO as major components. Experiments on the prebiotic synthesis indicate that the oxidation state of the atmosphere controls the yields of the synthesis of organic matter greatly [e.g., *Miller*, 1953; *Pinto et al.*, 1980; *Stribling and Miller*, 1987]. A reducing atmosphere, which contains reducing species, such as CH₄, H₂, and CO, allows efficient abiotic synthesis of organic compounds, but it is very inefficient to synthesize the organic matter in the atmosphere which does not contain reducing species.

[9] In the following, we first discuss the chemical composition of impact-degassed atmosphere. Second, we consider an influence of preexisting atmosphere that is formed during the main stage of accretion on the chemical composition of the early atmosphere. Third, we infer the chemical composition of the early atmosphere from the elemental abundance of the present Earth surface, and we discuss the life span of the early reducing atmosphere.

2. Late-Veneer Atmosphere

[10] Accretion of oxidizing material after the end of core formation (late veneer) has been suggested as a mechanism to supply not only excess siderophile elements in the Earth's mantle but also atmophile elements in the Earth's near surface [e.g., *Chyba*, 1990]. It is very likely that atmophile elements in the accreting material of late veneer will degass upon impact since partial vaporization of impactor will occur when the proto-Earth is larger than 75% of the present mass [e.g., *Abe*, 1993].

[11] At the time of later-veneer accretion, the average temperature of Earth's surface would not be high enough to allow chemical reactions to proceed efficiently since accretionary flux at that time is too small to sustain a massive

steam atmosphere [e.g., *Abe*, 1993]. However, materials involved in an impact vapor plume will be in chemical equilibrium immediately after the impact since the rates of chemical reactions are fast under high-temperature and high-pressure conditions of the impact vapor plume. Because an impact vapor plume cools as it expands, chemical equilibrium becomes increasingly more difficult to achieve. The chemical reactions of vapor plumes are quenched when reaction rates become too slow to attain chemical equilibrium.

2.1. Accreting Material

[12] To examine the atmospheric composition generated by the late veneer, we assume that the bulk composition of planetesimal accreted as the late veneer is similar to that of CI-chondritic material. It is widely accepted that the composition of the late-veneer material is similar to CI chondrite [e.g., *Chou et al.*, 1983].

[13] The composition of CI chondrite has been studied extensively, and its chemical composition is mostly established [e.g., *Wasson and Kallemeyn*, 1988]. However, the abundance of water is still controversial [e.g., *Kuramoto and Matsui*, 1996 and references therein]. Some groups of researchers found about 20 wt% of water in CI chondrite [*Wiik*, 1956], whereas 5–10 wt% of water has also been reported [*Boato*, 1954; *Kerridge*, 1985]. The variation in water abundance in CI chondrite may be related to the contamination of terrestrial water [*Kaplan*, 1971] although it is still controversial. Thus we consider two cases: dry case ~6 wt% H₂O, and wet case ~20 wt% H₂O (Table 1) in this study.

[14] To evaluate the atmospheric composition generated by the late veneer, we have to take into account not only atmophile elements but also iron and sulfur. Although most of the major atmophile elements would remain in the atmosphere, the atmospheric abundance of oxygen is controlled by the partition between fluid (i.e., gas and liquid) phases and solid phase. The change in the redox state of iron affects the abundance of oxygen in the atmosphere. Also, the abundance of iron, which can combine with oxygen, is determined by the abundance of sulfur combined with iron since iron combined with sulfur does not combine with oxygen.

[15] In this study, we calculate thermochemical equilibrium of a system that consists of six elements (H, C, N, O, S, and Fe). Since Mn, Co, Ni, and Cu are similar to Fe in chemical behavior, the abundances of these elements are added to that of Fe. Other major elements are removed from the reaction system as oxides because their affinity to oxygen is much stronger than Fe. To remove these elements together with their combining oxygen, the following valences are assumed: Na(+1), Mg(+2), Al(+3), Si(+4), P(+5), K(+1), Ca(+2), Ti(+4), and Cr(+3) [*Railsback*, 2003]. Minor elements not mentioned here are neglected in our calculation.

[16] The elemental abundances used in our calculation are summarized in Table 1. The chemical composition of CI chondrite given by *Wasson and Kallemeyn* [1988] is used to estimate the elemental abundance of the wet case. The H₂O content of the wet case corresponds to ~18 wt%. We assume that the H₂O content of dry case is 5.8 wt% as reported by *Kerridge* [1985]. The elemental abundance of the dry case is created by removing some H₂O from the composition of the wet case.

Table 1. Model Composition of Two Components^a

Element	Component R	Component O	
		Wet Case	Dry Case
H	4.000	1.219	0.612
C		0.164	0.291
N		0.007	0.012
O	≡1	≡1	≡1
S		0.113	0.201
Fe		0.215	0.380

^aAll values listed are in mole and are normalized to O ≡ 1.

2.2. Calculation of Chemical Equilibrium

[17] To examine the atmospheric composition generated by the late veneer, we have calculated the equilibrium chemical composition at a variety of temperatures and pressures, ranging from 300 to 2500 K and 1 to 100 bar, respectively. The conditions of quench of chemical reactions in the impact vapor plumes are determined not only by reaction rates but also by the cooling rate of vapor plume. Although several studies estimated the effective quenching temperature to be higher than 1000 K for impact vapor plumes [Fegley *et al.*, 1986; Zahnle, 1990], it depends on various parameters, such as size of impactor and impact velocity. Although a kinetic model that involves all the reaction paths relevant to each elemental composition is necessary for precise determination of the molecular composition, equilibrium molecular composition at different *P-T* conditions gives us a general view of the reaction system and serves as the baseline of more complicated studies.

[18] To obtain the molecular composition at equilibrium, we employed a thermodynamic energy minimization procedure that considers 30 species (Table 2) and determines the complete equilibrium composition of a system that minimizes the total Gibbs free energy as a function of temperature, pressure, and elemental composition. We used the thermodynamic data on the JANAF Tables [Chase, 1998].

[19] It is important to note that the oxygen fugacity of the system is not assumed but is calculated in the model. In principle, it cannot be determined which buffer reaction controls the oxygen fugacity of the system until the actual equilibrium calculation is conducted. Thus procedures that assume a buffer reaction of oxygen fugacity a priori are inappropriate for examining the chemical composition of the atmosphere. In this study, we calculate the partitioning of oxygen between fluid and solid phases, and the oxygen fugacity of the system is self-consistently determined.

