

Origin and Early Evolution of Terrestrial Planet Atmospheres and Oceans

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ABSTRACT

Planet atmospheric compositions are determined by the availability of a gas species, its molecular weight and the mass (or gravity force) of a planet. Both Mercury and the Moon are not massive enough to hold any gas species to form an atmosphere. The observed atmospheric compositions of all other terrestrial planets (Venus, Earth and Mars) are consistent with the calculated lower bounds of the critical mass (CM) for various atmospheric gas species. The proto-atmospheres of Venus, Earth and Mars during accretion should be composed primarily of CO₂. The Martian mass is significantly smaller than the lower bound of CM for gaseous H₂O. Thus, Mars is not capable of retaining H₂O in its atmosphere. In terms of today's atmospheric compositions, the Earth appears to be the only "abnormal" planet in our Solar System. This may suggest that the fate of the Earth might be unique among the terrestrial planets by the fact that the Earth has an over-massive Moon. The capture of the Moon by a giant impact process might produce Earth's indigenous hot supercritical H₂O-CO₂ ocean that quickly reacted with feldspar, the most abundant surface mineral, and eventually removed all CO₂ from Earth's proto-atmosphere.

Keywords: Atmospheres, Oceans, Terrestrial planets

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1. INTRODUCTION

The planets in our Solar System form two contrasted groups: an inner group (Mercury, Venus, Earth and Mars) of small planets with higher mean densities ($3.9 \sim 5.5 \text{ g/cm}^3$) and an outer group (Jupiter, Saturn, Uranus, and Neptune) of large planets with lower mean densities ($0.7 \sim 1.66 \text{ g/cm}^3$). The inner group, which includes the Moon, is also known as the terrestrial planets and the outer group as the major planets. The atmospheric compositions for the two groups are also distinct: the major planets are composed exclusively of H_2 and He, having a slightly different ratio between the two gas elements, and the terrestrial planets are composed of various different gas species. The seemingly different atmospheric compositions of the terrestrial planets may be an artifact. As shown in Table 1, the atmospheric compositions of Venus and Mars are nearly identical, both possess more than 95% CO_2 , and there is practical no atmosphere at all on Mercury as indicated by its atmospheric pressure ($\sim 10^{-15}$ bar). The latter is definitely due to Mercury's small mass (see explanations in the next section). Thus, except for the Earth, the general features of the planet atmospheric compositions in our Solar System are that the major planets consist exclusively of H_2 and He in slightly different ratios and that the terrestrial planets consist dominantly of CO_2 with N_2 as the second abundant component. As far as the atmospheric compositions are concerned, therefore, the Earth is the only "abnormal" planet in our Solar System.

2. ATMOSPHERE OF A PLANET

Whether a volatile gas species can form an atmosphere of a planet is determined by the following factors:

- 1) The availability of a volatile species, either forms as a compound or stands as an element, in the nearby areas inside or outside of a planet;
- 2) The surface temperature and/or pressure of a planet; and
- 3) The total mass, or the gravity force/attraction force, of a planet.

The reason for the first factor is self-evident. If a gas species is not available in the nearby areas of a planet, it is not possible to form the atmosphere of a planet. The surface temperature and/or pressure of a planet determine the states whether a volatile species exists as a solid,

liquid, or gas on the surface of a planet. The temperature also plays as a competing factor with the gravity force to hold a gas species in an atmosphere. It is the kinetic energy of temperature that causes a gas species to escape from the atmosphere of a planet. The higher the temperature, or the lighter the gas species, the faster a gas species escapes from an atmosphere. The atmospheric composition of a planet appears to be more determined by the total mass of a planet because the surface temperature drops rather quickly at higher altitudes. A less massive planet may also possess an atmosphere if its surface temperature is rather lower. Nonetheless, there is always some escape of a gas to the outer space for as long as the temperature is not zero. Providing the escape of a gas from an atmosphere is negligible, it is regarded as a component of an atmosphere. Thus, an atmosphere is a layer of gases around a material body that are mainly attracted by the gravity of the material body and retained for a long duration. In rare cases, like Mercury, the gases may also be imposed upon by the solar wind. The atmospheric composition of a terrestrial planet is generally related to the chemistry of primordial planetesimals that formed the solid body and the subsequent escape of gases during and after accretion. The proto-atmosphere of each planet might undergo much evolution over time.

