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# 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 $CO_2$. The Martian mass is significantly smaller than the lower bound of CM for gaseous $H_2O$. Thus, Mars is not capable of retaining $H_2O$ 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 $H_2O$-$CO_2$ ocean that quickly reacted with feldspar, the most abundant surface mineral, and eventually removed all $CO_2$ from Earth's proto-atmosphere.

## 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 - 5.5 g $cm^{-3}$) and an outer group (Jupiter, Saturn, Uranus, and Neptune) of large planets with lower mean densities (0.7 - 1.66 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 seemly 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 (~$10^{-15}$ 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 it 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 state of the species, i.e., 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

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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 (2014). 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 (2014) 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 (Fegley 1995) suggests that the true CM for He should be greater than $5.976 \times 10^{27}$ g. The lower bound CM for $H_2$ shown in Table 1 is 1.20 times the Earth's mass, and the CM for $H_2$ was estimated some 5 to 20 times that of the Earth's mass by Mizuno (1980) and Ikoma et al. (2000), respectively. The mass of Uranus is 14.5 times that of the Earth, which suggests the true value of CM for $H_2$ must be less than 15 times that of the Earth.

The atmosphere of Mercury might need further to be

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** | $7.35 \times 10^{25}$ |
| | | **Mercury** | $3.30 \times 10^{26}$ |
| | | ($O_2 + Na + H_2 + He = 10^{-15}$ bar) | |
| $CO_2$ (44.01) | $3.30 \times 10^{26}$ | | |
| Ar (39.95) | $3.64 \times 10^{26}$ | | |
| $O_2$ (32.00) | $4.54 \times 10^{26}$ | | |
| $N_2$ (28.01) | $5.19 \times 10^{26}$ | | |
| CO (28.01) | $5.19 \times 10^{26}$ | | |
| | | **Mars** | $6.419 \times 10^{26}$ |
| | | ($CO_2 + N_2 + Ar = 8 \times 10^{-3}$ bar) | |
| $H_2O$ (18.02) | $8.06 \times 10^{26}$ | | |
| $CH_4$ (16.05) | $9.05 \times 10^{26}$ | | |
| He (4.00) | $3.63 \times 10^{27}$ | | |
| | | **Venus** | $4.869 \times 10^{27}$ |
| | | ($CO_2 + N_2 = 93$ bar) | |
| | | **Earth** | $5.976 \times 10^{27}$ |
| | | ($N_2 + O_2 + H_2O + Ar = 1.013$ bar) | |
| $H_2$ (2.02) | $7.19 \times 10^{27}$ | | |
| | | Uranus | $8.68 \times 10^{28}$ |
| | | ($H_2 + He = ??$) | |

elucidated. The atmospheric pressure of Mercury is so small (~$10^{-15}$ bar) that there is practically "no" atmosphere on Mercury, and this is consistent with the lower bound of CM for $CO_2$. In other words, Mercury is not massive enough to hold $CO_2$, the heaviest nature gas species, in its atmosphere as assumed and observed. The appearance of trace amounts of $O_2$ and Na on Mercury is likely to be a transit and short-lived phenomenon, and the relatively abundant $H_2$ and He on Mercury may be imposed by the solar wind, as has long been speculated (e.g., Yung and DeMore 1998). Since the Moon is 78% less massive than Mercury, there must be virtually no atmosphere at all on the Moon.

## 3. THE SOURCES OF VOLATILES AND IMPACT PROCESSES

It is well known that $H_2O$ and $CO_2$ are the two most abundant volatiles on the terrestrial planets. $H_2O$ forms the Earth's oceans, and $CO_2$ 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 ($CaCO_3$) and other carbonate rocks (Boslough et al. 1982; Kotra et al. 1983; Lange and Ahrens 1986) 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 (Lange and Ahrens 1984) 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 $CO_2$ and $H_2O$ 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 $CO_2$ and $H_2O$ buried inside the terrestrial planets up until the impact pressure exceeded 600 - 700 kbar. Based on these experimental studies, assuming that the $H_2O$ content in the infalling materials is 0.33 wt%, Liu (1988) calculated that the total $H_2O$ buried inside Venus, Earth, and Mars should be ~$1.4 \times 10^{24}$ g which is equivalent to the mass of today's Earth oceans estimated by Holland (1984).

## 4. EVOLUTION OF TERRESTRIAL PLANET ATMOSPHERES

Using Venus, Earth, and Mars shown in Fig. 1 as an example, Liu (1988, 2009) developed a simple model that describes the evolution of $CO_2$ and $H_2O$ 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 $M_1$ and $R_1$ in Fig. 1. Continuous growth of the planets would cause a total release of $CO_2$ and $H_2O$ from the infalling planetesimals and the surface materials of the growing planets. The released $CO_2$ and $H_2O$ gas species would then escape from the growing planets to the outer-space, and be gone forever, because the growing planets were not massive enough to hold them to form a proto-atmosphere.