2.3. Atmospheric Composition

[20] Figures 1 and 2 show dry gas compositions as functions of quenching temperature. Although the fraction of water is not shown in these figures, the equilibrium compositions of atmospheres contain a large amount of water. The fraction of water in the gas phase was not shown because it changes greatly with temperature via a simple phase change (i.e., condensation and vaporization), not via chemical reactions as other chemical species do. The amount of water released from the accreting material depends on the quenching temperature and water content of the accreting material. When the accreting material contains ~6 wt% H₂O (dry case), approximately 50–100% of hydrogen is released as H₂O. When the accreting

material contains ~20 wt% H₂O (wet case), approximately 75–100% of hydrogen is released as H₂O.

[21] Here it is noted that the CI chondrites are generally considered to be one of the most oxidizing materials in the solar system based on the state of iron [e.g., Wasson, 1985]. The CI chondrites are the only clan of chondrites, with no members of which contain metallic iron; all the iron in the CI chondrites is oxidized [e.g., Weisberg *et al.*, 2006]. Thus the compositions of atmospheres obtained in the above calculation using the CI composition would be considered as the most oxidizing atmosphere generated by the accretion process. The most important point here is that considerable amounts of reducing species such as H₂, CO, and CH₄ are present in “CI-derived” atmosphere despite of the oxidizing nature of CI composition. The abundance of reducing species is insensitive to the pressure and the water content of CI chondrite. Although reducing gas species are minor for very low quenching temperatures (~300 K), it is likely that the quenching temperatures for impact vapor plumes are higher than 1000 K [Fegley *et al.*, 1986; Zahnle, 1990]. Therefore an atmosphere generated by the accretion of CI chondrite is likely to contain more than 30% of reducing species, such as H₂ and CO. The atmospheric H₂/CO ratio depends on the water content of CI chondrite; the H₂/CO ratio is high for high water content.

[22] The proportion of reducing species (for example, H₂ and CO) decreases as quenching temperature decreases from 1800 to 1400 K. The decrease in the proportion of reducing species is caused by the formation of iron sulfides. Although iron sulfides are unstable at high temperatures,

Table 2. Chemical Compounds and Their Phases Considered in This Study

Name	Chemical Formula
<i>Gas Phase</i>	
Hydrogen	H ₂
Water	H ₂ O
Oxygen	O ₂
Carbon monoxide	CO
Carbon dioxide	CO ₂
Methane	CH ₄
Nitrogen	N ₂
Ammonia	NH ₃
Sulfur	S
Sulfur	S ₂
Mercapto	SH
Hydrogen sulfide	H ₂ S
Sulfur oxide	SO
Sulfur dioxide	SO ₂
Sulfur oxide	S ₂ O
Carbon oxide sulfide	COS
Iron sulfide	FeS
Iron	Fe
Hydrogen	H
Hydroxyl	OH
<i>Condensed Phase</i>	
Water (liquid)	H ₂ O
Graphite	C
Pyrite	FeS ₂
Troilite	FeS
Iron sulfide (liquid)	FeS
Iron (crystal)	Fe
Iron (liquid)	Fe
Wüstite	Fe _{0.947} O
Magnetite	Fe ₃ O ₄
Hematite	Fe ₂ O ₃

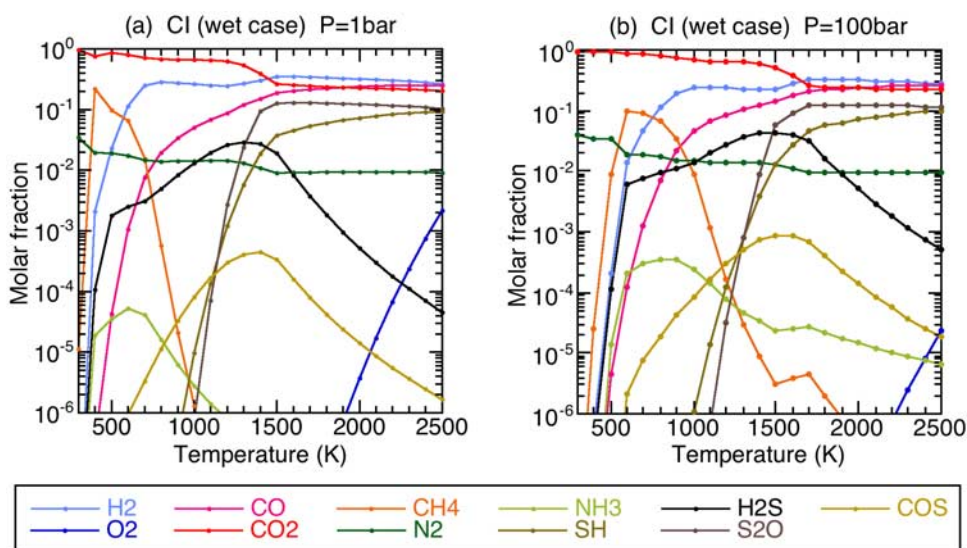


Figure 1. Equilibrium composition of dry gas phase at (a) 1 bar and (b) 100 bar total pressures. Water content in CI chondrite is about 20 wt% (wet case). This figure does not include water vapor since atmospheric water varies greatly due to condensation.

they are stable and formed from iron oxides in this temperature range. The transformation of iron oxides into iron sulfides releases oxygen from solid phases into the atmosphere. Since this released oxygen combines with reducing species, the proportion of reducing gas species in the atmosphere decreases.

[23] When quenching temperature is decreased from 1000 to 500 K, CH₄ is formed instead of H₂ and CO. The mixing ratio of CH₄ is more than several percent when quenching temperature is between 400 and 900 K. Although these temperatures are lower than the expected gas-phase quenching temperature of impact vapor plume, CH₄ may be produced by surface catalysis reaction [Sekine *et al.*, 2003; Kress and McKay, 2004].