The minimum planet mass required to retain a given gas species as a component of an atmosphere was defined as the critical mass (CM) of the planet for that gas species by Liu [1]. CM is gas species dependent, and is somewhat inversely proportional to the molecular weight of a gas species. The lower bounds of CM for various common gas species of the planets in our Solar System were estimated by Liu [1] and are given in Table 1. Thus, the true values of CM must be greater than those listed in Table 1. The mass of all terrestrial planets and that of Uranus, the least massive major planets, and their atmospheric composition and surface pressure are also given in Table 1 for comparison. For simplicity, atmospheric gases less than 1% are not shown and the gas species are listed in the order of decreasing abundance. Both CM's and the mass of planets are listed in order so that one is able to see what gas species can be retained in the planet's atmosphere based on the calculated CM's. Except for He, Table 1 shows that the calculated lower bounds of CM are consistent with the atmospheric composition of all planets observed. That Table 1 suggests that both Venus and Earth might be able to retain He in their atmospheres is merely an artifact. The fact that the Earth is

not massive enough to hold He in its atmosphere [2] suggests that the true CM for He should be greater than 5.976×10^{27} g. The lower bound CM for H₂ shown in Table 1 is 1.20 times the Earth's mass, and the CM for H₂ was estimated some 5 to 20 times the Earth's mass by Mizuno [3] and Ikoma et al. [4], respectively. The mass of Uranus is 14.5 times that of the Earth.

The atmosphere of Mercury might need further to be elucidated. The atmospheric pressure of Mercury is so small ($\sim 10^{-15}$ bar) that there is practically “no” atmosphere on Mercury, and this is consistent with the lower bound of CM for CO₂. In other words, Mercury is not massive enough to hold CO₂, the heaviest nature gas species, in its atmosphere as assumed and observed. The appearance of trace amounts of O₂ and Na on Mercury is likely to be a transit and short-lived phenomenon, and the relatively abundant H₂ and He on Mercury may be imposed by the solar wind, as has long been speculated, e.g. [5]. Since the Moon is 78% less massive than Mercury, there must be no atmosphere at all on the Moon.

3. THE SOURCES OF VOLATILES AND IMPACT PROCESSES

It is well known that H₂O and CO₂ are the two most abundant volatiles on the terrestrial planets. H₂O forms the Earth's oceans, and CO₂ constitutes more than 95% of Cytherean and Martian atmospheres. Assuming that the terrestrial planets all grew from similar primordial planetesimals via a similar accretion process, it is most likely that the planetesimals contain a small amount of carbonates and hydrous minerals. The latter minerals are commonly found in many stony meteorites on the Earth's surface today. During an early stage of accretion, the collisions among planetesimals and the impact of planetesimals onto the infant planet had to be small. Thus, the growing planets should maintain all carbonates and hydrous minerals. Further on the way of growing, the impacting force was increasing to a stage while decarbonation and dehydration would occur.

The shock-wave experimental studies of calcite (CaCO₃) and other carbonate rocks [6, 7, 8] indicate that decarbonation reactions begin at about 100 kbar and are complete near 700 kbar. The results from similar studies on serpentine and other hydrous minerals [9] found that dehydration reactions in hydrous minerals start generally at around 200 kbar, and complete dehydration occurs around 600 kbar. Thus, it can be concluded that all CO₂ and H₂O contained, respectively, in carbonates

and hydrates had to be buried inside the terrestrial planets (and probably all planets as well for as long as planetesimals contained carbonates and hydrates) during the early stage of accretion before the impact pressure reached over 100~200 kbar. Even after decarbonation and dehydration commenced, there should still be some amounts of both CO₂ and H₂O buried inside the terrestrial planets up until the impact pressure exceeded 600~700 kbar. Based on these experimental studies, assuming that the H₂O content in the infalling materials is 0.33 wt%, Liu [10] calculated that the total H₂O buried inside Venus, Earth and Mars should be $\sim 1.4 \times 10^{24}$ g which is equivalent to the mass of today's Earth oceans estimated by Holland [11].

