The inception of the oceans and CO_2-atmosphere in the early history of the Earth

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Abstract

After accretion and solidification of a "magma ocean", the proto-atmosphere of the Earth is modeled to compose of 560 bar of H_2O and 100 bar of CO_2. The existence of a CO_2-rich atmosphere in the early history of the Earth has been envisaged and supported by earlier studies. The results of the present study suggest that the oceans started to grow when the surface temperature of the Earth cooled to below approximately 300–450 °C. This study further suggests that CO_2 was removed away from the early atmosphere as a dense supercritical H_2O–CO_2 mixture during condensation (or the growing ocean), and then formed carbonate rocks in early geological history. The scenario of early growth of the oceans is in line with the geochemical evidence revealed recently from detrital zircons 4.4 Gyr old. A large-scale hydrosphere probably never existed on Venus, and not for long, on Mars. Thus, the atmospheres of these latter planets are composed mainly of carbon dioxide.
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1. Introduction

The origin and early evolution of the atmospheres and oceans of terrestrial planets are classic unsolved problems in the planetary sciences. These topics are also of great interest to science in general and have attracted attention from science-philosophers who have considered life in nature. Nearly all theories concerning these topics are model-dependent and constrained by various evidence, e.g., [1,2]. H_2O and CO_2 are the two most abundant volatile species on the surfaces of Earth, Venus and Mars, e.g., [3], and are the most vital elements (C, H and O) for life on the Earth.

It has been suggested favorably that the surface of a growing planet may be covered entirely by a "magma ocean" in the late stage of accretion [4,5]. Both H_2O and CO_2 in the proto-atmospheres of the terrestrial planets may be derived from the magma ocean upon solidification by outgassing, and the

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oceans were formed by condensation of the atmospheric H_2O when the Earth's surface was cooled below the condensation temperature. Venus is deficient in H_2O, relative to Earth, by a factor of 10^4 to 10^5. Although this deficiency may be accounted for by a speculative theory of hydrodynamic escape, Yung and DeMore [3] favored a theory of planetary evolution, which suggested that most water in the magma ocean is still trapped in the thick partial melting zone inside the present Venus, and only CO_2 and a small amount of H_2O were outgassed in the Cytherean atmosphere [6]. Both H_2O and CO_2 were outgassed into the proto-atmospheres of Earth and Mars after solidification of their magma oceans, but most water on the surface of Mars did not survive for long because of its small mass (a hydrogen-rich surface layer on Mars was confirmed by the Mars Odyssey mission [7,8]).

The atmospheres of both Venus and Mars are composed of more than 95% CO_2 [9,10]. In comparison, one may suggest that a similar CO_2-rich atmosphere (or as some more reduced carbonaceous gases, CO or CH_4, which should soon be oxidized to CO_2 by OH radicals produced from water vapor photolysis [11]) may have existed in the early history of the Earth. The CO_2-rich atmosphere of the Earth has been envisaged and supported by earlier studies [2,12].

The inception of oceans on the Earth by condensation has not been addressed in detail. 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 oxygen into the atmosphere, e.g., [13]. The abundance of oxygen in the Earth 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.

2. The model

The present atmosphere of Venus contains ca. 4.6×10^{20} kg CO_2 and that of Mars contains at least ca. 2.1×10^{16} kg CO_2. Thus, it is conveniently assumed that the early Earth atmosphere contained some 5.2×10^{20} kg CO_2 (or 100 bar, see also [2]), in

addition to H_2O, if Venus, Earth and Mars were formed via a similar accretion process with similar infalling materials, because the Earth is more massive than Venus. Holland's estimate gives about 20 bar of CO_2, which equates to ca. 9×10^{19} kg of CO_2, in the proto-atmosphere of the Earth [11].

One may start to consider these issues right after the solidification of the magma ocean and when both H_2O and CO_2 are the main constituents of the proto-atmosphere of the Earth. On the basis of a theory of planetary evolution, Liu [14] estimated that there was about 2.9×10^{21} kg H_2O (twice the amount of the present oceans) in the proto-atmosphere of the Earth, stripping the free water above the "water line" from the depth near 350 km. This amount of H_2O, together with CO_2, in the proto-atmosphere yielded a surface pressure of about 660 bar (560 bar due to H_2O and 100 bar due to CO_2) on the early Earth.

