## NOTES AND CORRESPONDENCE

# Critical Masses for Various Terrestrial Planet Atmospheric Gases and Water in/on Mars

Lin-gun Liu\*

Laboratory for High-temperature & High-pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou, China

Received 6 November 2013, revised 2 March 2014, accepted 11 April 2014

#### ABSTRACT

The lower critical mass boundaries (CM) for various atmospheric gas species on terrestrial planets are estimated. The CM is different for different gas molecules. Except for He, the observed atmospheric compositions of the terrestrial planets are consistent with these estimates. The lower CM boundary for gaseous H<sub>2</sub>O is calculated as  $8.06 \times 10^{26}$  g, which is significantly greater than the Martian mass ( $6.419 \times 10^{26}$  g). Thus, Mars is not capable of retaining H<sub>2</sub>O in its atmosphere. If the speculated ocean on Mars and the claimed H<sub>2</sub>O ice in the Martian soil are true, both the ocean and ice had to be derived earlier from H<sub>2</sub>O degassed from the Martian interior after the surface temperature cooled much below 100°C. These watery bodies cannot be sustained for long durations because evaporation and sublimation would turn them into gaseous H<sub>2</sub>O, which would be lost to outer-space. It is concluded that H<sub>2</sub>O in/on Mars is inherent and that the primordial planetesimals that formed Mars must have contained appreciable amounts of hydrous minerals, if the oceans and/or H<sub>2</sub>O ice on Mars are true.

Key words: Critical mass, Atmospheric composition, Water, Mars

Citation: Liu, L., 2014: Critical masses for various terrestrial planet atmospheric gases and water in/on Mars. Terr. Atmos. Ocean. Sci., 25, 703-707, doi: 10.3319/TAO.2014.04.11.01(T)

### **1. INTRODUCTION**

An atmosphere is a layer of gases around a material body mainly attracted by the material body's gravity 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 the 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. After accretion, meteorites constantly hit each planet and add minor gas species to the atmosphere during impact. It has been said, however, that a large quantity of "dirty snowballs" have impinged upon the Earth which eventually evolved to form the oceans after accretion (e.g., Frank et al. 1986a, b).

Once a gas species became available during and after

accretion, the planet's atmospheric evolution is controlled mainly by two competing factors; gravity and atmospheric temperature. The thermal motion of gas molecules is dependent on their molecular mass. The molecules of a gas move at a wide range of velocities at any given temperature and there will almost always be some slow gas leakage into space. Lighter molecules move faster than heavier ones with the same thermal kinetic energy, and so the former are lost from the atmosphere more rapidly than the latter. Therefore, greater gravity (or critical mass) is required to hold down lighter gases than heavier ones to form an atmosphere. The same is true in order to hold down the same molecules at higher temperatures rather than lower temperatures.

Venus is the hottest terrestrial planet (470°C) and Mars is the coldest (-55°C). These are, of course, the surface temperatures which are different from the atmospheric temperatures. It is extremely difficult to estimate what the exact atmospheric temperatures of these planets were during and after accretion. However, the terms "escape gases"

<sup>\*</sup> Corresponding author

*E-mail: lliu@earth.sinica.edu.tw* 

and "gases lost to outer space" used in the present text represent the temperature effects and the term of "gases lost to outer space became negligible" represents the gravity effect on atmospheric formation. Once the gases lost to outer space became negligible, the gravity effect overcomes that of temperature and the growing planet was enwrapped in a proto-atmosphere.

#### 2. CRITICAL MASS

 $H_2O$  and  $CO_2$  are the two most abundant volatiles on terrestrial planets. Based on the shock-wave study results on hydrates and carbonates, Liu (1988, 2009) developed a simple model that describes the evolution of  $H_2O$  and  $CO_2$ during and after accretion. Volatiles like  $H_2O$  and  $CO_2$  in primordial planetesimals should have existed as hydrates and carbonates, respectively, and been buried inside a growing planet when the impact pressure was less than 600 - 700 kbar. The equivalent mass of the growing planets is shown as  $M_1$ in Fig. 1, using Venus, Earth and Mars as examples. Liu (1988) estimated that the amount of  $H_2O$  equivalent to the entire Earth's ocean water was buried inside  $M_1$  of Venus, Earth and Mars.

