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# Origin and Evolution of Earth's Atmosphere and Oceans

Lin-gun Liu

1. Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan, ROC

**Abstract**: Both Venus and Mars most likely retain their proto-atmospheres with more than 95% $CO_2$ plus a few percent of $N_2$. The Earth is situated between the two; there is no compelling reason that the Earth's proto-atmosphere should be any different from those of Venus and Mars. Thus, today's Earth atmosphere is rather different from her proto-atmosphere. After completion of accretion, the magma ocean on the Earth surface started to solidify. Then a Mars-like impactor hit the Earth to form the Moon. The Moon-making giant impact also released a large quantity of supercritical $H_2O$ from the magma ocean entrapped inside the Earth. The supercritical $H_2O$ thus released would then quickly react with $CO_2$ in the proto-atmosphere to form a supercritical $H_2O$-$CO_2$ mixture. When the Earth's surface cooled down to 450-300 °C, the dense supercritical $H_2O$-$CO_2$ mixture precipitated to form the Earth's indigenous oceans which were hot soda supercritical $H_2O$. When the surface temperature further cooled down, the indigenous oceans expanded at the expense of $CO_2$ in the proto-atmosphere. The atmospheric pressure also decreased simultaneously. The removal of $CO_2$ from the proto-atmosphere was accelerated and then completed when the indigenous oceans reacted with the most abundant surface mineral plagioclase to form carbonates and clay minerals, leaving $Na^+$ in the oceans. Once $CO_2$ in the proto-atmosphere was completely removed, $N_2$ naturally became the most abundant component in the Earth's atmosphere as observed today. Some supercritical $H_2O$ at high altitude would likely dissociate into $O_2$ and $H_2$. The latter would then escape to the outer-space and $O_2$ remained in the atmosphere. Alternatively, $O_2$ in the Earth's atmosphere may be explained by the increase in photosynthetic organisms in the oceans, metabolizing carbon from $CO_2$ and releasing $O_2$ into the atmosphere.

**Keywords:** Earth, atmosphere, oceans, terrestrial planet

## INTRODUCTION

The origin and evolution of the atmospheres and oceans of terrestrial planets are classic unsolved problems in planetary sciences. These topics are also of great interest to science in general and have attracted attention from scientists who have considered life in nature. Nearly all theories concerning these topics are model dependent and constrained by various evidence and investigations (e.g., Holland, 1984; Kasting and Ackerman, 1986; Pepin, 1991; Liu, 2004; 2009; 2023). $H_2O$ and $CO_2$ are the two most abundant volatile species on the surfaces of terrestrial planets and are the most vital elements (C, H and O) for life on the Earth.

Our Solar System consists of 4 inner terrestrial planets (Mercury, Venus, Earth and Mars) and 4 outer major planets (Jupiter, Saturn, Uranus and Neptune). The atmospheres of the major planets are exclusively composed of $H_2$ and He with slightly different ratios. The atmospheres of the terrestrial planets appear to be somewhat irregular. Except for the Earth, however, in reality the atmospheric compositions of the terrestrial planets are also rather similar; both Venus and Mars are composed of more than 95% $CO_2$ and followed by a few percent of $N_2$ and Mercury is virtually in vacuum due to its small mass. Thus, it appears that the Earth's atmosphere is the only abnormality in our Solar System, in particular the Earth is situated between Venus and Mars and the latter two have nearly the identical atmospheric composition.