3. Vaporization at high pressures

The vaporization temperature of H_2O, CO_2 and H_2O–CO_2 mixture at sufficiently high pressures can be inferred from data on specific volume and/or density of these materials at various temperatures and pressures determined by experimental studies and thermodynamic calculations [15–17]; and many references cited therein]. Although discrepancies exist among the available experimental data, Blencoe et al. [17] concluded that an excellent agreement was also found in some studies. As an example, the specific volume of H_2O at various pressures and temperatures relevant to the present study is shown in Fig. 1 [15,18]. Although the critical point of H_2O is located at 221.19 bar and 374.1 °C, Fig. 1 clearly shows that the specific volumes of supercritical H_2O as a function of temperature at pressures greater than 221.19 bar are similar to that below the critical point. In Fig. 1, the volume–temperature relationship is marked by a discontinuity near 366 °C at 200 bar, but similar discontinuities in the volume–temperature relationships at 250 and 300 bar are also obvious. When the pressure increases to 400 bar or above, a discontinuity becomes an inflection along the volume–temperature relationships. Thus, although there is no so-called liquid above the critical point, at a given pressure, a supercritical H_2O can still possess a
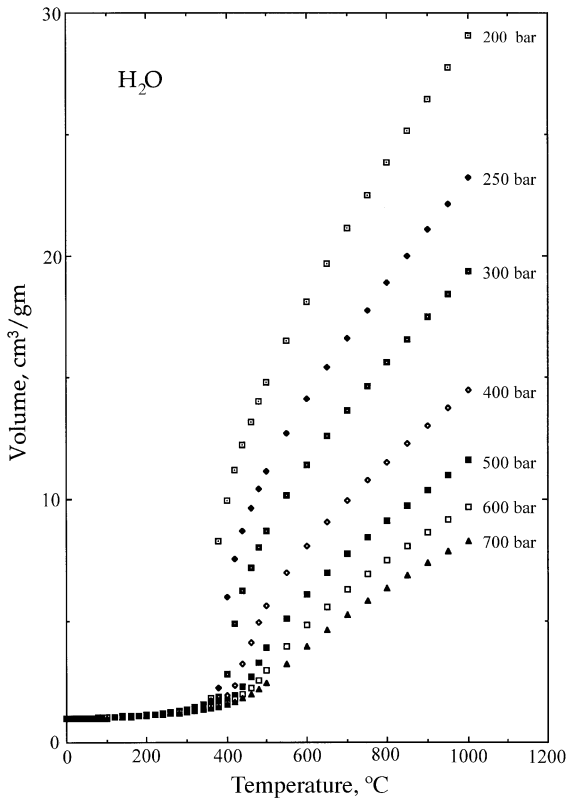
Fig. 1. Specific volume of H_2O as a function of temperature at various pressures after [15,18].

volume that is similar to a liquid below a certain temperature. Just like a liquid, such a "dense" supercritical H_2O should be able to "precipitate" to the surface when the early Earth cooled down below these temperatures. The corresponding temperatures thus derived as a function of pressure are shown by the short-dashed curve in Fig. 2 (it might be called a second- or higher-order transition boundary), together with the vaporization temperatures of H_2O at various pressures as shown by the solid curve (a first-order transition boundary). The critical point is marked by an x. Similar data for CO_2 up to 300 bar are also shown in Fig. 2.

4. Inception of the oceans

The temperature for the onset of the "dense" supercritical H_2O (the short-dashed curve in Fig. 2)

appears insensitive to pressure variation above about 500 bar. If H_2O and CO_2 were to coexist as an ideal mixture (or inert to each other), according to Fig. 2, the first drop of "dense" supercritical H_2O appeared (or the inception of the oceans) on the Earth when the surface temperature cooled to about 450 ± 20 °C ("a" in Fig. 2). The atmospheric pressure must drop at high altitude. So, "dense" supercritical H_2O clouds might have already existed in the proto-atmosphere, 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, the temperature and pressure on the surface would have followed the line from "a" to "b" in Fig. 2, and all H_2O in the air would have condensed as water
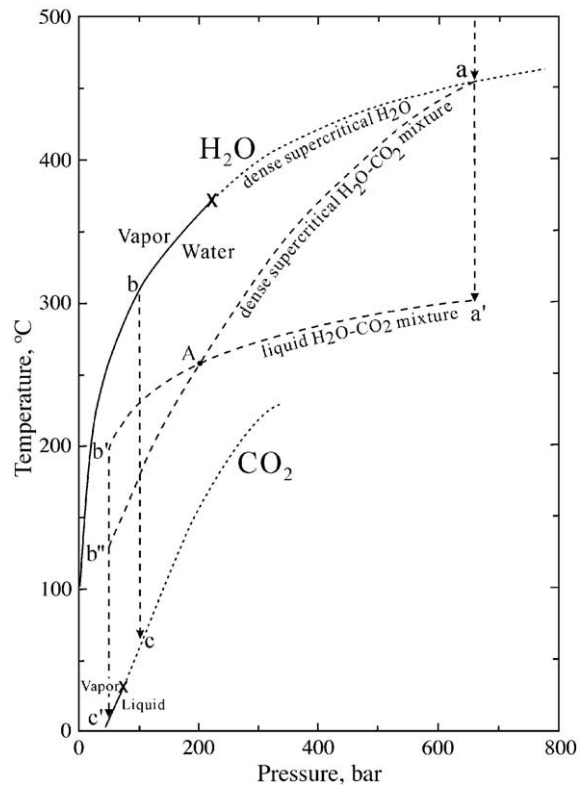