4. EVOLUTION OF TERRESTRIAL PLANET ATMOSPHERES

Using Venus, Earth and Mars shown in Fig. 1 as an example, Liu [10, 12] developed a simple model that describes the evolution of CO₂ and H₂O during and after accretion. These volatiles should have been buried inside a growing planet when the impact pressure was less than 600~700 kbar, and the equivalent mass and radius of the growing planet are respectively shown as M₁ and R₁ in Fig. 1. Continuous growth of the planets would cause a total release of CO₂ and H₂O from the infalling planetesimals and the surface materials of the growing planets. The released CO₂ and H₂O gas species would then escape from the growing planets to the outer-space, and gone forever, because the growing planets were not massive enough to hold them to form a proto-atmosphere.

4.1 MARTIAN ATMOSPHERE

As accretion continued, the radius of the growing planets would increase from R₁ to R₂, and the mass between them is marked as M₂. When the total mass (M₁ + M₂) reached the CM for CO₂ (it must be greater than the lower bound 3.30×10^{26} g listed in Table 1), a growing planet would hold CO₂ to form its first proto-atmosphere. CO₂ contained in M₂ would be lost and would escape to the outer-space forever. In other words, the CO₂ proto-atmosphere was derived primarily from carbonates originally contained in the planetesimals that formed M₃. Following CO₂, as suggested in Table 1, Ar and then O₂ and N₂ would add to the proto-atmosphere during accretion (the relative abundance, however, is determined primarily upon the availability of

source materials). This is practically what one observes in today's Cytherean and Martian atmospheres.

If a planet continued to grow, $(M_1 + M_2)$ would increase and reach the CM for H_2O (it must be greater than the lower bound 8.06×10^{26} g listed in Table 1), then the growing planet should hold the escaping gaseous H_2O in its proto-atmosphere. The mass of Mars is 6.419×10^{26} g. Therefore, Mars is never massive enough to hold gaseous H_2O in its atmosphere. Today's atmospheric composition of Mars (CO_2 , N_2 , Ar, O_2 and CO) and the absence of H_2O , CH_4 , He and H_2 in Martian atmosphere are in complete agreement with the lower bounds of CM's calculated and listed in Table 1.

4.2 MAGMA OCEAN

Hofmeister [13] and Matsui and Abe [14] suggested that, due to impacting, Earth's surface commenced to be covered by "magma ocean" when the growing Earth exceeded ~40% (a radius of ~2550 km) of its final radius. Once the magma ocean was formed, the solid-solid impact models of both decarbonation and dehydration described earlier become an impact of solid planetesimals into the liquid magma ocean. Not only the mechanism of a solid-liquid impact differs drastically from those of a solid-solid impact, but also silicate melts are capable of dissolving an appreciable amount of H_2O at high pressures. When an impactor hit the magma ocean on a growing planet, instead of producing large quantities of impact-induced dusts and releasing volatiles to the proto-atmosphere as would be expected in a solid-solid impact, an impactor would penetrate into the magma ocean to greater depths. High-pressure experimental studies indicate that at least 6 wt% H_2O can be dissolved in silicate melts at 3 kbar and the solubility increases with increasing pressure for all silicate melts known [15]. However, no appreciable amounts of CO_2 are known to dissolve in silicate melts at high pressures. Thus, nearly all the H_2O released during impacting and penetration would be dissolved in the magma ocean and most of the CO_2 released would escape from the magma ocean. In other words, even if the impact pressure exceeded 100 kbar, escape of H_2O from the growing planets and/or loss of H_2O to outer-space would not happen once the surface was covered by magma ocean. Escape and loss of CO_2 to outer-space, on the other hand, would take place once the impact pressure exceeded 100 kbar regardless of the formation of a magma ocean on the surface during accretion. CO_2

