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Atmospheres and Oceans of Terrestrial Planets-II

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Abstract: Both Venus and Mars most likely retain their proto-atmospheres which comprise more than 95% CO_2 plus a few percent of N_2. Mercury being so small and so close to the Sun for so long has only trace amounts of O_2 and Na. This might imply that its rocky parts (crust + mantle) became thinner and thinner with time due to sublimation. The Earth's CO_2-rich proto-atmosphere was removed by a large quantity of supercritical H_2O released from the Moon-making giant impact process. The supercritical H_2O released from this impact reacted with Earth's CO_2-rich proto-atmosphere to form a supercritical H_2O-CO_2 mixture which yielded the hot and soda indigenous ocean when the Earth's surface temperature cooled down to 450~300 ^oC. The Earth, however, retains N_2 from her proto-atmosphere. The ancient Martian oceans, on the other hand, might be derived from the entrapped magma oceans via a degassing process when the Martian surface temperature cooled much below 100 ^oC.

Keywords: terrestrial planets, atmospheres, oceans, H_2O, CO_2.

INTRODUCTION

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. The Earth is the only planet that possesses the oceans today.

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. 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 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 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 planet, 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.

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}
		($O_2 + Na + H_2 + He \approx 10^{-15}$ 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}
		($CO_2 + N_2 + Ar = 8 \times 10^{-3}$ bar)	
H_2O (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}
		($N_2 + O_2 + H_2O + Ar = 1.013$ 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. CO_2 in both Venus and Mars is more than 95%.

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 × 1027g. 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 (1980) and Ikoma et al. (2000). The mass of Uranus is 14.5 times that of the Earth, which suggests that the true value of CM for H_2 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. H_2 possesses the smallest molecular weight, thus the discrepancy between the CM for H_2 listed in Table 1 and the other estimates is the greatest.

THE EARLY STAGE OF ACCRETION

H_2O and CO_2 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 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 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 (1988) 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 (1984).

THE PROTO-ATMOSPHERE

Venus, Earth and Mars

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 an astrophysicist is able to observe the accretion of a similar 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. CO_2 and H_2O 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 x 10^{26} g to hold CO_2, the heaviest natural volatile, as the first component in a proto-atmosphere. The evolution of the CO_2 proto-atmosphere thus described during and right after accretion is shown in Fig.1, using Venus, Earth, and Mars as an example (Liu 1988, 2009). CO_2 would have been buried inside a growing planet when the impact pressure was less than 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 from the infalling planetesimals and the surface materials of the growing planets. The released CO_2 would then escape from the growing planets to outer-space, and be gone forever, because the growing planets were not massive enough to hold them to form a proto-atmosphere. When the planets grew to R_2 and $(M_1 + M_2) > CM$ for CO_2, the proto-atmosphere of CO_2 would then commence to envelope the growing planets. So, the CO_2 proto-atmosphere was derived from the planetesimals that formed M_3. This model easily explains the very thin atmosphere of Mars because its M_3 is so mall. The present CO_2 partial pressure on Venus is ~90 bar. Assuming Venus retains its proto-atmosphere today, the CO_2 partial pressure of the Earth's proto-atmosphere is calculated to be 114 bar (Liu, 2009).

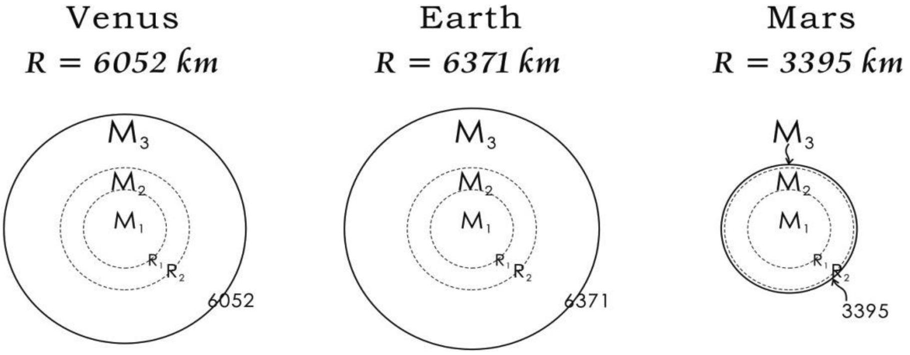

Fig. 1: Imaginary internal structure of Venus, Earth and Mars during and right after accretion. R_1 is the radius beyond which (or at which the impact pressure > 700 kbar) complete decarbonation of the infalling planetesimals and the surface materials of the growing planets occurred. M_1 is the mass 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.

After the CO_2 proto-atmosphere commenced to envelope the growing planets, further on the way to accretion, Table 1 suggests that the proto-atmosphere would add Ar when a planet grew over 3.64 x 10^{26} g, and would then add O_2 and N_2 if an infant planet continued to grow and the volatiles are available,. Except for O_2, 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 approximately 4.5 Gyr old. The atmospheres of both Venus and Mars are composed of more than 95% CO_2 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 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.

