

## NOTES AND CORRESPONDENCE

### Atmosphere-Ocean-Crust Interactions in Earth's Early Life

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#### ABSTRACT

For as long as infalling planetesimals contained some hydrous and carbonate minerals, Earth's proto-atmosphere had to be formed during accretion and was composed primarily of CO<sub>2</sub>. H<sub>2</sub>O was released and incorporated into the proto-atmosphere to form H<sub>2</sub>O-CO<sub>2</sub> supercritical fluid after accretion when the event of a giant Moon-forming impact took place. When Earth's surface cooled down to about 450 - 300°C, the indigenous ocean began to form and it was a hot ocean of either a dense supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture or a fluid H<sub>2</sub>O-CO<sub>2</sub> mixture. The hot ocean interacted both on the surface with CO<sub>2</sub>-dominated proto-atmosphere and on the bottom with feldspars in the crust. The latter removed CO<sub>2</sub> from the ocean to form carbonates and clay minerals on the crust. The interactions on the surface would quickly dissolve CO<sub>2</sub> into the indigenous ocean from the atmosphere and would evaporate H<sub>2</sub>O into the atmosphere. This would effectively remove all CO<sub>2</sub> in the proto-atmosphere via the ocean to the crust. The interactions among atmosphere, ocean and crust would exchange not only materials but heat between different bodies. This in turn might have helped Earth cool down more rapidly than its neighbor Venus.

Key words: Early atmosphere, Ocean, Crust, Interactions

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#### 1. INTRODUCTION

Certain aspects of the role of H<sub>2</sub>O during Earth's accretion have been addressed by Holland (1984), Fukai and Suzuki (1986), and Liu (1987, 1988). Much less attention has been paid to the role of CO<sub>2</sub> during accretion. For as long as the infalling planetesimals contained some hydrous and carbonate minerals, the accreting Earth had to preserve both H<sub>2</sub>O and CO<sub>2</sub> in its infancy. In other words, all H<sub>2</sub>O and CO<sub>2</sub> in the infalling planetesimals were buried inside the growing Earth (inside the radius R<sub>1</sub> of Fig. 1) because the impacting pressures were not large enough to drive out the volatiles. Assuming that the infalling planetesimals contained 0.3 wt% H<sub>2</sub>O, Liu (1988) estimated that a mass of H<sub>2</sub>O equivalent to that of the present-day oceans on Earth (~1.4 × 10<sup>24</sup> g) was buried inside the mass M<sub>1</sub> of Fig. 1. It is

not possible that all H<sub>2</sub>O and CO<sub>2</sub> in the infalling planetesimals had been lost to outer-space after Earth continued to grow from R<sub>1</sub> and onwards. Therefore, in addition to the observable water in the near-surface geochemical reservoirs (hydrosphere + crust), there must be many times of the present-day oceans inside the Earth. Liu (1987) calculated that the Earth's total H<sub>2</sub>O is at least a factor of 5 greater than the H<sub>2</sub>O content in the near-surface geochemical reservoirs of the present-day Earth (2 × 10<sup>24</sup> g). A majority of Earth scientists today believe that there is much water in the form of hydrous minerals in the Earth's deep interior.

Atmosphere-ocean-crust interactions occur not only today, but happened even more vigorously after completion of accretion and solidification of the Earth when the oceans were formed after the giant Moon-forming impact.

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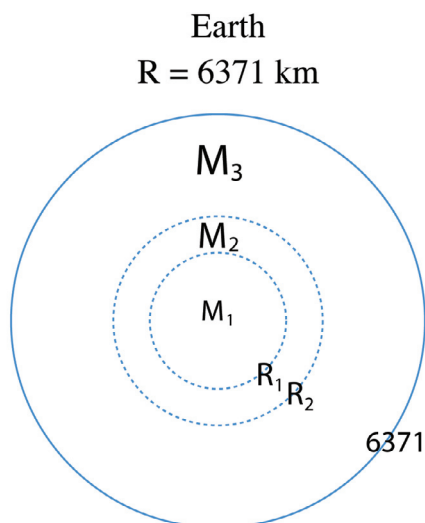


Fig. 1. Imaginary internal structure of Earth during and right after accretion.  $R_1$  is the radius beyond which complete dehydration and decarbonation of the infalling planetesimals and the surface of the growing planets occurred, and  $M_1$  is the mass contained within  $R_1$ .  $R_2$  is the radius beyond which the composition of the growing Earth (except hydrogen) is frozen, and  $M_2$  is the mass retained between  $R_1$  and  $R_2$ . Earth's  $\text{CO}_2$ -dominated proto-atmosphere was derived from mass  $M_3$ . The growing Earth began to be covered by the "magma ocean" at the vicinity of  $R_1$ .