Fig. 2. The vaporization temperature for both H_2O and CO_2 as a function of pressure (the solid curves). x marks the critical conditions of these materials. The short-dashed lines indicate the temperatures below which the "dense" supercritical H_2O and CO_2 exist. See text for the long-dashed lines, the paths a→b→c and a'→b'→c' and A.

at "b". Then the first "dense" supercritical CO_2 would have appeared when the temperature on the surface cooled from "b" to "c".

In reality, however, the early Earth atmosphere was a nonideal H_2O–CO_2 mixture with X_{CO_2} (molar fraction of CO_2)=0.068. According to Duan et al. [16], a true liquid with the critical composition X_{CO_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 ("a′" in Fig. 2), and the temperature and pressure on the surface of the early Earth may have followed a path somewhat similar to the long-dashed line from "a′" to "b′" in Fig. 2. The CO_2-dominated atmosphere of the early Earth (like, maybe, today's Venus and Mars) would condense to liquid when the temperature on the surface cooled down from "b′" to "c′" (or nearby).
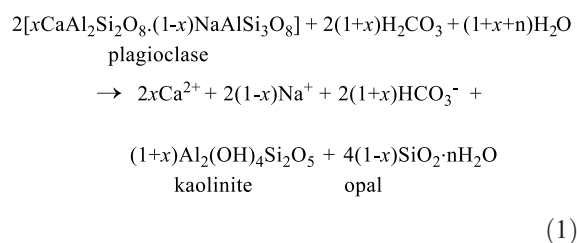
Alternatively, the latter case (from "a′" to "b′" and "c′") may not occur either. As those for pure H_2O shown in Figs. 1 and 2, it is likely that a "dense" supercritical H_2O–CO_2 mixture with X_{CO_2}=0.068 might exist at temperatures much higher than 300 °C at 660 bar (above the critical condition). Once a "dense" supercritical H_2O–CO_2 mixture appeared on the surface, the surface pressure would drop and the corresponding "critical temperature" would also increase [16]. In this case, the temperature and pressure on the surface of the early Earth may have followed a path somewhat similar to the long-dashed line from "a" to "b‴" in Fig. 2. Finally, all H_2O in the early atmosphere condensed in the ocean at "b‴" (arbitrarily in Fig. 2), and the first CO_2-rich liquid should have appeared when temperature on the surface dropped from "b‴" to "c′" (or nearby). However, even the latter case probably never happened, because carbonization reactions (see below) may have already removed all atmospheric CO_2, and the CO_2-rich liquid never appeared on the surface. Furthermore, the "dense" supercritical H_2O–CO_2 mixture and/or liquid H_2O–CO_2 mixture may have been in the form of either H_2CO_3 or HCO_3^-.

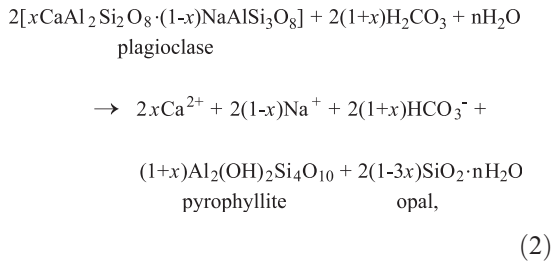The solubility of CO_2 in water at various temperatures and pressures has been determined and calculated in many studies. Available experimental data and calculated models were summarized and reviewed in a recent paper [19]. To be consistent with the data of CO_2 solubility in pure water, one may consider a case where the temperature cooled to 260 °C and the total atmospheric pressure dropped from 660 to 200 bar ("A" in Fig. 2). According to Duan and Sun [19], the CO_2 solubility in water is 1.685 mol/kg water (equivalent to X_{CO_2}=0.028) at 260 °C and 200 bar. The equilibrium vapor phase should have an $X_{CO_2} \approx 0.6$ at the same temperature and pressure condition [16]. However, the whole atmosphere is not under the same temperature and pressure condition, and the mass balance would require the average atmospheric composition being composed of the H_2O–CO_2 mixture with X_{CO_2}=0.174. In the real situation, these compositions are further complicated by: (1) the pressure at the deep parts of the ocean must increase and therefore change the CO_2 solubility significantly; (2) the formation of carbonates via the processes outlined in the following Eqs. (1)–(3) may have removed a lot of the dissolved CO_2 from the ocean; and (3) once carbonization reactions (transfer of atmospheric CO_2 to carbonates via the ocean) took place, the ocean was no longer pure water and the CO_2 solubility in aqueous NaCl solution [19] must be taken into consideration. However, these details do not seem to affect the main theme to be addressed in the present paper.