The Earth is situated between Venus and Mars and there is no compelling reason that the proto-atmosphere of Earth should be any different from those of Venus and Mars as shown in Fig 1. Then, where did the more than 95% CO_2 in the Earth's proto-atmosphere go?

The next most important stage of accretion is when the mass of terrestrial planets grew over 8.06 x 10^{26} g, below which H_2O would not become one of the proto-atmospheric components. The mass of Mars is 6.419 x 10^{26} g. Therefore, H_2O should never be a component of the proto- and today's Martian atmospheres.

Mercury

According to Table 1, Mercury is not massive enough to hold CO_2 in its atmosphere. Therefore, there is no so-called proto-atmosphere on Mercury and it is virtually in vacuum (manifested by its atmospheric pressure of ~10^{-15} bar) as observed today. However, the significance of the trace amounts of O_2, Na, H_2 and He detected on the smallest terrestrial planet may be worthwhile exploring.

These volatiles are likely to be a transit and short-lived phenomenon, and H_2 and He are commonly explained as due to impinging by the solar wind. The presence of O_2 and Na on its surface is not totally unexpected and can be quite significant because Mercury is so small and so close to the Sun and is exposed to higher temperatures (> 470 ^oC) for so long (~4.5 Gyr). O_2 itself is a volatile and was suggested to be the most abundant element by weight in the whole Earth (Ringwood, 1979; Liu, 1982a). Na is also rather abundant in the shallow parts of the Earth (Liu, 1982b) and is known to be a rather volatile metal element.

Slow sublimations of Mercury's rocky parts (crust and/or mantle) might yield trace amounts of O_2 and Na, due to exposure to very high temperatures for so long. The speculation of sublimation is also substantiated by the presence of even less abundant elements like K, Mg and Ca on Mercury's surface. All these elements are classified as the light elements, which are concentrated in the Earth's surface, by Liu (1982b). The sublimated volatiles and light elements would then escape into outer-space. Therefore, the rocky parts of Mercury would become thinner and thinner with time, which might attribute to the great average density of Mercury (5.43 g/cm^3) in our Solar system, second to the Earth (5.52 g/cm^3).

MAGMA OCEAN

Hofmeister (1983), Matsui and Abe (1986) among others suggested that, due to impacting of planetesimals onto the growing planet during accretion, the Earth's surface commenced formation of 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", 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). On the other hand, 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 to be incorporated in the proto-atmosphere. 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.’ Right after the completion of accretion, the planets must have cooled down and solidified. The magma ocean, on the other hand, was most likely entrapped inside the planet.

The fact that the Martian radius is 3395 km and its mass is 6.419×10^{26} g suggests that 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.

Except for Mercury, it can be speculated that, after the completion of accretion and the early stage of solidification, all H_2O 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 CO_2-dominated proto-atmosphere. There is no compelling reason that the Earth should be an exception, and a similar CO_2-dominated proto-atmosphere should have existed in the early history of the Earth. The CO_2-dominated atmosphere of the Earth has also been envisaged and supported by earlier studies (Holland, 1984; Kasting and Ackerman, 1986; Liu, 2004).

CO_2 in the early atmosphere of the Earth is generally believed to be removed mainly by photosynthetic organisms in the oceans, metabolising carbon from CO_2 and releasing O_2 into the atmosphere (e.g., Abell, 1975). The abundance of O_2 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 CO_2 in the early Earth atmosphere. Furthermore, this mechanism should not be confused with the CO_2-dominated proto-atmosphere of the Earth after accretion and before the formation of the oceans. Liu (2009, 2014; 2023) envisaged that the Moon-making giant impact process released almost all H_2O from the partially solidified magma ocean in the early history of the Earth.

ORIGIN OF THE EARTH’S OCEANS

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 how “dirty snowballs” would choose to bombard the Earth alone, but not her nearest neighbor Venus which is severely deficient in H_2O today.

Liu (2004, 2009), on the other hand, postulated that the Earth’s oceans were derived from supercritical H_2O released from the Moon-making giant impact process. Liu (2004) also modeled that the partial pressure of CO_2 in the proto-atmosphere of the Earth was 100 bar (or some 5.2×10^{23}g) and the supercritical H_2O released from the giant impact was 560 bar (twice the amount of today’s oceans). The moment when the supercritical H_2O entered the CO_2-dominated proto-atmosphere, they would react with each other to form a supercritical

H_2O-CO_2 mixture. When the temperature cooled down to 450±20 °C, the supercritical H_2O-CO_2 mixture was dense enough to precipitate on the Earth’s surface to form the indigenous ocean. Alternatively, the supercritical H_2O-CO_2 mixture would become liquid at around 300 °C and 660 bar (Duan et al., 1992). Thus, when the Earth’s surface temperature cooled down to 450~300 °C, the supercritical H_2O-CO_2 mixture would precipitate on the surface to form the hot and soda indigenous ocean, which would then expand at the expanse of CO_2 from the proto-atmosphere and the atmospheric pressure would also decrease simultaneously. The corresponding temperature and pressure paths are shown in Fig. 2.