The volatiles contained in the planetesimals that formed  $M_2$  were released as  $H_2O$  and  $CO_2$  gases that would potentially escape from a growing planet and be lost to outer space during accretion. The gravity of the total mass ( $M_1 + M_2$ ) is large enough that the escaped  $H_2O$  and  $CO_2$  from  $M_3$  would be retained to form the proto-atmosphere of a growing planet. In other words, the proto-atmosphere was derived primarily from volatiles originally contained in the planetesimals that formed  $M_3$ . The total mass ( $M_1 + M_2$ ) is thus defined as the critical mass (CM) of a planet beyond which gases lost to outer space is negligible. The masses of  $M_1$  and  $M_2$  are both gas-species dependent and so is the CM. Based on a theoretical calculation Donahue (1986) concluded that gas loss (ex-

cept hydrogen) should occur so slowly from growing planets greater than about  $10^{26}$  g and that the composition becomes practically frozen except for continuous growth. The CM for H<sub>2</sub> was estimated as some 5 - 20 times that of the Earth's mass by Mizuno (1980) and Ikoma et al. (2000), respectively.

 $CO_2$  has the largest molecule mass among the known common atmospheric gas species, and therefore, it requires the smallest CM to retain a  $CO_2$  atmosphere. Liu (2009) suggested that today's atmospheres on both Venus and Mars should have retained all of the  $CO_2$  (more than 95% on both), in addition to other minor volatiles such as nitrogen and argon, as in their proto-atmospheres derived from M<sub>3</sub>. If the primordial planetesimals that formed Venus and Mars are similar, then

$$CO_2(V)/M_3(V) = CO_2(M)/M_3(M)$$
 (1)

where V and M inside the parentheses represent Venus and Mars, respectively, and  $CO_2$  (V) and  $CO_2$  (M) are today's total atmospheric CO<sub>2</sub> on Venus and Mars. In principle, the masses of both  $M_3(V)$  and  $M_3(M)$  can be calculated exactly. Numerically, however,  $M_3(M)$  has to be rather small because  $CO_2(M)$  is more than four orders of magnitude less than  $CO_2(V)$ . Consequently, the CM  $(M_1 + M_2)$  for  $CO_2$ thus calculated  $(6.415 \times 10^{26} \text{ g})$  is so close to the Martian mass  $(6.419 \times 10^{26} \text{ g})$  (see Liu 2009). However, the Martian atmospheric pressure (average ~8 mbar) varies from time to time and some solid CO2 always exists on the Martian poles. This suggests that the CM for CO<sub>2</sub> thus calculated represents the upper bound and that the true CM for CO<sub>2</sub> must be smaller than  $6.415 \times 10^{26}$  g. Instead of attempting to estimate the true value of CM for CO<sub>2</sub>, it is assumed that the lack of CO<sub>2</sub> on Mercury is due mainly to its small gravity. Thus, the mass of Mercury may be regarded as the lower CM boundary for CO<sub>2</sub>.



Fig. 1. Imaginary internal structure of the terrestrial planets during and right after accretion, using Venus, Earth and Mars and volatile CO<sub>2</sub> 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 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 CO<sub>2</sub> content in the growing planets are frozen, and  $M_2$  is the mass retained between  $R_1$  and  $R_2$ .  $CO_2$  in the proto-atmospheres was derived from mass  $M_3$ . ( $M_1 + M_2$ ) is the CM beyond which the loss of CO<sub>2</sub> to outer space is negligible.

The present study estimated the lower CM boundaries for all relevant gas species (Ar,  $O_2$ ,  $N_2$ , CO,  $H_2O$ , He, and  $H_2$ ) using the gravitational law:

$$F = G \times (M_1 + M_2) \times (\text{molecular mass})/r^2 \text{ or}$$

$$(M_1 + M_2) = F \times r^2/G \text{ (molecular mass)}$$
(2)

where F is the attraction force, G the gravitational constant,  $(M_1 + M_2)$  the CM, and r the average distance of a gas species to the center of a growing planet (R<sub>2</sub> or > R<sub>2</sub> in Fig. 1). Substituting both the masses of Mercury and CO<sub>2</sub> molecule, one obtains a value of F × r<sup>2</sup> for CO<sub>2</sub> from Eq. (2). By holding F × r<sup>2</sup> thus obtained as a constant in Eq. (2), (M<sub>1</sub> + M<sub>2</sub>) is inversely proportional to molecular mass. The CM's for all other gas species can then be calculated and are listed in Table 1. A greater F is required to hold down lighter molecules and so F should increase with decreasing gas species molecular mass. Not only (M<sub>1</sub> + M<sub>2</sub>), but also r increases with decreasing molecular mass. Holding both F and r, calculated for CO<sub>2</sub>, as constants in the calculation suggests that all CM's listed in Table 1 represent the lower boundaries for all gas species.

#### **3. ATMOSPHERIC COMPOSITION**

The masses of all terrestrial planets, 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.