[24] If the chemical equilibrium is attained at very low temperatures (for example, 300 K), reducing gas species that exist at high temperature are converted into graphite. Therefore there is an extremely large amount of reducing species in the condensed phase even though the atmosphere is composed of oxidizing species, such as CO₂ and N₂. However, no mechanism has been suggested to accelerate the production of graphite at such low temperatures.

[25] The range of volume mixing ratio of ammonia (NH₃) calculated here is several to several hundred parts per million. The sensitivities of NH₃ abundance to temperature and pressure are similar to those of CH₄. The abundance of NH₃ is maximized in the temperature range from 600 to 900 K at the pressures used in this study (1–100 bar). The

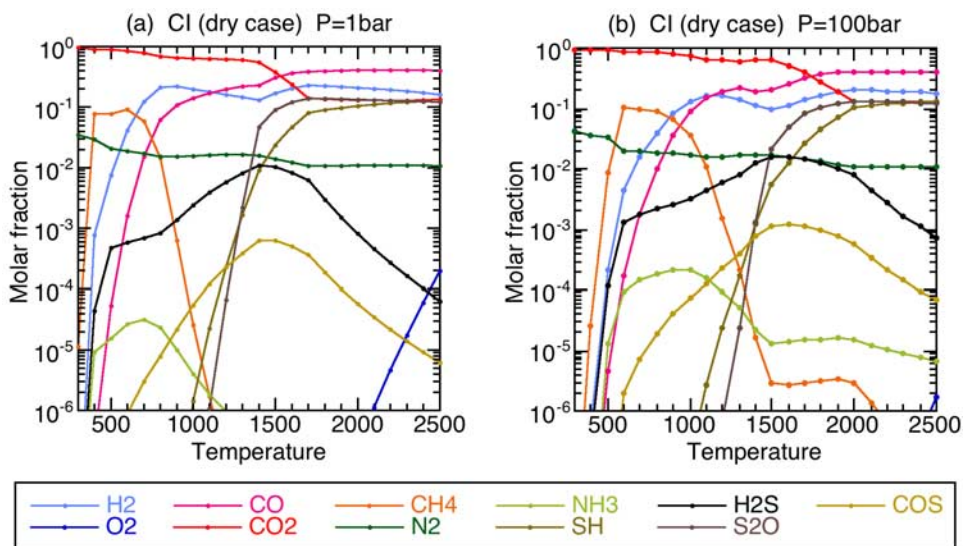


Figure 2. Equilibrium composition of dry gas phase at (a) 1 bar and (b) 100 bar total pressures. Water content in CI chondrite is about 6 wt% (dry case). This figure does not include water vapor since atmospheric water varies greatly due to condensation.

abundance of NH_3 increases with pressure. When pressure is higher than 10 bar, NH_3 mixing ratio is higher than 1 ppm for a wide range of temperature.

2.4. Oxygen Deficit

[26] The results of chemical equilibrium calculations demonstrate that the Earth's early atmosphere would contain a significant amount of reducing species even if atmosphere is entirely generated by the accretion of CI chondrites. The reason why this occurs is the following. As mentioned above, all the iron in the CI chondrites is oxidized [e.g., *Wasson*, 1985; *Weisberg et al.*, 2006]. However, CI chondrite also contains reducing components such as organic matter; the components in CI are not in chemical equilibrium to each other, no matter which temperature is assumed. The gases formed through the decomposition of organic matter are intrinsically reducing. The redox state of degassed atmosphere from CI is determined by the relative abundance of oxygen in the oxidized iron to that of reducing organic matter.

[27] The deficit in oxygen is easily demonstrated by a simple calculation used by *Kasting et al.* [1993]. It is appropriate to assume that carbon content of 3.5 wt% in CI chondrite represents the abundance of reduced carbon in CI chondrite since almost all carbon in CI chondrite is in reduced forms [e.g., *Kerridge*, 1985; *Wasson and Kallemeyn*, 1988]. If reduced carbon is oxidized by conversion of ferric iron to ferrous iron, two moles of ferric iron is required to oxidize 1 mol of reduced carbon.



Therefore about 32.6 wt% of ferric iron is required to oxidize 3.5 wt% of reduced carbon. However, a typical iron content in CI chondrite is about 20 wt% [*Wasson and Kallemeyn*, 1988]. The abundance of ferric iron in CI chondrite is not sufficient to oxidize all the carbon in CI chondrite. Even though some of the reducing gases are oxidized through the reaction with iron oxides, the abundance of oxygen stored in iron oxides is not enough to oxidize all the reducing gases released from organic matter.

[28] It is inevitable that an atmosphere generated by the late veneer contains a considerable amount of reducing gases since oxygen is deficient even in CI chondrites, which are one of the most oxidizing materials among the primitive materials in the solar system. Thus the formation of reducing atmospheres by accretion is a very robust consequence. Even when chemical equilibrium is not attained in the vapor plume, the atmosphere will contain reducing species as a result of oxygen deficit.

3. The Influence of the Preexisting Atmosphere

[29] It is not obvious whether the very early atmosphere and ocean formed before the accretion of the late veneer are completely lost or not [*Hashimoto and Abe*, 1995]. Here the late veneer is defined as the mass that is not reacted with metallic iron, so the preexisting atmosphere (including ocean) prior to the later-veneer accretion is the atmosphere that was reacted with metallic iron. In this section, we examine the influence of survived preexisting atmosphere

on the chemical composition of the early atmosphere at the end of the late-veneer accretion.

3.1. Atmospheres Before the Late Veneer

[30] The formation of atmosphere by accretion of volatile-containing planetesimals must have begun in the early stage of Earth formation [e.g., *Abe et al.*, 2000]. Atmosphere elements degas from accreting planetesimals, when impact generates sufficiently high-temperature and high-pressure conditions. Shock experiments indicate that degassing begins when the mass of the proto-Earth is as large as 10% of the present size [*Lange and Ahrens*, 1982; *Ahrens et al.*, 1989]. It is consistent with argon isotope data which suggest that most of the terrestrial atmosphere was formed by 4.0 billion years ago [e.g., *Hamano and Ozima*, 1978].

[31] The atmosphere formed during the main accretionary phase is probably reducing since a large amount of metallic iron, which later becomes the core of the Earth, would be contained in the planetesimals [e.g., *Dreibus and Wänke*, 1989]. Then, a large amount of H_2 would be formed during planetary accretion by the reaction of metallic iron with H_2O [e.g., *Dreibus and Wänke*, 1989]. Thus the atmosphere formed during the main accretionary phase is expected to be reducing even when the atmosphere is generated solely by degassing.