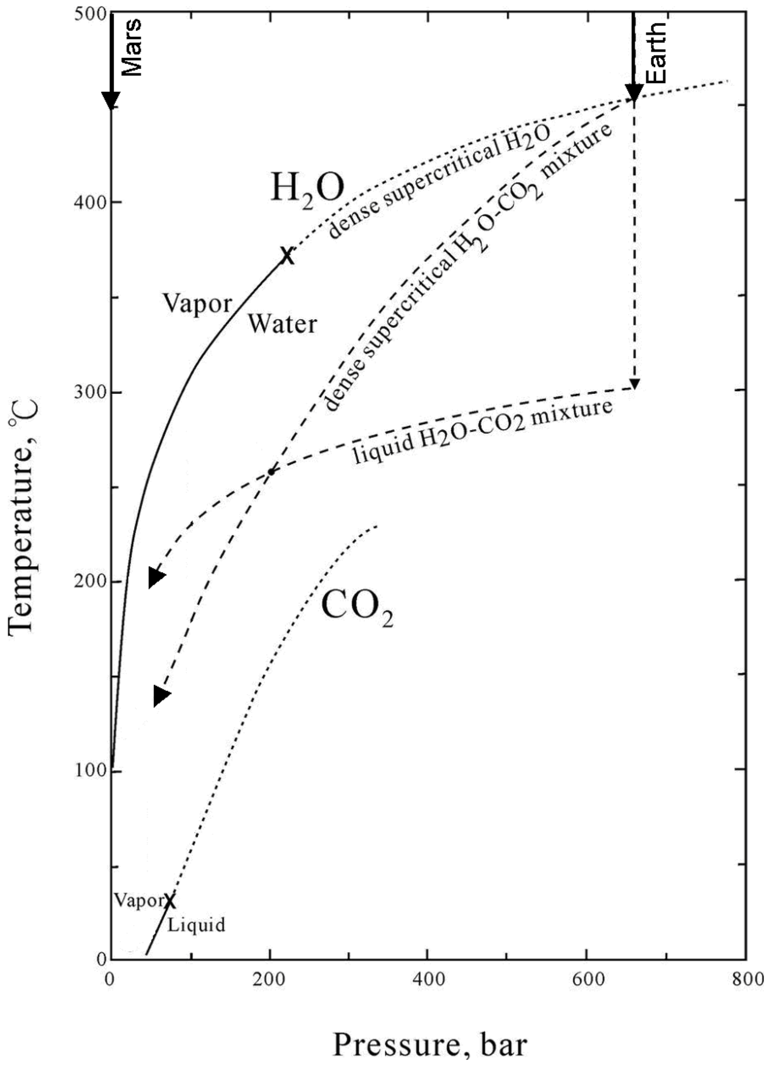

Figure 2: The vaporization temperature for both H_2O and CO_2 as a function of pressure (the solid curvers). *X* marks the critical conditions of these materials. The short-dashed lines indicate the temperatures below which the “dense” supercritical H_2O and CO_2 exist. The long-dashed lines represent the paths of “dense” and liquid supercritical H_2O-CO_2 mixtures. The Earth model of a supercritical 560 bar H_2O + 100 bar CO_2 mixture and the Martian proto-atmosphere are also marked.

The indigenous oceans would not only just expand, but would also react with the most abundant surface mineral plagioclase and yield carbonates and clay minerals on the

Earth's surface, leaving Na^+ in the ocean. It is this ocean that quickly removed all CO_2 from the Earth's proto-atmosphere. Once CO_2 was removed, N_2 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 of her proto-atmosphere.

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 4.3 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 (~90 bar) 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.

Relative to CO_2, the abundance of the Earth's H_2O oceans suggests that there might be much more hydrous minerals than carbonate minerals in the primordial planetesimals. Or, perhaps, the dirty snowballs might somehow also contribute some H_2O to today's Earth oceans.