With the exception of He, Table 1 shows that the calculated CM's are consistent with the atmospheric compositions of all observed terrestrial planets. As shown in Table 1, the atmospheric pressure of Mercury is so small (~10<sup>-15</sup> bar) that there is practically "no" atmosphere on Mercury. This is consistent with the lower CM boundary for CO<sub>2</sub>. In other words, Mercury is not massive enough to hold CO<sub>2</sub> in its atmosphere as assumed and observed. The appearance of trace amounts of O<sub>2</sub> and Na on Mercury is likely to be a transit and short-lived phenomenon. The relatively abundant amounts of H<sub>2</sub> 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 more than 20% less massive than Mercury, there is not much point in showing the details on the Moon's atmosphere in Table 1. The calculated CM's suggest that both Mercury and the Moon possess practically no atmospheres as "observed".

Table 1 shows that Mars is massive enough to hold  $CO_2$ ,  $N_2$ , and Ar in its atmosphere as observed. The CM for gaseous H<sub>2</sub>O shown in Table 1 appears to be reasonable

Table 1. Comparison of the lower CM boundaries for various gas species with the mass of Mercury, Venus, Earth, Moon and Mars and their respective atmospheric composition and surface pressure.

Gases (molecular mass)	Critical Mass (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 <sub>2</sub> (44.01)	$3.30 \times 10^{26}$			
Ar (39.95)	$3.64\times10^{26}$			
O <sub>2</sub> (32.00)	$4.54 \times 10^{26}$			
N <sub>2</sub> (28.01)	$5.19\times10^{26}$			
CO (28.01)	$5.19\times10^{26}$			
		Mars	$6.419 \times 10^{26}$	
		$(CO_2 + N_2 + Ar = 8 \times 10^{-3} \text{ bar})$		
H <sub>2</sub> O (18.02)	$8.06 \times 10^{26}$			
He (4.00)	$3.63 \times 10^{27}$			
		Venus	$4.869 \times 10^{27}$	
		$(CO_2 + N_2 = 93 \text{ bar})$		
		Earth	$5.976 \times 10^{27}$	
		$(N_2 + O_2 + H_2 O_2)$	$(N_2 + O_2 + H_2O + Ar = 1.013 bar)$	
H <sub>2</sub> (2.02)	$7.19 \times 10^{27}$			

because  $H_2O$  is observed on Earth, but not on Mars (0.03%). Venus is known to be deficient in  $H_2O$ . It has been suggested that nearly all of Venus  $H_2O$  is still entrapped inside the partial melting zone because Venus may not yet have reached 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. Ar,  $O_2$ , and  $H_2O$  are missing from its atmosphere. In considering the thick  $CO_2$  atmosphere on Venus (90 bar), the small amount of Ar would become trace (<<1%) and the absence of other gases may simply be due to a lack of availability or even less abundant than Ar.

Subject to availability, Table 1 shows that Earth should retain all gas species except H<sub>2</sub>, in its atmosphere. Indeed, the Earth's atmosphere possesses all four species Ar, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. The content of both CO<sub>2</sub> and CO in the Earth's atmosphere is too small (<< 1%) to be listed in Table 1. As has been suggested, most of the CO<sub>2</sub> in the Earth's protoatmosphere was removed to form carbonates via the formation of oceans shortly after accretion (Liu 2004, 2009). The trace amount of CO in the Earth's atmosphere is simply due to the lack of availability and/or is controlled by the fO<sub>2</sub> of the system via the 2CO + O<sub>2</sub> = 2CO<sub>2</sub> reaction (e.g., Yung and DeMore 1998).

Table 1 shows that both Venus and the Earth should retain He in their atmospheres. This appears to contradict the fact that the Earth is not massive enough to hold He in its atmosphere (Fegley 1995). However, this is simply an artifact because the CM's listed in Table 1 are the lower boundaries.

Except for Mercury, none of the atmospheres of the terrestrial planets have a significant amount of  $H_2$ . Table 1 shows that the CM for  $H_2$  should at least be 1.2 times that of the Earth's mass. This is consistent with the CM estimates for  $H_2$  mentioned earlier.

