

The Proto-Atmosphere of Terrestrial Planets

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ABSTRACT

The theoretically derived composition of the proto-atmosphere, which evolved during accretion, of terrestrial planets is composed primarily of CO₂, Ar and N₂ when the mass of a planet became greater than 3.30×10^{26} g. This is identical to the atmospheric compositions of Venus and Mars observed today. Therefore, both Venus and Mars most likely retained their proto-atmospheres till now. The Earth is situated between Venus and Mars, there is no reason whatsoever that the Earth's proto-atmosphere should be any different from those of Venus and Mars. Yet, today's Earth atmospheric composition is drastically different from her proto-atmosphere. Mercury is not massive enough to hold even CO₂ to form a proto-atmosphere. Therefore, Mercury is virtually in vacuum. A "magma ocean" has been proposed to commence and cover the surface of the Earth when her radius grew over ~2550 km. All H₂O in the primordial planetesimals would dissolve in the "magma ocean" during accretion. Thus, H₂O would never be one of the proto-atmospheric components even if the mass of terrestrial planets was over 8.06×10^{26} g. Any significant amount of H₂O on the surface of all terrestrial planets must be added or derived via other mechanisms after the completion of accretion. The Earth's hot and soda indigenous ocean of supercritical H₂O-CO₂ mixture was most likely derived from the giant impacting process that produced the Moon. It is this ocean that removed all CO₂ from the Earth's proto-atmosphere.

Keywords: terrestrial planets, atmospheres, H₂O, CO₂.

INTRODUCTION

It has been said that, right after accretion, a large quantity of "dirty snowballs" impinged upon the Earth which subsequently evolved to form the oceans (e.g., [1, 2]). This "added" mechanism speculation, however, provides no explanation as to why Venus and Mars were not bombarded with "dirty snowballs" after accretion. Nor can it explain the drastically different atmospheric compositions between the Earth and her immediate neighbors of Venus and Mars. The "added" mechanism also implies that the Earth had a second-stage of accretion with primordial planetesimals being replaced by "dirty snowballs" and that the same second-stage of accretion did not occur on Venus. Liu [3] conclude that Mars is not massive enough to hold H₂O in its atmosphere (see later Table 1). So, if there were some kinds of ancient ocean on Mars, this ocean cannot be added by "dirty snowballs" and it has to be derived from another mechanism such as degassing [4].

H₂O and CO₂ are the two most abundant volatiles on the terrestrial planets and contain the most vital elements (C, H and O) for life on the Earth. 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 (e.g., C1 chondrite) on the Earth today.

THE IMPACK PROCESSES

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 in their infant planets. Further as their growth continued, the impacting force was increasing to a stage where decarbonation and dehydration occurred.

The shock-wave experimental studies of calcite (CaCO_3) and other carbonate rocks [5-7] 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 [8] 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 terrestrial 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 planetesimals is 0.33 wt%, Liu [9] calculated that the total H_2O 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 [10].

ATMOSPHERE OF A PLANET

An atmosphere is defined as 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. Therefore, it is the total mass of a planet that determines the atmospheric composition for as long as the volatiles are available.

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 [3]. 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 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 [11] suggests that the true CM for He should be greater than the Earth's mass, 5.976×10^{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 respectively estimated some 5 to 20 times that of the Earth's mass by Mizuno

[12] and Ikoma et al. [13]. The mass of Uranus is 14.5 times that of the Earth, which suggests that the true value of CM for H₂ must be less than 15 times that of the Earth. 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. H₂ possesses the smallest molecular weight, thus the discrepancy between the CM for H₂ listed in Table 1 and the other estimates is the greatest.

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 \approx 1 bar)	

*Atmospheric composition is listed in the order of abundance, less than 1% is not included. CO₂ in both Venus and Mars is more than 95%.