## 2. EVENTS DURING ACCRETION

### 2.1 Dehydration and Decarbonation

After the Earth grew over the size exceeding  $R_1$ , it is conceivable that both dehydration and decarbonation of the primordial planetesimals and the surface of the growing Earth had to take place when infalling materials impacted the growing planet. On the basis of results of shock-wave experiments on various hydrous minerals, Lange and Ahrens (1984) proposed that impact-induced dehydration of Earth began when Earth grew to about 20% of its final radius. Complete dehydration (total loss of  $\text{H}_2\text{O}$  to outer-space) during accretion began at about one-half of the present radius. The radius  $R_1$  shown in Fig. 1 marks the inception of complete dehydration during accretion. Shock-wave experiments on carbonate minerals revealed similar results (see a summary by Liu 2004); decarbonation began at slightly different pressures. Thus, complete decarbonation during accretion would take place at a slightly different value of  $R_1$ .

Both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  would have been released from the materials of Earth's surface and the infalling planetesimals and would have escaped from Earth's gravitational field after Earth grew beyond  $R_1$ ; thereafter, they should have been lost to outer-space. According to Donahue (1986), however, loss of gas (except hydrogen) should occur so slowly from growing planets greater than about  $10^{26}$  g (the equivalent mass of  $M_1 + M_2$  in Fig. 1), that the composition of a growing planet becomes practically frozen except for continuous

growth. Thus, the gravitational force of the growing Earth was strong enough to hold the escaping volatiles to form Earth's proto-atmosphere when Earth grew over the size of  $R_2$ . In other words, Earth's proto-atmosphere had to be derived from volatiles released from materials of  $M_3$ .  $\text{CO}_2$  is heavy, therefore, the proto-atmosphere had to first consist primarily of  $\text{CO}_2$  (see next section for other reasons).

### 2.2 Magma Ocean on the Growing Earth

The idea of Earth being covered by large-scale melting, or the "magma ocean" during accretion has been suggested favorably by Hofmeister (1983) and Abe and Matsui (1985) among others. Matsui and Abe (1986) suggested that the "magma ocean" began when Earth grew to about 40% of its final radius. In other words, before the Earth reached to complete dehydration during accretion, the heat generated by impact force between the infalling planetesimals and the growing Earth was large enough to cause large-scale melting. The complete dehydration during accretion of Earth estimated by Lange and Ahrens (1984) was based on results of a solid-solid impact observed in the laboratory, which should be very different from that of a solid-melt impact. When an impactor hit the "magma ocean" on the growing Earth, instead of producing large quantities of impact-induced dusts and releasing volatiles to outer-space as would be expected in a solid-solid impact, the infalling planetesimals would most likely penetrate deep into "magma ocean" and then release volatiles in silicate melts. Silicate melts are capable of dissolving a large amount of  $\text{H}_2\text{O}$ , but not  $\text{CO}_2$ , at high pressures (Liu 1987, 2009). For example, various silicate melts are capable of dissolving 6 wt%  $\text{H}_2\text{O}$  at 0.3 GPa and the solubility increases with increasing pressure for all silicate melts known (Liu 1987). In other words, once the growing Earth was covered by the "magma ocean," most of the  $\text{H}_2\text{O}$  would be preserved in the melts;  $\text{CO}_2$  was expelled out from the growing Earth which eventually formed Earth's proto-atmosphere. The proto-atmosphere, that formed after the composition became frozen, would envelope the growing Earth and would consist primarily of  $\text{CO}_2$  (This  $\text{CO}_2$  proto-atmosphere is preserved on both Venus and Mars today).

The conclusion that nearly all the  $\text{H}_2\text{O}$  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.

## 3. SOLIDIFICATION AND INDIGENOUS OCEAN

After the completion of accretion, the Earth stopped growing and started to cool down. Soon the "magma ocean"

began to solidify from Earth's surface. The onset of solidification on Earth would not drive out H<sub>2</sub>O from the "magma ocean" to form oceans on Earth's surface. Instead, H<sub>2</sub>O would be entrapped inside the "magma ocean" or a partial melting zone beneath the solid surface, increasing the H<sub>2</sub>O content in the partial melting zone. Then there was another big event happened at this early stage - the giant Moon-forming impact on Earth (Benz et al. 1986, 1987). The giant impact had changed the destiny of Earth and made it very different from its two neighbors, Venus and Mars, today.

It is most likely that the Earth was only partially solidified before its capture of the Moon. The giant impact would have probably evaporated the "magma ocean" and other solid silicates. A large amount of H<sub>2</sub>O, if not all, would have incorporated in the CO<sub>2</sub>-dominated proto-atmosphere to form supercritical H<sub>2</sub>O-CO<sub>2</sub> fluid, whilst the silicates condensed to form the Moon. The supercritical H<sub>2</sub>O-CO<sub>2</sub> fluid was formed due to the relatively high pressure and temperature imposed on the Earth's surface by its proto-atmosphere.