MARTIAN ACIENT OCEANS

Today's surface temperature of Mars is well below the melting temperature of H_2O. Therefore, it is impossible for liquid water to be present on the Martian surface. Actually, even the naked H_2O ice cannot exist on the Martian surface either because sublimation would soon remove all the ice. This conclusion, however, appears to be in contradiction with many observed morphologic features of Mars and the recent NASA missions to Mars. Squyres (1984) and Carr (1986) have long speculated that many surface geological features of Mars suggest the existence of an ancient ocean on Mars. The NASA 2008 and 2016 missions confirmed the existence of H_2O ice in the Martian soil. Based on photos taken by Perseverance rover, an ancient delta-lake system and flood deposits have been speculated at Jezero crater on Mars by Mangold et al. (2021). It was inferred that Jezero crater itself was an ancient lake, which was connected to a sizeable river. The latter, in turn, implies that there was an ancient ocean on Mars as advocated earlier by Squyres (1984), Carr (1986), and Liu (1988). The disappearance of an ancient ocean, river and lake on Mars appears to contradict the earlier NASA claims of H_2O ice in the Martian soil, unless H_2O ices were sealed in some kinds of cavities in the Martian soil as suggested by Liu (2014).

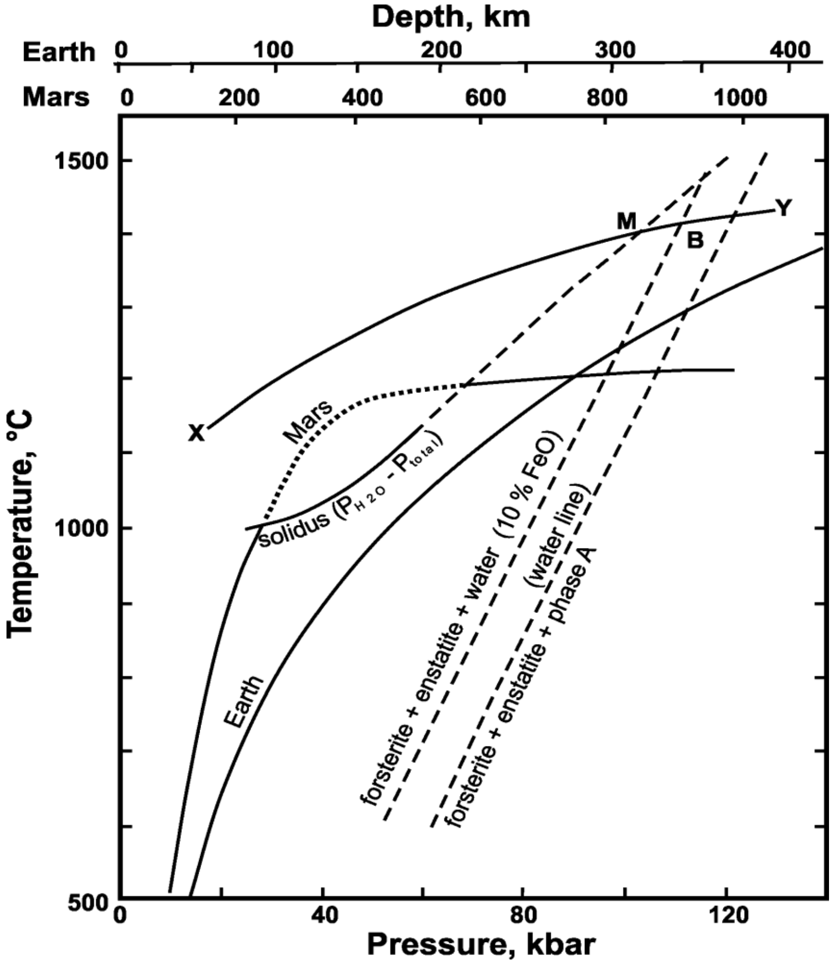

Fig 3: The thermal models for Mars and the Earth are compared with the mantle solidus and the water line. The solid portions of the latter two represent the experimental determinations. XY represents a hypothetical temperature profile that intersects the mantle solidus at M, or a depth of 845 km, right after completion of accretion of Mars. Thus, M corresponds to the bottom of a magma ocean. XY also intersects the water line at B.

Mars is the most distant terrestrial planet in our Solar System and is also relatively small. Thus, it would be expected that Mars cooled down much faster than the other terrestrial planets. Liu (2014, 2022) showed that the Martian temperature profile intersects its mantle solidus near 230 and 580 km (Fig. 3). 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. If ordinary hydrous minerals were not formed, the up-moving water would be capable of forming a 2000 m depth ocean on Martian surface via degassing processes (Liu, 2022). Because Martian atmospheric pressure is very low, there never appears supercritical H_2O on its surface and the more than 95% CO_2 atmosphere remains intact throughout its life (see Fig. 2).

The short-lived Martian oceans can easily be rationalized due to the fact that Mars is not massive enough to hold gaseous H_2O in its atmosphere. Liu (2014, 2019) also concluded that the Martian oceans should be inherent, or was derived from its interiors, and cannot be added by “dirty snowballs” after accretion, because Mars is never massive enough to retain gaseous H_2O in its atmosphere. Any H_2O added by snowballs would be evaporated and lost to outer-space during bombardment.

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