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## Atmospheres and Oceans of Terrestrial Planets

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#### Introduction

It is widely known that 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 H2 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<sub>2</sub> and followed by a few percent of N<sub>2</sub> 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.

H<sub>2</sub>O and CO<sub>2</sub> are the two most abundant volatiles on the terrestrial planets. The former forms the Earth's oceans, and the latter 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. These minerals are commonly found in many stony meteorites (e.g., chondrites) 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 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 latter reactions were experimentally observed by shock-wave studies of carbonates and hydrous minerals. Based on the results of these studies, it can be concluded that all CO<sub>2</sub> and H<sub>2</sub>O 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, at which the total decarbonation and dehydration take place.

Liu estimated that when the mass of a planet grows over  $3.30 \times 10^{26}$  g it would hold CO<sub>2</sub>, the heaviest natural volatiles, to form the protoatmosphere of the growing planet [1]. Mercury is not massive enough to hold CO<sub>2</sub> in its atmosphere and thus virtually becomes vacuum (manifested by its atmospheric pressure of ~10<sup>-15</sup> bar). The trace amounts of O<sub>2</sub>, Na, H<sub>2</sub> and He on Mercury's surface are likely to be a transit and short-lived phenomenon, and H<sub>2</sub> and He may even be imposed by the solar wind.

The observed atmospheric compositions of Venus and Mars are composed of more than 95% CO<sub>2</sub>. This appears to suggest that both Venus and Mars might have maintained their proto-atmospheres until now. Earth is situated 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 what has happened to the CO<sub>2</sub>-dominated Earth's proto-atmosphere? We will address this issue later.

So far we have focused at the decarbonation reactions at high pressures, then what has happened when dehydration reactions occurred at impact pressures exceeding 600 - 700 kbar during accretion? First, according to Liu [1], the mass of a growing planet must be greater than 8.06 x  $10^{26}$  g in order to hold gaseous H<sub>2</sub>O in its atmosphere. In other words, even Mars is not massive enough to hold gaseous H<sub>2</sub>O in its atmosphere. The issue of H<sub>2</sub>O, however, is further complicated by the presence of the magma ocean when the radius of a growing planet exceeds ~2550 km. When an impactor hit the magma ocean on a growing planet, it would penetrate into the magma ocean to greater depths. High-pressure experimental studies indicate that at least 6 wt% H<sub>2</sub>O can be dissolved in silicate melts at 3 kbar and the solubility increases with increasing pressure for all silicate melts known. No appreciable

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Pressure, bar

**Figure 1**. The vaporization temperature for both  $H_2O$  and  $CO_2$ as a function of pressure (the solid curves). X marks the critical conditions of these materials. The short-dashed lines indicate the pressure-temperature conditions (beyond the critical points) at which the 'dense' supercritical  $H_2O$  and  $CO_2$  exist. The long-dashed lines indicate the possible routes that dense supercritical  $H_2O$ - $CO_2$  mixture and/or liquid  $H_2O$ - $CO_2$  mixture may precipitate on the Earth's surface from its proto-atmosphere after accretion. Mars total atmospheric pressure of both  $H_2O$  and  $CO_2$  right after accretion and solidification is too small to shown in the present scale (indicated by an arrow along the vertical axis). At such a low pressure,  $H_2O$  and  $CO_2$  would act rather independently except possibly for forming some  $HCO_3$ . Thus, H2O degassed from Mars would condense directly to form an ocean when Mars surface cooled down below 100°C, leaving behind  $CO_2$ , in the proto-atmosphere.

amounts of  $CO_2$  are known to dissolve in silicate melts at high pressures, on the other hand. Thus, nearly all the H<sub>2</sub>O released during impacting and penetration would be dissolved in the magma ocean and most of the CO<sub>2</sub> released would escape from the magma ocean to incorporate in the proto-atmosphere.

Right after the completion of accretion, the planets must have cooled down and solidified. The magma ocean, on the other hand, is most likely entrapped inside the planet. Liu showed that the Martian temperature profile intersects its mantle solidus near 230 and 580 km [2]. In other words, there probably exists a partial melting zone inside Mars. Supercritical  $H_2O$  fluid is freely moving upwards and forms ordinary hydrous minerals near surface regions, when the P–T conditions and chemical environments are suitable, and the remaining unreacted water would be capable of forming a 2000 m depth oceans on Martian

surface via degassing processes. The Martian short-lived oceans can easily be rationalized due to the fact that Mars is not massive enough to hold gaseous H<sub>2</sub>O in its atmosphere.

The entrapped magma ocean inside Venus probably remains intact due to its high surface and internal temperatures. Most, if not all, of Cytherean  $H_2O$  is dissolved in the entrapped magma ocean. This may account for the fact that Venus is deficient in  $H_2O$ , relative to Earth, by a factor of  $10^4$  to  $10^5$ .

The origin of the Earth's oceans is totally different from Martian short-lived oceans due to the fact that Earth possesses the largest satellite (relative to Earth's mass). Earth's large Moon is generally believed to be formed by a striking from a Mars-like impactor at a very early stage of the Earth's evolution, so-called the Moon-forming giant impact hypothesis. Whilst the rocky debris formed the Moon, the giant impact also released most of the Earth's volatiles into its CO<sub>2</sub>-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<sub>2</sub>O dissolved in the entrapped magma ocean, somewhat like today's Venus, escaped into the Earth's CO<sub>2</sub> proto-atmosphere.

Liu has modeled the proto-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  $CO_2[3]$ . Today's Cytherean atmospheric pressure is roughly of 90 bar  $CO_2$  and the partial pressure of  $CO_2$  in the proto-atmosphere of the Earth was estimated to be 114 bar.

Figure 1 shows that the first drop of dense supercritical H<sub>2</sub>O appeared (or the inception of the H<sub>2</sub>O oceans) on the Earth when the surface temperature cooled to about  $450 \pm 20$  °C, if H<sub>2</sub>O and CO, were to coexist as an ideal mixture (or inert to each other). Experimental and thermodynamic studies, however, show that H<sub>2</sub>O and CO<sub>2</sub> are able to form supercritical H<sub>2</sub>O-CO<sub>2</sub> mixtures in the temperature range between 450 and 300 °C at 660 bar. Thus, either dense supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture or liquid supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture may precipitate to form the indigenous hot soda oceans on Earth. The inception of such  $H_2O-CO_2$  oceans would somewhat remove  $CO_2$  from the  $CO_2$ dominated proto-atmosphere of the Earth. Then, the removal was later accelerated and completed when the indigenous oceans reacted with plagioclase, the most abundant mineral on the Earth, to form carbonate and clay minerals. As shown in Figure 1, no supercritical H<sub>2</sub>O or supercritical CO<sub>2</sub> was involved in the formation of the early Martian oceans by degassing process. Thus, the CO<sub>2</sub>-dominated proto-atmosphere of Mars is essentially intact.

Liu 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 [4]. This is because the CO<sub>2</sub>-dominated proto-atmosphere of a planet cannot be removed due to the absence of oceans which require a large quantity of supercritical  $H_2O$  fluid at high temperature and relatively higher atmospheric pressures. Bio-evolution itself is a chaotic process. The progress of evolution can go in any direction and is only constrained by environments. 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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