[32] If Earth accreted in the solar nebula, hydrogen-rich atmosphere also could have been formed by gravitational capture of solar nebula gas [e.g., *Hayashi et al.*, 1979]. Although solar nebula gas cannot be a major source of the present terrestrial atmosphere, it has been suggested that some part of captured solar nebula gas might be retained as a source of rare gases [e.g., *Porcelli and Pepin*, 2000]. Since H_2 in a solar-type atmosphere will react with Fe-bearing silicate on the planetary surface [e.g., *Sasaki*, 1990], the composition of the resulting atmosphere is similar to that of the atmosphere generated by degassing during the main accretionary phase.

[33] There are several processes that may dissipate a hydrogen-rich atmosphere formed during the main accretionary phase. Hydrogen in the upper atmosphere is heated by strong radiation of X ray and extreme ultraviolet (XUV) from the young Sun and is lost hydrodynamically to the space; i.e., hydrodynamic escape [e.g., *Sekiya et al.*, 1980, 1981]. This process was believed to dissipate efficiently in a short time (about several million years) a hydrogen-rich atmosphere. However, it has been suggested that an escape of hydrogen from early Earth's atmosphere would occur much slower than previously thought [*Tian et al.*, 2005].

[34] Another mechanism that dissipates the atmosphere is impact erosion [e.g., *Melosh and Vickery*, 1989; *Ahrens*, 1993]. Impact erosion of atmosphere would reduce the relative contribution of the preexisting atmosphere to the current terrestrial atmosphere. However, the degree of the impact erosion of Earth's atmosphere throughout its history is difficult to estimate accurately. There are a couple of important factors controlling the efficiency of the atmospheric erosion by impacts. First, the large mass of Earth prevents this process from occurring efficiently. It requires impact velocities higher than twice the escape velocity [*Vickery and Melosh*, 1990; *Melosh et al.*, 1993], but such an extremely high velocity impact is expected to be rare [e.g., *Chyba*, 1991]. Second, the condition of Earth's surface at the

time of large impacts also changes the erosion efficiency greatly. When Earth is covered with an ocean, the erosion efficiency is much greater than the case when Earth is covered with a dense steam atmosphere [Genda and Abe, 2003, 2005]. Thus, although an extremely large impact, such as moon-forming giant impact, may remove a significant fraction of the preexisting atmosphere, the fraction of the lost atmosphere to the total mass of the atmosphere due to such a giant impact depends on the condition of Earth's surface. Despite these uncertainties, Earth's atmosphere during and after the late-veneer accretion phase is predicted to be reducing as we discuss in the following sections 3.2 and 3.3.

3.2. Two-Component Model for Atmospheric Composition

[35] In order to consider the influence of the preexisting atmosphere formed before the accretion of late veneer, we use a model in which the composition of the early atmosphere is described as mixtures of two chemically different components, R and O. Since metallic iron has a predominant influence on the elemental abundance of atmosphere, we choose the component R to be the component equilibrated with molten metallic iron and the component O to be the volatile directly degassed from accreting planetesimals during the late stage not equilibrated with metallic iron.

[36] The mixing ratio of the two components f is defined as the fraction of the late-veneer contribution to the volatile inventory in the Earth surface and mantle (i.e., atmosphere, ocean, crust, and mantle). Although f can be defined by using any volatile element, hydrogen is chosen in this study.

$$f \equiv \frac{N_H^O}{N_H^R + N_H^O} \quad (2)$$

where N_H^O is the number of hydrogen supplied by the component O, and N_H^R is that supplied by the component R. If the atmosphere and ocean generated during the main accretionary phase are completely dissipated after the end of accretion of core-forming metallic iron, the atmosphere is generated entirely by the late veneer. Then, the atmosphere does not contain any component that is equilibrated with molten metallic iron, f value is unity. In contrast, f value is less than unity if the very early atmosphere formed during the accretion of core-forming metallic iron has not been completely lost.

[37] The elemental abundance in the component R is determined by equilibrium between the atmosphere and molten metallic iron. When the atmosphere and metallic iron are in equilibrium, oxygen fugacity is buffered by iron oxidation reaction. The abundances of carbon and nitrogen in the gas phase are also controlled by the solubility of these elements in molten metallic iron.

[38] We assume that the component R consists of equal amounts of H_2 and H_2O (Table 1). When metallic iron and silicates exist simultaneously, oxygen fugacity would be close to that of the iron-wüstite buffer [Holland, 1984; Abe *et al.*, 2000]:



where $x = 0.947$. The ratio of H_2/H_2O under the condition of iron-wüstite buffer will be larger than unity at high temperatures (i.e., >1000 K) [Sasaki, 1990]. In a real system, where other species coexist, the activity of wüstite is nearly equal to the molar fraction of FeO in silicate melts, and oxygen fugacity is possibly smaller than that controlled by the iron-wüstite buffer. Thus the assumed ratio of $H_2/H_2O = 1$ is an underestimate for a component-R atmosphere; a real component-R atmosphere may be more reducing than our model.

[39] We also assume that carbon and nitrogen are not present in the component-R atmosphere since solubilities of carbon and nitrogen in molten metallic iron are much larger than that of hydrogen [e.g., Wood, 1993]. However, some carbon and nitrogen would remain in the atmosphere. The influence of these remaining carbon and nitrogen in the component R is discussed below (section 3.4).

3.3. Molecular Composition of Mixed Atmosphere

[40] The preexisting atmosphere will chemically interact with the material accreted later since vapor plumes generated by impacts of planetesimals interact intensely with the surrounding atmosphere during their downrange motion and buoyancy uprise [Sugita and Schultz, 2003]. Although such high-temperature conditions are local and transient, such impacts occur frequently at the final stage of the Earth accretion. Since it is difficult to estimate the extent of interaction between the preexisting atmosphere and accreting material, we examined an extreme case that shows that the materials accreted later are chemically equilibrated with the preexisting atmosphere. This situation will occur when repeated impacts efficiently promote the chemical reaction between the accreting material and the preexisting atmosphere.