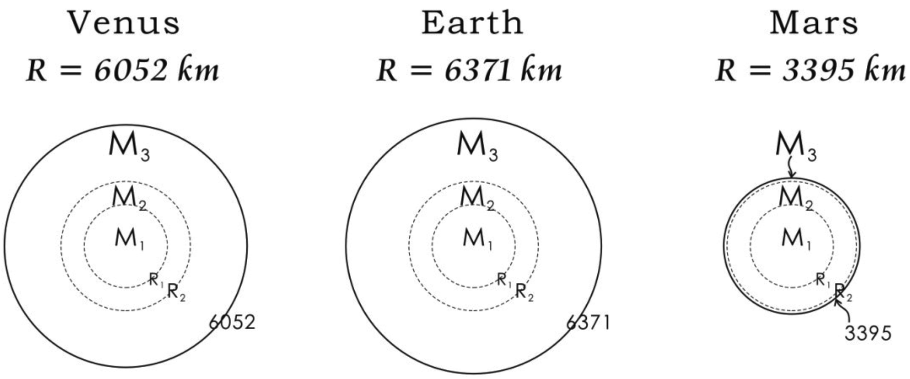

Fig. 1. Imaginary internal structure of the terrestrial planets during and right after accretion, using Venus, Earth and Mars and volatile $CO_2$ as an example. $R_1$ is the radius beyond which (or at which the impact pressure > 600 kbar) complete decarbonation of the infalling planetesimals and the 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 $M_3$. Except for $M_3$, all R's and M's are gas species dependent.

### 4.1 Martian Atmosphere

As accretion continued, the radius of the growing planets would increase from $R_1$ to $R_2$, and the mass between them is marked as $M_2$. When the total mass ($M_1 + M_2$) reached the CM for $CO_2$ (it must be greater than the lower bound $3.30 \times 10^{26}$ g listed in Table 1), a growing planet would hold $CO_2$ to form its first proto-atmosphere. $CO_2$ contained in $M_2$ would be lost and would escape to the outer-space forever. In other words, the $CO_2$ proto-atmosphere was derived primarily from carbonates originally contained in the planetesimals that formed $M_3$. Following $CO_2$, as suggested in Table 1, Ar and then $O_2$ and $N_2$ 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 $8.06 \times 10^{26}$ 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 $6.419 \times 10^{26}$ 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 the Martian atmosphere are in complete agreement with the lower bounds of CM's calculated and listed in Table 1.

### 4.2 Magma Ocean

Hofmeister (1983) and Matsui and Abe (1986) suggested that, due to impacting, Earth's surface commenced to be covered by a "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 (Liu 1987). 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 a 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 $3.30 \times 10^{26}$ 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 (1984) in his calculation of the solubility of various gases in the molten Earth. Fukai and Suzuki (1986) 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 (Liu 1988, 2009). 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 they are 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 THE 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% $CO_2$ 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., Benz et al. 1986, 1987), 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., Benz et al. 1986, 1987);
(2) The iron core of the impactor was incorporated into Earth's interior as shown in the computer simulation (Liu 1992);
(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 $H_2O$ dissolved in the entrapped magma ocean, somewhat like today's Venus, escaped into the Earth's $CO_2$ 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 (2004) has modeled the proto-atmosphere of the Earth after the giant impact and has postulated that it comprised 560 bar of $H_2O$ (twice the amount in the present oceans) and 100 bar of $CO_2$ (or some $5.2 \times 10^{23}$ g). Because of the relatively high pressure and temperature imposed on the Earth's surface by this proto-atmosphere, the released $H_2O$ after the giant impact would react with the existing $CO_2$ proto-atmosphere to form a supercritical $H_2O$-$CO_2$ mixture although $H_2O$ and $CO_2$ 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 $H_2O$-$CO_2$ 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 $H_2O$-$CO_2$ mixture, or the "hot soda water". The hot supercritical $H_2O$-$CO_2$ 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 would 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 $5.19 \times 10^{26}$ 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., Frank et al. 1986a, b). 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 the other objection in the next section.

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

As mentioned earlier, the lower bound CM for gaseous $H_2O$ ($8.06 \times 10^{26}$ 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., Squyres 1984; Carr 1986). The NASA 2008 and 2016 missions also confirmed the existence of $H_2O$ ice in the Martian soil. If these speculations and findings are true, the Martian $H_2O$ must have been derived from $H_2O$ originally buried inside $M_1$ through degassing processes as envisaged by Liu (1988). There is no $M_3$ for $H_2O$ during and after the accretion of Mars. The Martian $H_2O$ is thus inherent and cannot be added by "dirty snowballs" after accretion, because Mars is not massive enough to retain gaseous $H_2O$ in its atmosphere and any $H_2O$ added by snowball bombardment would be evaporated and lost to outer-space. If the Martian $H_2O$ 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 $H_2O$ degassed from the Martian interior after the surface cooled below 100°C and the supply of liquid $H_2O$ 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-m ocean on Mars. The oceans or $H_2O$ 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 $H_2O$, which would be lost to outerspace. 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 $CO_2$ or $H_2O$ on their surfaces. On the other hand, it is still quite possible that carbonates and/or hydrates may exist on the surfaces and in the interiors of these planets.

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