released from decarbonation due to impact had to be retained and formed the proto-atmosphere when the planets grew to over 3.30×10^{26} g. The conclusion that nearly all the H_2O in the infalling planetesimals would be preserved in the silicate melts when they impacted on the magma ocean was also reached by Holland [11] in his calculation of the solubility of various gases in the molten Earth. Fukai and Suzuki [16] also concluded that 'nearly 100% of the accreted water was incorporated in the interior of the Earth, leaving only a very small proportion in the form of atmosphere (p. 9225)'. Although these conclusions were resulted from studies of the Earth, the same results should also be applicable to Venus and Mars because their radii all exceed 2550 km.

4.3 CYTHEREAN ATMOSPHERE

Venus is known to be deficient in H_2O . It has been suggested that nearly all the H_2O of Venus is still entrapped inside the partial melting zone because Venus may not yet have reached its complete solidification [10, 12]. The Cytherean atmosphere possesses primarily CO_2 and N_2 plus the clouds that are composed of sulphuric acid and various other corrosive compounds, but Ar, O_2 , and H_2O are missing from its atmosphere. In considering the thick CO_2 atmosphere of Venus (90 bar), the small amount of Ar would become trace ($<<1\%$) and the absence of other gases may simply be due to either a lack of availability or even less abundant than Ar.

Since today's atmospheric compositions of Venus and Mars follow almost exactly what Table 1 would expect, it is highly possible that both Venus and Mars might have kept their proto-atmospheres until today. Earth is located between Venus and Mars and there does not seem to have any compelling reasons why the proto-atmosphere of the Earth should be different from those of Venus and Mars. In other words, the proto-atmosphere of the Earth should also be consisted of more than 95% CO_2 plus N_2 , Ar and so forth. The fact that today's atmosphere composition of the Earth is so different from those of Venus and Mars hints that the fate of the Earth might be different from those of Venus and Mars.

5. ORIGIN OF EARTH'S OCEANS

It has been mentioned earlier, as far as today's atmospheric compositions are concerned, the Earth is the only "abnormal" planet in

our Solar System. Yet, we also conclude that there are no compelling reasons that the Earth's proto-atmosphere should be any different from those of today's Venus and Mars. Then, how did the more than 95% CO₂ vanish from the Earth's proto-atmosphere?

The fate of the Earth might be unique among the terrestrial planets by the fact that the Earth has the Moon. As envisaged in the giant impact hypothesis, e.g. [17, 18], the Moon might be formed by a striking from a Mars-like impactor at a very early stage of the Earth's evolution. The consequences of the Moon-forming giant impact should at least be as follows:

- 1) The Earth acquired the Moon, e.g. [17, 18];
- 2) The iron core of the impactor incorporated into Earth's interior as shown in the computer simulation [19];
- 3) The release of most of the Earth's volatiles into the proto-atmosphere. It is highly likely that the Earth was not completely solidified before its capture of the Moon. Most, if not all H₂O dissolved in the entrapped magma ocean, somewhat like today's Venus, escaped into the Earth's CO₂ proto-atmosphere.

The first consequence is self evident. The second consequence may provide a reasonable explanation for Earth's bigger iron core, relative to its rocky mantle. Thus, the Earth has the highest mean density among all planets in our Solar System. The third consequence produced the Earth's oceans.

Liu [20] has modeled the proto-atmosphere of the Earth after the giant impact and has postulated that it comprised 560 bar of H₂O (twice the amount in the present oceans) and 100 bar of CO₂ (or some 5.2×10^{23} g). Because of the relatively high pressure and temperature imposed on the Earth's surface by this proto-atmosphere, the released H₂O after the giant impact would react with the existing CO₂ proto-atmosphere to form a supercritical H₂O-CO₂ mixture although H₂O and CO₂ are not mutually soluble at ambient conditions. When the Earth cooled down further and the surface temperature reached about 450~300 °C, the heavy supercritical H₂O-CO₂ mixture in the proto-atmosphere commenced to precipitate on the surface to form the indigenous ocean. Thus, the indigenous ocean on the Earth was hot (300~450 °C) and composed of a heavy supercritical H₂O-CO₂ mixture, or the "hot soda water". The hot