[41] Using the CI chondrite composition for the component O, we calculated the chemical composition of mixed atmosphere (Figures 3 and 4). Since the value of f represents the fraction of the metallic-iron-free material accreted, the abundance of reducing species decreases as the value of f increases. When quenching temperature is higher than ~ 1000 K, the abundance of H_2 increases with f due to the survival of H_2-H_2O atmosphere. However, the abundance of CH_4 increases significantly when quenching temperature is lower than ~ 800 K. At low temperatures, hydrogen in the H_2-H_2O atmosphere combines with carbon delivered by late-stage accretion. If some catalytic reactions can produce CH_4 at low temperatures [e.g., Sekine *et al.*, 2003, 2006], the survival of H_2-H_2O atmosphere probably leads to CH_4 -rich atmosphere at the end of accretion.

3.4. Estimation of f Value

[42] The fraction f of the late-veneer contribution (i.e., component O) can be estimated from the relative abundance of atmophile elements. There are marked differences in siderophilicity among atmophile elements. The atmosphere of the component R is depleted in siderophile elements since it has been removed by dissolving in metallic iron. However, the atmosphere that originated from the component O is not depleted in siderophile elements. Therefore we can evaluate f , the fraction of late-veneer contribution, using two atmophile elements with different siderophilicity.

[43] We choose hydrogen as a representative of weakly siderophile elements, and we select carbon and nitrogen for

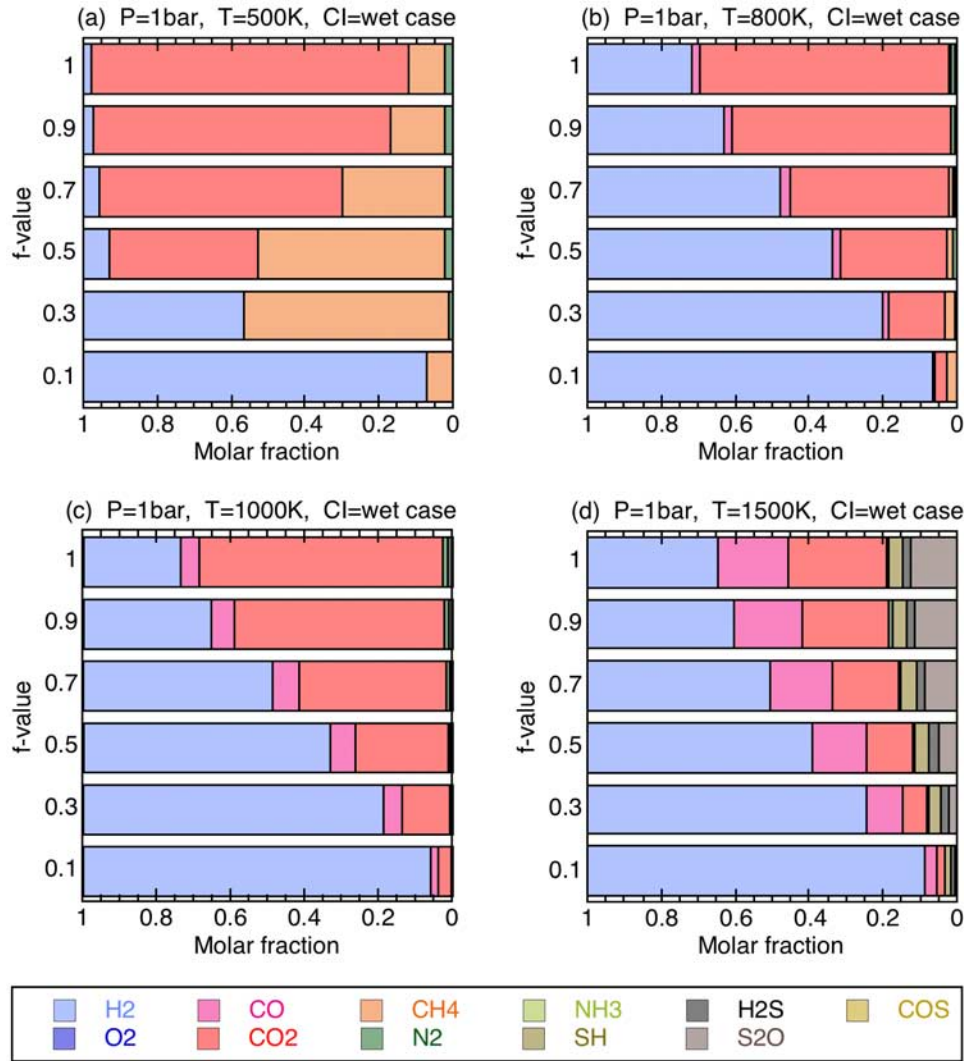


Figure 3. Dry gas composition for various values of parameter f . Water content of CI chondrite is about 20 wt% (wet case). Total pressure and temperature of each system are (a) $P = 1$ bar, $T = 500$ K, (b) $P = 1$ bar, $T = 800$ K, (c) $P = 1$ bar, $T = 1000$ K, and (d) $P = 1$ bar, $T = 1500$ K. This figure does not include water vapor since atmospheric water varies greatly due to condensation.

those of strongly siderophile elements. If metallic iron absorbed all of the carbon and the nitrogen in the atmosphere of the component R but no hydrogen (see section 3.2), then the f value is given by

$$f = \left(\frac{N_H^O}{N_X^O} \right) \left(\frac{N_X^{Earth}}{N_H^{Earth}} \right) \quad (4)$$

where N_i^O and N_i^{Earth} are the numbers of i th element ($i = H, X; X = C, N$) in the component O and the Earth surface and mantle, respectively. The derivation of equation (4) is given in Appendix A.

[44] To evaluate f value, we use the elemental abundance in the Earth surface and mantle given in Table 3 [Ronov and Yaroshevsky, 1976; Holland, 1978; Kargel and Lewis, 1993]. Here we consider the Earth surface as the sum of the atmosphere, the ocean, and the crust. We also take into account the hydrogen and carbon in the mantle since water

and carbon would be exchanged between the crust and the mantle [e.g., Kasting and Holm, 1992; Sleep and Zahnle, 2001]. Using the composition of component O given in Table 1, we calculated the values of f (Table 4). The calculated f values for wet CI composition and dry CI composition are about 0.3 and 0.1, respectively, which are significantly lower than unity. In other words, despite the model uncertainties, the present elemental abundance of the Earth surface and mantle requires a significant contribution from the atmosphere that was generated when metallic iron was present.