THE PROTO-ATMOSPHERE

The proto-atmosphere is defined as an atmosphere evolved during accretion of a planet. No one knows what the components of a proto-atmosphere should be unless astrophysicist is able to observe the accretion of a planet in another solar system. As discussed earlier, in the early stage of accretion, carbonates and hydrous minerals in primordial planetesimals would undergo decarbonation and dehydration reactions when the impact pressures reached 100~200 kbar and complete decarbonation and dehydration would take place when the impact pressures are over 600~700 kbar. CO₂ and H₂O thus released would escape from the growing planets and not form a proto-atmosphere of a growing planet until the mass of an infant planet exceeds 3.30×10^{26} g to hold CO₂ as the first component in a proto-atmosphere. Further on the way of accretion, if the volatiles are available, Table 1 suggests that the proto-atmosphere would add Ar when a planet grew over 3.64×10^{26} g, and would then add O₂ and N₂ if an infant planet continued to grow. Except for O₂, which would react to form oxides, the components of such a

proto-atmosphere derived from Table 1 are identical to the Cytherean and Martian atmospheres observed today. Thus, it is highly likely that both Venus and Mars retain their proto-atmospheres which are somewhat 4.5 b.y. old. The atmospheres of both Venus and Mars are composed of more than 95% CO₂ suggesting 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 N₂ in the Martian atmosphere suggests that the source material of Ar (probably radioactive ⁴⁰K) is less abundant than nitrate minerals in the primordial planetesimals. Table 1 demonstrates that Mercury is not massive enough to hold CO₂ to form a proto-atmosphere during accretion. Therefore, Mercury is virtually in vacuum as observed today.

The next most important stage of accretion is when the mass of terrestrial planets grew over 8.06×10^{26} g, below which H₂O would not become one of the proto-atmospheric components. The mass of Mars is 6.419×10^{26} g. Therefore, H₂O should never be a component of the proto- and today's Martian atmospheres. This issue was further complicated when Hofmeister [14], Matsui and Abe [15] among others suggested that, due to impacting, Earth's surface commenced to be covered by a "magma ocean" when the growing Earth exceeded ~40% of its final radius (a radius of ~2550 km). Once the growing planets were covered by a "magma ocean", nearly all H₂O released from the infalling planetesimals during accretion would be dissolved in the "magma ocean" [16]. The facts that the Martian radius is 3395 km and its mass is 6.419×10^{26} g suggest that H₂O never existed as one of the proto-atmospheric components on all terrestrial planets during accretion. Therefore, any significant amount of H₂O on the surface of all terrestrial planets must be added or derived via other mechanisms after the completion of accretion.

Except for Mercury, it can be speculated that, after the completion of accretion and the early stage of solidification, all H₂O should be dissolved in the partially solidified magma oceans and/or in the solid hydrous minerals in all terrestrial planets, which were enveloped by their CO₂-dominated proto-atmosphere. There is no compelling reason that the Earth should be an exception, and a similar CO₂-dominated proto-atmosphere should have existed in the early history of the Earth. The CO₂-dominated atmosphere of the Earth has also been envisaged and supported by earlier studies [10, 17-18]. Then, what has caused today's Earth unique atmospheric composition?

CO₂ in the early atmosphere of the Earth is generally believed to be removed mainly by photosynthetic organisms in the oceans, metabolising carbon from CO₂ and releasing oxygen into the atmosphere (e.g., [19]). The abundance of oxygen in the Earth's atmosphere may be explained by the occurrence of organisms, which, however, can probably account for only a very small amount of the missing CO₂ in the early Earth atmosphere. Furthermore, this mechanism should not be confused with the CO₂-dominated proto-atmosphere of the Earth after accretion and before the formation of the oceans. Then, how did the more than 95% CO₂ vanish from the Earth's proto-atmosphere? Liu [20, 21] envisaged that the Moon-making giant impact process released almost all H₂O from the partially solidified magma ocean in the early history of the Earth. Supercritical H₂O thus released would react with the CO₂-dominated proto-atmosphere to form a supercritical H₂O-CO₂ mixture. When the Earth's surface temperature cooled down to 450~300 °C, the supercritical H₂O-CO₂ mixture was dense enough to precipitate

on the surface to form the hot and soda indigenous ocean, which would react with the most abundant mineral plagioclase and yield carbonates and clay minerals on the Earth's surface. It is this ocean that quickly removed all CO₂ from the Earth's proto-atmosphere. Once CO₂ was removed, N₂ in the proto-atmosphere would naturally become the most abundant component in the Earth's atmosphere as observed today. Thus, like Venus and Mars retain all of their proto-atmospheres, the Earth might have also retained a partial proto-atmosphere.

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