## ATMOSPHERE OF A PLANET

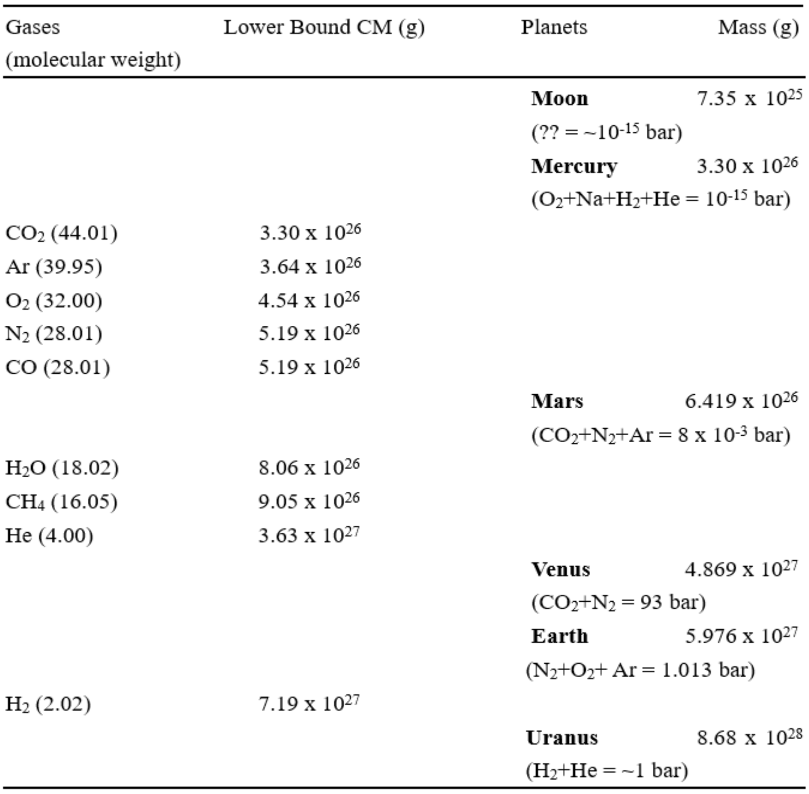
If volatiles are available, whether a volatile is qualified to be a component of an atmosphere of a terrestrial planet is determined by the mass of a planet and the molecular weight of a volatile. The latter criterion becomes invalid, if a planet is massive enough to hold $H_2$ in its atmosphere. The relative abundance of each volatile in an atmosphere, on the other hand, is determined by the abundance of each volatile in the primordial planetesimals that formed a terrestrial planet via accretion. The proto-atmosphere is defined as an atmosphere evolved during accretion of a planet. Direct observation of the growth of a proto-atmosphere is practically impossible.

The minimum planetary 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. In view of the way that the lower bounds of CM were estimated, the smaller the molecular weight the greater the discrepancy between the true values and the lower bounds 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 the Earth's mass, $5.976 \times 10^{27}$g.

If the volatiles are available, theoretically, Table 1 shows when a terrestrial planet grows to over $3.30 \times 10^{26}$ g, $CO_2$ would be the first volatile to form the proto-atmosphere. Ar would be added to the proto-atmosphere, when the planet grows to over $3.64 \times 10^{26}$ g. If the planet continues to grow, $O_2$, $N_2$, CO, $H_2O$, ...would then be added to the proto-atmosphere (Liu, 2025).

Both Mercury and the Moon are not massive enough to hold $CO_2$ to form their proto-atmospheres. Therefore, Mercury and the Moon are basically in vacuum as manifested by their atmospheric pressure of $\sim 10^{-15}$ bar. The atmospheres of both Venus and Mars are composed of more than 95% $CO_2$ plus a few percents of $N_2$ as observed today. This is nearly identical to the theoretical proto-atmosphere described above. A minor amount of Ar is indeed present in the Martian atmosphere, the lack of $O_2$ in the atmospheres of both Venus and Mars is readily understood because $O_2$ is easily and quickly reacted with other materials, e.g, CO, during accretion. If so, one may conclude that both Venus and Mars are most likely to retain their proto-atmosphere until today. The abundant $CO_2$ in the Cytherean and Martian atmospheres suggests that the primordial planetesimals should contain a fair amount of carbonate minerals. The lack of Ar in the Cytherean atmosphere and Ar is less abundant than or equal to $N_2$ in the Martian atmosphere suggests that the source material of Ar (probably radioactive $^{40}K$) is less abundant than nitrate minerals in the primordial planetesimals.

**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**<br>(?? = ~$10^{-15}$ bar) | $7.35 \times 10^{25}$ |
| | | **Mercury**<br>($O_2$+Na+$H_2$+He = $10^{-15}$ bar) | $3.30 \times 10^{26}$ |
| $CO_2$ (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**<br>($CO_2$+$N_2$+Ar = $8 \times 10^{-3}$ bar) | $6.419 \times 10^{26}$ |
| $H_2O$ (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**<br>($CO_2$+$N_2$ = 93 bar) | $4.869 \times 10^{27}$ |
| | | **Earth**<br>($N_2$+$O_2$+ Ar = 1.013 bar) | $5.976 \times 10^{27}$ |
| $H_2$ (2.02) | $7.19 \times 10^{27}$ | | |
| | | **Uranus**<br>($H_2$+He = ~1 bar) | $8.68 \times 10^{28}$ |

The Earth is located right between Venus and Mars. There is no compelling reason that the Earth's proto-atmosphere should be any different from those of Venus and Mars. Then, where is the more than 95% $CO_2$ of the Earth's proto-atmosphere gone?

## IMPACT DURING ACCRETION

### Early Stage of Accretion

It is well known that $H_2O$ and $CO_2$ are the two most abundant volatiles on the terrestrial planets. 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, e.g. CI chondrites, on the Earth's surface today.