[45] As discussed above in section 3.2, the value of f calculated by equation (4) is an overestimate since some amounts of carbon and nitrogen remain in the atmosphere of component R and some hydrogen components dissolve in molten metallic iron. When we take this overestimation of f into account, a larger amount of the atmosphere generated under the presence of metallic iron (i.e., before and during

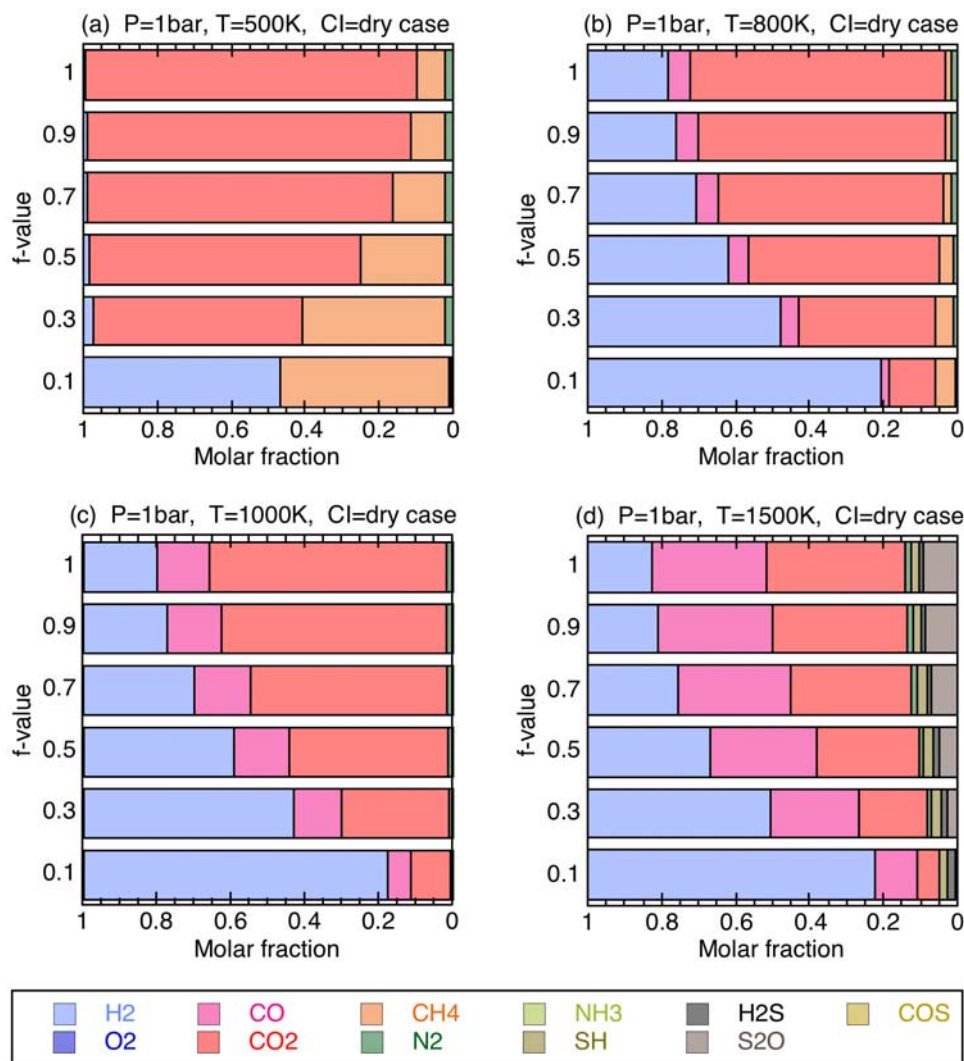


Figure 4. Dry gas composition for various values of parameter f . Water content in CI chondrite is about 6 wt% (dry case). Total pressure and temperature of each system are (a) $P = 1$ bar, $T = 300$ K, (b) $P = 1$ bar, $T = 800$ K, (c) $P = 1$ bar, $T = 1300$ K, and (d) $P = 1$ bar, $T = 1500$ K. This figure does not include water vapor since atmospheric water varies greatly due to condensation.

core formation) needs to remain in the present terrestrial atmosphere than our calculated f values indicate.

[46] It is also likely that the f value of the early atmosphere is much smaller than that estimated from the present elemental abundance because hydrogen in the early atmosphere was likely lost by escape. The elemental abundance might be also altered by exchange of atmophile elements between the mantle and the core. Although it is difficult to evaluate precisely the influence of the exchange between the mantle and the core, its influence is likely to be much smaller than the effect of hydrogen escape. Thus the hydrogen in the surface layers of the Earth must have decreased over the course of its evolution; the ratios of hydrogen to carbon/nitrogen would be much higher in the past (see section 4.1).

4. Discussion and Implication

4.1. The Life Span of Reducing Atmosphere

[47] A reducing early atmosphere is indicated by the elemental abundance of atmophile elements in the Earth

surface and mantle. Such a reducing atmosphere needs to have evolved to an oxidizing atmosphere found today. It is likely that the early reducing atmosphere is oxidized through hydrogen escape [e.g., *Catling et al.*, 2001; *Tian et al.*, 2005]. Since hydrogen is the lightest element, it is preferentially lost to the space. Preferential loss of hydrogen relative to other atmophile elements increases the relative abundance of oxygen in the atmosphere. When hydrogen photodissociated from water vapor is lost, the remaining oxygen, a by-product of photodissociation, would oxidize the atmosphere.