#### 4. H<sub>2</sub>O IN/ON MARS

It is interesting to find that the calculated CM for gaseous H<sub>2</sub>O (8.06 ×  $10^{26}$  g) is significantly greater than the masses of Mars, Mercury and the Moon. Accordingly, these planets are not capable of retaining gaseous H<sub>2</sub>O in their atmospheres. This should have profound implications for the origin and evolution of H<sub>2</sub>O in/on these planets. 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 recent Phoenix Mission confirms the existence of H<sub>2</sub>O ice in the Martian soil (NASA-Phoenix News & Media Resources 2008). If these speculations and findings are true, the Martian H<sub>2</sub>O must have been derived from H<sub>2</sub>O originally buried inside M<sub>1</sub> as shown in Fig. 1 through a degassing process because there is no  $M_3$ for H<sub>2</sub>O during and after the Mars accretion according to this study. The total amount of H2O buried inside Mars was estimated to be equivalent to the Earth's oceans ( $\sim 1.4 \times 10^{24}$  g) by Liu (1988). The Martian H<sub>2</sub>O is thus inherent and cannot be added by "dirty snowballs" after accretion and solidification, because Mars is less massive than its CM for gaseous H<sub>2</sub>O and any added H<sub>2</sub>O would be evaporated and lost to outer-space during impact.

If there were indeed oceans on Mars, they had to be derived from H<sub>2</sub>O degassed from the Martian interior after the surface cooled much below 100°C and the supply of liquid H<sub>2</sub>O had to be greater than evaporation. The oceans or H<sub>2</sub>O ice (when the surface temperature dropped below 0°C) on the Martian surface cannot be sustained for long duration because evaporation and sublimation would turn the oceans and ice into gaseous H<sub>2</sub>O, which would be lost to outer-space. It is most likely that life might not have been developed in such short-lived oceans on Mars. The existence of either oceans or H<sub>2</sub>O ice on Mars would imply that the primordial planetesimals that formed Mars must have contained appreciable amounts of hydrous minerals. Similar scenarios may also apply to any H<sub>2</sub>O found on Mercury and the Moon. Because H<sub>2</sub>O in/on Mars is inherent, it is highly likely that the Earth's H<sub>2</sub>O is also inherent rather than added by "dirty snowballs".

Acknowledgements I am indebted to M. H. Lee and T. P. Mernagh for their critical comments and reading of an earlier version of this manuscript, which was finalized while the author was affiliated with Amperex Technology Limited in Dongguan, Guangdong, China.

#### REFERENCES

- Carr, M. H., 1986: Mars: A water-rich planet? *Icarus*, **68**, 187-216, doi: 10.1016/0019-1035(86)90019-9. [Link]
- Donahue, T. M., 1986: Fractionation of noble gases by thermal escape from accreting planetesimals. *Icarus*, **66**, 195-210, doi: 10.1016/0019-1035(86)90151-X. [Link]
- Fegley, B., 1995: Properties and composition of the terrestrial oceans and of the atmospheres of the Earth and other planets. In: Ahrens, T. J. (Ed.), Global Earth Physics: A Handbook of Physical Constants, AGU Reference Shelf 1, American Geophysical Union, Washington, D.C., 320-345, doi: 10.1029/RF001p0320. [Link]
- Frank, L. A., J. B. Sigwarth, and J. D. Craven, 1986a: On the influx of small comets into the Earth's upper atmosphere. I. Observations. *Geophys. Res. Lett.*, 13, 303-306, doi: 10.1029/GL013i004p00303. [Link]
- Frank, L. A., J. B. Sigwarth, and J. D. Craven, 1986b: On the influx of small comets into the Earth's upper atmosphere. II. Interpretation. *Geophys. Res. Lett.*, 13, 307-310, doi: 10.1029/GL013i004p00307. [Link]
- Ikoma, M., K. Nakazawa, and H. Emori, 2000: Formation of giant planets: Dependences on core accretion rate and grain opacity. *Astrophys. J.*, 537, 1013-1025.

- Liu, L., 1988: Water in the terrestrial planets and the moon. *Icarus*, **74**, 98-107, doi: 10.1016/0019-1035(88)90032-2. [Link]
- Liu, L., 2004: The inception of the oceans and CO<sub>2</sub>-atmosphere in the early history of the Earth. *Earth Planet. Sci. Lett.*, **227**, 179-184, doi: 10.1016/j.epsl.2004.09.006. [Link]
- Liu, L., 2009: Origin and early evolution of the atmospheres and oceans on the terrestrial planets. In: Denis, J. H. and P. D. Aldridge (Eds.), Space Exploration Research,

Nova Publishers, New York, 385-400.

- Mizuno, H., 1980: Formation of the giant planets. *Prog. Theor. Phys.*, **64**, 544-557, doi: 10.1143/PTP.64.544. [Link]
- Squyres, S. W., 1984: The history of water on Mars. *Annu. Rev. Earth Planet. Sci.*, **12**, 83-106, doi: 10.1146/annurev.ea.12.050184.000503. [Link]
- Yung, Y. L. and W. B. DeMore, 1998: Photochemistry of Planetary Atmospheres, Oxford University Press, New York, 480 pp.