The planets started to grow by collisions among primordial planetesimals at an early stage of accretion. Soon an infant planet was formed. 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 in their infant planets. 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 takes place at 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 infant planets 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).

In order to hold the impact released $H_2O$ in the proto-atmosphere, Table 1 shows that the mass of a growing planet must be greater than $8.06 \times 10^{26}$ g which is greater than the Martian mass. Therefore, Mars is never massive enough to hold $H_2O$ to form its atmosphere (Liu, 2014; 2022).

## Magma Ocean during Accretion

Hofmeister (1983), Matsui and Abe (1986) and among others 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 does the mechanism of a solid-liquid impact differ 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. 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)'.

The facts that the Martian radius is 3395 km and its mass is 6.419 x $10^{26}$ g suggest that the magma ocean on terrestrial planets commenced before Martian mass grew over the CM for $H_2O$. Thus, $H_2O$ never existed as one of the proto-atmospheric components on all terrestrial planets during accretion. Therefore, any significant amount of $H_2O$ on the surface of all terrestrial planets must be added or derived via other mechanisms after the completion of accretion. Frank et al. (1986a; b) proposed that the Earth's oceans were added by "dirty snowballs" after accretion, and this idea has gained strong support by a majority of astrophysicists in the past 40 years. If this speculation were true, today's Earth atmosphere would most likely be composed of more than 95% $CO_2$ as on Venus and Mars; not to mention "dirty snowballs" would choose to bombard the Earth alone, but not her nearest neighbor Venus. Liu (2014, 2019, 2022), on the other hand, concluded that the ancient Martian oceans should be inherent, or was derived from its interiors, and cannot be added by "dirty snowballs" after accretion because snowballs would be evaporated and lost to outer-space during bombardment.

## ORIGIN OF THE EARTH'S OCEANS

### The Moon-Making Impact Process

The fate of the Earth might be unique among the terrestrial planets by the fact that the Earth has the Moon (Liu, 2023). As envisaged in the giant impact hypothesis (e.g., Benz et al. 1986, 1987), the Moon might be formed by a strike 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 her relatively larger 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, while the rocky debris formed the Moon (Liu 1992);
3. The release of most of the Earth's volatiles into the CO2-rich 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 $CO_2$-dominated proto-atmosphere.

Liu (2004) has modeled the atmosphere of the Earth during and after the giant Moon-making impact process and has postulated that it comprised 560 bar of $H_2O$ (twice the amount of today's oceans) and 100 bar of $CO_2$ (or some 5.2 × $10^{23}$g). Today's Cytherean atmospheric pressure is roughly 90 bar $CO_2$ and the partial pressure of $CO_2$ in the proto-atmosphere of the Earth was estimated to be 114 bar by Liu (2009). In their modeling of the Earth's early evolution after the giant impact, Zahnle et al. (2007) also adopted the value of 100 bar of $CO_2$ in their study.

## Inception of the Oceans

If $H_2O$ and $CO_2$ were to coexist as an ideal mixture (or inert to each other), the first drop of dense supercritical $H_2O$ appeared (or the inception of the $H_2O$ oceans) on the Earth when the surface temperature cooled to about 450 ± 20 °C. The atmospheric pressure must drop during the onset of the indigenous oceans. So, "dense" supercritical $H_2O$ clouds might have already existed in the proto-atmosphere at high altitude, if the temperature at high altitude was cool enough. However, these cloud droplets would not be able to arrive on the surface until the surface temperature dropped below about 450 °C. When the Earth further cooled down, all $H_2O$ in the air would have condensed as water on the Earth's surface. If this scenario were to be true, the Earth's $CO_2$ proto-atmosphere would not be removed.

In reality, however, the 560 bar $H_2O$ and 100 bar $CO_2$ impose relatively high pressure on the Earth's surface above 450 °C, the released $H_2O$ after the giant impact would react with the already 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. Thus, the early Earth atmosphere was a nonideal supercritical $H_2O$-$CO_2$ mixture with $XCO_2$ (molar fraction of $CO_2$) = 0.068. According to Duan et al. (1992), a true liquid with the critical composition $XCO_2$ = 0.32 ought to appear in such a mixture when the temperature drops below about 300 °C at 660 bar (it acts as a critical point in a $H_2O$-$CO_2$ mixture), and a true vapor-liquid mixture also appears at about 210 °C at 660 bar. In this case, the first drop of liquid $H_2O$-$CO_2$ mixture appeared (or the inception of the oceans) on the Earth when the surface temperature cooled to about 300 °C. Alternatively, the latter case may not occur either and a "dense" supercritical $H_2O$-$CO_2$ mixture with $XCO_2$ = 0.068 might exist at temperatures much higher than 300 °C at 660 bar (above the critical condition). Once a "dense" supercritical $H_2O$-$CO_2$ mixture appeared on the surface, the atmospheric pressure would drop and the corresponding "critical temperature" would also increase (Duan et al., 1992). So, the Earth's indigenous oceans were hot soda supercritical $H_2O$.