supercritical $\text{H}_2\text{O}-\text{CO}_2$ would react rather quickly with the most abundant mineral, feldspar, to form carbonates and clay minerals at the bottom of the indigenous ocean. In order to keep a chemical balance, CO_2 in the proto-atmosphere have to continue dissolving into the indigenous ocean. This would effectively remove all CO_2 from the proto-atmosphere. Thus, the atmosphere of the early Earth after the formation of the ocean should be composed primarily of gaseous hot H_2O , which would most likely dissociate into O_2 and H_2 at high altitude and H_2 would then escape from the Earth to outer-space. The removal of the CO_2 proto-atmosphere from the Earth appears to require the presence of a large quantity of H_2O and might have helped the Earth to cool down much faster than the neighboring Venus even if their relative distances from the Sun are taken into consideration. Consequently, the internal temperatures of the Earth are much lower than those of Venus at the same depth. This hypothesis can be tested when surface rocks of Venus and Mars are surveyed in some details. Compared with the Earth, there should not be much carbonate rocks on Venus and Mars.

Table 1 shows that after CO_2 , N_2 is the second most abundant gas species in today's Cytherean and Martian atmospheres. The complete removal of CO_2 from the Earth's proto-atmosphere would naturally leave N_2 as the most abundant gas species in the Earth's atmosphere as observed today. N_2 in terrestrial planet atmospheres should be derived from nitrate minerals in primordial planetesimals during accretion when the growing planets exceeded 5.19×10^{26} g.

It has been said, however, that a large quantity of "dirty snowballs" has impinged upon the Earth which eventually evolved to form the oceans after accretion, e.g. [21, 22]. This speculation provides no explanation as to why Venus and Mars were not bombarded with "dirty snowballs" after accretion. Nor can it explain the abundant CO_2 in today's Cytherean and Martian atmospheres. See other objection in the next section.

6. WATER IN/ON MARS, MERCURY AND THE MOON

As mentioned earlier, the lower bound CM for gaseous H_2O (8.06×10^{26} g) is significantly greater than the masses of Mars, Mercury and the Moon. Accordingly, these planets are not capable of retaining gaseous H_2O in their atmospheres. On the other hand, it has long been known that many surface features of Mars suggest the existence of a speculated

ocean on Mars in the past, e.g. [23, 24]. The NASA 2008 and 2016 missions also confirmed the existence of H₂O ice in the Martian soil. If these speculations and findings are true, the Martian H₂O must have been derived from H₂O originally buried inside M₁ through degassing processes as envisaged by Liu [10]. There is no M₃ for H₂O during and after the accretion of Mars. The Martian H₂O is thus inherent and cannot be added by “dirty snowballs” after accretion, because Mars is not massive enough to retain gaseous H₂O in its atmosphere and any H₂O added by snowball bombardment would be evaporated and lost to outer-space. If the Martian H₂O is inherent, there are no compelling reasons to believe that the Earth’s oceans were derived from “dirty snowballs”.

If there were indeed oceans on Mars, they had to be derived from H₂O degassed from the Martian interior after the surface cooled below 100 °C and the supply of liquid H₂O had to be greater than evaporation. The radius of Mars is 0.53 times that of the Earth. It takes only about 1/10 the total Earth’s oceans to form an average 1000-meter ocean on Mars. The oceans or H₂O ice (when surface temperature dropped below 0 °C) on Martian surface cannot be sustained for a long duration because evaporation and sublimation would turn them into gaseous H₂O, which would be lost to outer-space. It is most likely that life might not have been developed in such short-lived oceans on Mars.

Both Mercury and the Moon practically have no atmospheres at all. It would be impossible for the existence of either CO₂ or H₂O on their surfaces. On the other hand, it is still quite possible that carbonates and/or hydrates may exist in the interiors of these planets.