[48] A small value of f indicates that most of the hydrogen in the Earth's surface are delivered during the main accretionary phase. The atmosphere formed during planetary accretion (component-R atmosphere) would contain a large amount of H_2 as a result of the reaction of metallic iron with H_2O . Since such an early atmosphere would contain more H_2 than H_2O in mole [e.g., *Dreibus and Wänke*, 1989; *Sasaki*, 1990; *Abe et al.*, 2000], the

Table 3. Distribution of Carbon, Nitrogen, and Hydrogen in the Earth Surface and Mantle^a

	Hydrogen	Carbon	Nitrogen
Atmosphere		5.8×10^{16}	2.8×10^{20}
Hydrosphere	1.6×10^{23}	3.3×10^{18}	1.6×10^{18}
Crust	6.7×10^{22}	1.0×10^{22}	1.4×10^{20}
Mantle	1.5×10^{23}	1.2×10^{22}	1.1×10^{20}
Earth Surface	2.2×10^{23}	1.0×10^{22}	4.3×10^{20}
Earth Surface + Mantle	3.7×10^{23}	2.2×10^{22}	5.4×10^{20}

^aAll values listed are in mole.

amount of dissipated hydrogen must be more than that in the present terrestrial ocean. In addition to the dissipation of H₂, there is a need to oxidize the reduced carbon, such as C, CO, and CH₄. There is also probably a need for oxidizing the mantle since ferric iron in the mantle would be produced by oxidation of ferrous iron. These oxidation processes will consume a great number of oxygen atom [Kasting *et al.*, 1993] and require more hydrogen to escape.

[49] The timescale for hydrogen escape, which is the timescale for oxidization of the reducing atmosphere, is controlled by the energy available to drive the escape flow since escape of hydrogen from a hydrogen-rich atmosphere is energy-limited [Tian *et al.*, 2005]. Since hydrogen in the upper atmosphere is heated by radiation of XUV from the young Sun, the upper limit of mass loss rate is controlled by the solar XUV flux.

[50] The escape of hydrogen from very early Earth's atmosphere might occur at a very high rate since the XUV emission of the young Sun is estimated to be about 100 times that of the present Sun [Ribas *et al.*, 2005]. However, the hydrogen escape depends greatly on whether the Earth was surrounded by a protoplanetary disk gas. Before the protoplanetary disk gas was dissipated, the XUV radiation was absorbed by the disk gas and could not have a great influence on the planetary atmosphere. When once the disk gas was dissipated, the strong radiation would start to affect the planetary atmosphere. The timing of disk gas dissipation is not observationally constrained yet. However, theoretical models of terminal phase of terrestrial planet formation require the presence of thin disk gas around the terrestrial planets; high eccentricities of terrestrial planets resulting from the final stage of planet formation through mutual collision of Mars-sized protoplanets (i.e., giant impacts) are very difficult to reduce without remnant protoplanetary disk gas [Kominami and Ida, 2004; Nagasawa *et al.*, 2005].

[51] If a massive hydrogen escape occurs on very early Earth, it might change the composition of preexisting atmosphere significantly. If accretion of metallic iron was ended and metallic iron disappeared from the Earth surface before the dissipation of the protoplanetary disk gas, the strong solar XUV radiation would deplete the atmospheric H₂ from the preexisting atmosphere. Although some H₂O would be lost by photodissociation of H₂O and resulting hydrogen would escape from the Earth, most of the H₂O likely remains on the Earth because of the cold trap, which effectively prevents a massive loss of H₂O.

[52] If a massive hydrogen escape generates a H₂O-rich preexisting atmosphere, the atmospheric composition subsequent to the late-veener accretion would be similar to that of a case for $f = 1$ regardless of the actual value of f . As shown in section 2, an atmosphere with $f = 1$ has the most oxidizing composition among the atmosphere predicted for the early Earth, but it is still very reducing and rich in H₂ and/or CH₄. It is worth noting that such a H₂O-rich preexisting atmosphere does not lead to oxidation of the atmosphere generated by the late-veener accretion since H₂O does not have excess oxygen to oxidize the reducing species. Thus, even in an extreme case where H₂ in the preexisting atmosphere is completely lost and only H₂O is left behind on the Earth before the accretion of the late veneer, the resulting atmosphere after the late veneer accretion would be reducing (i.e., rich in CH₄ and/or H₂).

[53] It is noted that a reducing atmosphere at the time of late-veener accretion would likely survive more than a few hundred million years. When the heavy bombardment of planetesimals is almost ended about 3.8 billion years ago, the solar XUV flux decreased to about 10 times the present value [Ribas *et al.*, 2005]. On the basis of the calculation made by Tian *et al.* [2005], the hydrogen escape flux would be about 6×10^{15} molecules m⁻² s⁻¹ for a solar XUV level 10 times that of today. Then, dissipation of hydrogen equivalent to that in the terrestrial ocean needs 500 million years. Thus it is likely that ancient terrestrial atmosphere had contained reducing species at least for a few hundred million years.

4.2. Implication for Early Earth

[54] The formation of a reducing early atmosphere does not depend on the reaction kinetics since the reducing early atmosphere is formed as a result of the deficiency of oxygen. The result of our model indicates that the early atmosphere would contain a significant amount of reducing species, such as H₂, CO, CH₄, and NH₃. Such a reducing atmosphere would lead to efficient abiotic synthesis of organic compounds for the origin of life.

[55] It has also been suggested that reducing gases, such as CH₄ and NH₃, have been important greenhouse gases on the early Earth [e.g., Sagan and Mullen, 1972; Kiehl and Dickinson, 1987; Sagan and Chyba, 1997; Pavlov *et al.*, 2000]. The geologic record tells us that liquid water was present on the early Earth [e.g., Mojzsis *et al.*, 2001; Wilde *et al.*, 2001]. However, standard models of solar evolution indicate that the luminosity of the Sun was ~70% of the current value at the time when the Sun is formed and has

Table 4. Estimated Value of f From the Elemental Abundance Near the Earth Surface

	Water Content	Reservoir	f Value
H/C	Wet case	Surface	0.34
		Surface + mantle	0.44
	Dry case	Surface	0.10
		Surface + mantle	0.13
H/N	Wet case	Surface	0.34
		Surface + mantle	0.25
	Dry case	Surface	0.10
		Surface + mantle	0.07

increased monotonically [e.g., *Gough*, 1981]. To compensate for the fainter solar luminosity, strong greenhouse effect is required on the early Earth to raise the surface temperature to above the freezing point of water [e.g., *Kasting and Toon*, 1989].