## Removal of $CO_2$ from Earth's Proto-Atmosphere

When the Earth's surface temperature further cooled down, the indigenous oceans expanded at the expense of the $CO_2$ proto-atmosphere. Once the oceans commenced to expand, the atmospheric pressure would also decrease simultaneously. The removal of $CO_2$ from the Earth's proto-atmosphere was accelerated and then completed when the hot soda indigenous oceans reacted with the most abundant surface mineral plagioclase to form carbonates and clay minerals, leaving $Na^+$ in the oceans (Liu, 2004; 2023).

So, like the ancient Martian oceans, the Earth's oceans are also inherent and derived from its interiors, but via different mechanisms after the completion of accretion. The ancient Martian oceans were derived by a slow degassing process at rather lower temperature and pressure (Liu, 2014; 2022), yet the Earth's oceans were produced by the Moon-making giant impact process involving a larger quantity of supercritical $H_2O$. This is why the $CO_2$-dominated proto-atmosphere of Mars remains intact and the Earth's $CO_2$-dominated proto-atmosphere was completely removed. Once the Earth's $CO_2$ proto-atmosphere was removed, $N_2$ would naturally become the most abundant component of the Earth's atmosphere as observed today. The atmosphere of the early Earth after the formation of the oceans and removal of the $CO_2$ proto-atmosphere might be composed of supercritical or some hot gaseous $H_2O$, which would most likely dissociate into $O_2$ and $H_2$ at high altitude and $H_2$ would then escape from the Earth to the outer-space and $O_2$ remained in the Earth's early atmosphere. Alternatively, the abundance of $O_2$ in the Earth atmosphere may be explained by the occurrence of photosynthetic organisms in the oceans, metabolizing carbon from $CO_2$ and releasing oxygen into the atmosphere (e.g., Abell, 1975).

The inception of oceans on the Earth right after accretion and solidification of the magma ocean thus envisaged is consistent with the geochemical evidence revealed from detrital zircons 4.4 Gyr old (Wilde et al., 2001; Mojzsis et al., 2001). It has been found that these very old zircon crystals were formed from acidic magmas having undergone low-temperature interaction in the presence of water, implying a large reservoir of liquid water on the surface of the Earth some 4.4 Gyr ago.

It has been estimated that the $CO_2$ locked in the carbonate rocks on the Earth is about 2/3 that of the $CO_2$ contents in the present Cytherean atmosphere (Ronov and Yaroshevsky, 1976; Holland, 1984). Then, where can one find the remaining 1/3 or more $CO_2$ in the Earth, if terrestrial planets were formed via a similar accretion process with similar infalling materials? Both Ronov and Yaroshevsky (1976) and Holland (1984) have only considered carbonate rocks in the shallow parts of the Earth. The existence of magnesite ($MgCO_3$) at depths greater than 200 km has been favoured by many studies (Gillet, 1993; Redfern et al., 1993; Liu and Lin, 1995). Thus, these deep sources of carbonate and diamond may account for the remaining 1/3 or more $CO_2$ in the Earth's interior. Carbonate rocks are ubiquitous on the Earth's surface. If a detailed geological survey could be conducted on Mars one day, it is highly likely that carbonate rocks would hardly be found on Mars because nearly all $CO_2$ still exists in the Martian atmosphere.

Liu (2023) stated that the abnormality of the Earth (different atmospheric composition, possessing the oceans, the largest satellite, and the greatest average density) implies its uniqueness or rareness which, in turn, may disappoint many scientists who are interested in searching for life on other planets. As demonstrated in this study, if the proto-atmosphere of a terrestrial planet is dominated by $CO_2$ and if this $CO_2$-dominated proto-atmosphere cannot be removed due to the absence of oceans which require a large quantity of supercritical $H_2O$ fluid at high temperatures and relatively higher atmospheric pressures, life is unlikely to evolve on such a planet. Bio-evolution itself is a chaotic process. The progress of evolution can go in any direction and is constrained only by environments. A change of environments may modify the evolution route, create new species, or lead to total extinction. Even if one day life is found on other planets, there is no warranty that a human-like species may be evolved on that planet.

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