7. CONCLUSION

The majority of the materials that form today’s terrestrial planet atmospheres and oceans should be inherent (derived from planetesimals). An amount of H₂O that is roughly equivalent to today’s Earth oceans should be buried inside Venus, Earth and Mars during the early stage of accretion. After accretion, the proto-atmospheres of Venus, Earth and Mars likely consisted of more than 95% CO₂ which are probably kept by both Venus and Mars till today. The fate of the Earth, on the other hand, had been changed by the Moon-forming giant impact. After the giant impact, the Earth gained its Moon and released most of its H₂O contents

into the CO₂ proto-atmosphere. At such temperature and pressure conditions, H₂O and CO₂ would form a supercritical H₂O-CO₂ fluid which would later precipitate to yield the indigenous oceans when Earth's surface temperature cooled down to 450°C - 300°C. The hot indigenous ocean reacted with feldspars, the most abundant surface minerals, to form carbonates, thus removing all CO₂ from Earth's proto-atmosphere eventually. The gravity force of Mars is too small to hold gaseous H₂O in its atmosphere, but this does not necessarily imply that Mars' interior or its surface materials do not contain H₂O. Both Mercury and the Moon are not massive enough to hold appreciable amount of gas species to form an atmosphere.

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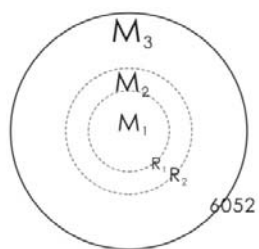
Table 1 Comparison of the lower bounds of the CM for various gas species with the mass of Mercury, Venus, Earth, Moon, Mars and Uranus and their respective atmospheric composition and surface pressure

Gases (molecular weight)	Lower Bound CM (g)	Planets	Mass (g)
		Moon	7.35×10^{25}
		Mercury	3.30×10^{26}
		(O ₂ +Na+H ₂ +He = 10^{-15} bar)	
CO ₂ (44.01)	3.30×10^{26}		
Ar (39.95)	3.64×10^{26}		
O ₂ (32.00)	4.54×10^{26}		
N ₂ (28.01)	5.19×10^{26}		
CO (28.01)	5.19×10^{26}		
		Mars	6.419×10^{26}
		(CO ₂ +N ₂ +Ar = 8×10^{-3} bar)	
H ₂ O (18.02)	8.06×10^{26}		
CH ₄ (16.05)	9.05×10^{26}		
He (4.00)	3.63×10^{27}		
		Venus	4.869×10^{27}
		(CO ₂ +N ₂ = 93 bar)	
		Earth	5.976×10^{27}
		(N ₂ +O ₂ +H ₂ O+Ar = 1.013 bar)	
H ₂ (2.02)	7.19×10^{27}		
		Uranus	8.68×10^{28}
		(H ₂ +He = ??)	

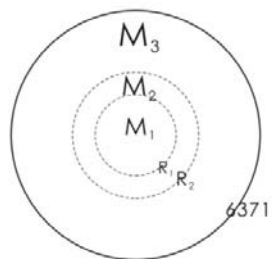
FIGURE CAPTIONS

Figure 1 Imaginary internal structure of the terrestrial planets during and right after accretion, using Venus, Earth and Mars and volatile CO_2 as an example. R_1 is the radius beyond which (or at which the impact pressure > 600 kbar) complete decarbonation of the infalling planetesimals and the surface materials of the growing planets occurred. M_1 is the mass contained within R_1 , and CO_2 buried as carbonates inside R_1 . R_2 is the radius beyond which the escaping of CO_2 to the outer-space in the growing planets became negligible, and M_2 is the mass between R_1 and R_2 . $(M_1 + M_2)$ is the CM for CO_2 . CO_2 in the proto-atmospheres was derived from M_3 . All R 's and M 's are gas species dependent.

Venus
 $R = 6052 \text{ km}$



Earth
 $R = 6371 \text{ km}$



Mars
 $R = 3395 \text{ km}$

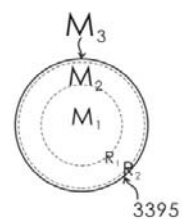


Fig. 1, Liu