[56] It would be an important future work to estimate the actual mixing ratio of relevant molecules, such as CH₄ and NH₃. It is necessary to use a modeling of chemical kinetics to estimate the precise chemical composition consequent on the planetesimal impact since temperature and pressure dependences of each reaction path are different. Chemical interaction between the preexisting atmosphere and the accreting material also deserves further study since the extent of interaction between impact vapor plume and surrounding atmosphere does affect the atmospheric composition, especially the mixing ratio of CH₄.

4.3. Implication for Venus and Mars

[57] It is likely that the early atmospheres of Venus and Mars are also reducing similarly to that of the Earth since the atmospheres on both planets would also be generated by degassing of planetesimals.

[58] The formation process of the Venusian atmosphere would be similar to that of the Earth's atmosphere since the mass and the heliocentric distance of Venus are similar to the Earth. Then, the Venusian atmosphere should also evolve from a reducing one into the present oxidizing one. Hydrogen escape must be an essential process for evolution of the Venusian atmosphere since the present Venusian atmosphere contains almost no hydrogen [e.g., *Kasting and Pollack*, 1983; *Kasting*, 1988].

[59] If the Venusian CO₂ atmosphere is generated from CI chondrite, the amount of hydrogen accreted is as large as $2.3\text{--}8.1 \times 10^{19}$ kg. That is 0.15–0.52 times of the mass of hydrogen in the terrestrial ocean. A hydrogen escape rate estimated for a solar XUV level 10 times the present based on the calculation made by *Tian et al.* [2005] indicates that it takes 40–130 million years to dissipate hydrogen from Venus. When f value is not unity, the timescale for hydrogen escape is $1/f$ times longer (see Appendix B). If the f value for the Venusian atmosphere is similar to that of the terrestrial atmosphere, it takes more than a billion years to dissipate hydrogen from the Venusian atmosphere.

[60] It would be worth mentioning that nonthermal escape processes might significantly enhance the rate of hydrogen escape on Venus since Venus could have lost its magnetic field very early in its history. It has been also suggested that the solar wind may have been much more massive in the distant past [*Wood et al.*, 2002]. Without the protection of magnetic field, very strong solar wind would probably have caused strong hydrogen escape in addition to the hydrodynamic escape although the details of nonthermal escape processes need to be worked on.

[61] The early atmosphere of Mars would also contain reducing gases although formation process of the Martian atmosphere may be somewhat different from those on Earth and Venus. The mass of Mars, a tenth of the mass of the Earth, is rather small for impact vaporization to occur, but it is large enough to cause impact degassing and impact melting [e.g., *Abe*, 1993]. Chemical reactions would proceed in a high-temperature region near impact points [*Kuramoto and Matsui*, 1996].

[62] Reducing gases in the Martian early atmosphere could have been important in warming the surface of early Mars since fluvial features on the Martian surface indicate that surface condition of early Mars was warm and wet [e.g., *Carr*, 1996]. Radiative warming by reducing gases, such as CH₄ and NH₃, will be favorable for providing the necessary greenhouse warming since it is difficult to warm early Mars by the greenhouse effect of a dense CO₂ atmosphere [*Kasting*, 1991].

5. Conclusion

[63] The Earth's early atmosphere is likely to contain a significant amount of reducing species, such as H₂, CO, and CH₄, when the accretion is mostly completed. This conclusion is robust because reducing atmosphere is generated even if atmosphere is not contributed by captured solar nebula gas or H₂ generated by reaction with metallic iron and is solely generated by accretion of CI chondrite. Since CI chondrites are the most oxidizing kind of meteorites, the atmosphere generated by CI chondrites will be the most oxidizing primitive atmosphere that is allowed in the currently accepted planetary formation theories.

[64] The elemental abundance of the present Earth surface and mantle strongly suggests that most of atmophile elements in the present terrestrial atmosphere were once equilibrated with metallic iron. Since the ratios of hydrogen to carbon and nitrogen in the Earth surface and mantle are higher than those of the probable carrier (i.e., CI-like material) of Earth's volatile components, mechanism(s) that change the relative abundance of atmophile elements are needed. Dissolution of carbon and nitrogen into the molten metallic iron during the main accretionary phase is the most probable process that can account for the elemental abundance of the Earth.

[65] The most plausible process that changes the early reducing atmosphere into the present oxidizing one is hydrogen escape. When hydrogen photodissociated from water vapor is lost, the remaining oxygen, a by-product of photodissociation, would oxidize the atmosphere. It is indicated that early atmosphere is rich in hydrogen since this oxidation process requires a large amount of hydrogen to escape. If escape flux of hydrogen is energy-limited, the timescale of hydrogen escape would be as long as about a billion years. Thus, once a reducing atmosphere is created, it may exist for about a billion years on the early Earth.

Appendix A: Derivation of Equation (4)

[66] Since N_H^R and N_H^O are the numbers of hydrogen supplied by the components R and O, respectively, the number of hydrogen in the Earth surface and mantle, N_H^{Earth} , is given by

$$N_H^{Earth} = N_H^R + N_H^O \quad (A1)$$

while the number of carbon or nitrogen in the Earth surface and mantle is given by

$$N_X^{Earth} = N_X^O \quad (A2)$$

since we assumed that carbon and nitrogen are not present in a component-R atmosphere. Using these two equations, we can reformulate equation (2) as:

$$\begin{aligned} f &\equiv \frac{N_H^O}{N_H^R + N_H^O} \\ &= \frac{N_H^O}{N_H^{Earth}} \\ &= \frac{N_H^O}{N_H^{Earth}} \frac{N_X^{Earth}}{N_X^O} \\ &= \left(\frac{N_H^O}{N_H^{Earth}} \right) \left(\frac{N_X^{Earth}}{N_X^O} \right) \end{aligned} \quad (A3)$$

Appendix B: Timescale for Hydrogen Escape

[67] When escape flux is energy-limited, the timescale for hydrogen escape is in proportion to the amount of hydrogen accreted. We can reformulate equation (A3) and obtain an expression for the amount of hydrogen accreted in terms of the amount of carbon accreted and the value of f :

$$N_H^{Earth} = \left(\frac{N_H^O}{N_C^O} \right) \left(\frac{1}{f} \right) N_C^{Earth} \quad (B1)$$

This indicates that the amount of hydrogen accreted is inversely proportional to the value of f , when the amount of carbon accreted is some fixed value.

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