5. Carbonization via the oceans

Plagioclase is the most abundant mineral species on the Earth's surface. Conversion of plagioclase by weathering processes produces Ca^{2+} and Na^+ via the following reactions (see also, e.g., [20,21]):

$$2[x CaAl_2Si_2O_8 \cdot (1\text{-}x)NaAlSi_3O_8] + 2(1\text{+}x)H_2CO_3 + (1\text{+}x\text{+}n)H_2O$$
$$\text{plagioclase}$$
$$\rightarrow \ 2x Ca^{2+} + 2(1\text{-}x)Na^+ + 2(1\text{+}x)HCO_3^- +$$
$$(1\text{+}x)Al_2(OH)_4Si_2O_5 + 4(1\text{-}x)SiO_2 \cdot nH_2O$$
$$\text{kaolinite} \qquad \text{opal}$$

$$(1)$$

where $0 \leq x \leq 1$; or

$$2[x\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot (1\text{-}x)\text{NaAlSi}_3\text{O}_8] + 2(1+x)\text{H}_2\text{CO}_3 + n\text{H}_2\text{O}$$
$$\text{plagioclase}$$

$$\rightarrow \ 2x\text{Ca}^{2+} + 2(1\text{-}x)\text{Na}^+ + 2(1+x)\text{HCO}_3^- +$$

$$(1+x)\text{Al}_2(\text{OH})_2\text{Si}_4\text{O}_{10} + 2(1\text{-}3x)\text{SiO}_2 \cdot n\text{H}_2\text{O}$$
$$\text{pyrophyllite} \qquad\quad \text{opal,}$$

$$(2)$$

where $0 \leq x \leq 0.333$ (when $0.333 < x \leq 1$, opal on the right-hand side should be moved to the left-hand side and the amount of H_2O should be adjusted accordingly), and the following reaction forms carbonates in a "dense" supercritical H_2O–CO_2 mixture,

$$\text{Ca}^{2+} \ + \ 2\,\text{HCO}_3^- \ \rightarrow \ \text{CaCO}_3 \ + \ \text{CO}_2 \ + \ \text{H}_2\text{O}.$$
$$\text{calcite}$$

$$(3)$$
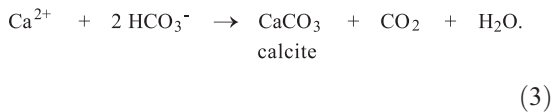
It is most likely that these reactions took place in the growing ocean, particularly at the pressure and temperature conditions prevailing in the early Earth as shown in Fig. 2. Thus, unless a large quantity of photosynthetic organisms would have also developed at similar pressure and temperature conditions in the growing ocean, the presence or absence of a CO_2-atmosphere on Venus, Earth and Mars hinges on the absence or presence of oceans in the early history of these planets. Conversely, the presence of CO_2-dominated atmospheres on both Venus and Mars may be taken as evidence supporting the hypothesis that a large-scale hydrosphere probably never existed on Venus and that the hydrosphere did not survive for long on Mars. Partial loss of the Earth atmosphere in the event of a giant Moon-forming impact is also plausible.

The inception of oceans on the Earth right after accretion and solidification of the magma ocean envisaged in the present paper appears to be consistent with the geochemical evidence revealed recently from detrital zircons 4.4 Gyr old [22,23]. 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 carbonate rocks on the Earth is about 2/3 that of the CO_2 contents in the present Cytherean atmosphere [12,24]. 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 [24] and Holland [12] have considered carbonate rocks in the shallow parts of the Earth. The existence of magnesite ($MgCO_3$) at depths greater than 200 km has been favored by many recent studies [25–27] and diamonds derived from the Earth's lower mantle are also proposed [28–30]. Thus, these deep sources of carbonate and diamond may account for the remaining 1/3 or more CO_2 in the Earth's interior. Because the Martian oceans did not survive for long, only a small amount of Martian CO_2-atmosphere has been converted to carbonate rocks. Consequently, one would expect that there should be nearly no carbonate (and probably no diamond as well) at all on Venus.

Acknowledgements

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