Liu (2004, 2009) has modeled the proto-atmosphere of the Earth after the giant impact as comprised 560 bar of H<sub>2</sub>O (twice the amount in the present oceans) and 100 bar of CO<sub>2</sub> (or some  $5.2 \times 10^{23}$  g). The latter figure appears to be reasonable in terms of the amount of CO<sub>2</sub> stored in near surface carbonates and all known organics ( $\sim 3 \times 10^{23}$  g). Today's Cytherean atmosphere is composed of 96.5% CO<sub>2</sub> that is equivalent to  $4.7 \times 10^{23}$  g of CO<sub>2</sub>. Zahnle et al. (2007) also adopted a hot  $\sim 100$  bar CO<sub>2</sub> proto-atmosphere in their modeling of the Earth's early evolution after the giant impact.

When the Earth cooled down further and the surface temperature reached about 450 - 300°C, either a heavy supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture or a fluid H<sub>2</sub>O-CO<sub>2</sub> mixture in the proto-atmosphere started to precipitate on the surface to form the indigenous ocean (Fig. 2; see also Liu 2004). Thus, the indigenous ocean on the Earth was hot (300 - 450°C) and composed of a heavy supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture, or the "hot soda water."

The scenario of the early growth of the oceans is in general agreement with the geochemical evidence revealed from detrital zircons 4.4 Gyr old (Mojzsis et al. 2001; Wilde 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.

#### 4. ATMOSPHERE-OCEAN-CRUST INTERACTIONS

Once Earth's surface was covered by "hot soda water" or the indigenous ocean, the hot ocean of a supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture would then react rather quickly with the most abundant mineral of the crust, feldspar, to form carbonate and clay minerals at the bottom of the ocean. Plagioclase is a common feldspar species on the Earth's sur-

face. Conversion of plagioclase by ocean-crust interactions produces Ca<sup>2+</sup> and Na<sup>+</sup> (Liu 2004). The former reacted with supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture, forming CaCO<sub>3</sub> and precipitating on the crust. To maintain equilibrium, the removal of CO<sub>2</sub> at the bottom of the ocean would prompt a quick dissolve of CO<sub>2</sub> from the atmosphere to the indigenous ocean. This in turn would effectively remove all the CO<sub>2</sub> from the proto-atmosphere via ocean to the crust. A diminishing of the CO<sub>2</sub> proto-atmosphere from the Earth appears to require the presence of a large quantity of H<sub>2</sub>O which would have formed a supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture at high pressure and high temperature. The continuous removal of CO<sub>2</sub> from the proto-atmosphere would gradually change the composition of Earth's early atmosphere which would consist primarily of H<sub>2</sub>O. H<sub>2</sub>O vapor in the atmosphere would then

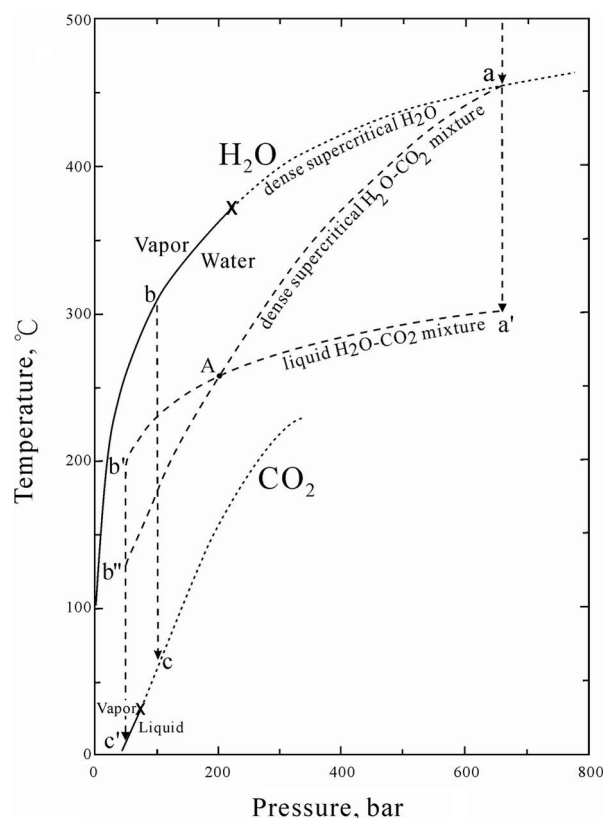


Fig. 2. The vaporization temperature for both H<sub>2</sub>O and CO<sub>2</sub> as a function of pressure (the solid curves). X marks the critical conditions of these materials. The short-dashed lines indicate the pressure-temperature conditions (beyond the critical points) at which the 'dense' supercritical H<sub>2</sub>O and CO<sub>2</sub> exist. The long-dashed lines indicate the possible routes that dense supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture and/or liquid H<sub>2</sub>O-CO<sub>2</sub> mixture may precipitate on the Earth's surface from its proto-atmosphere after accretion. The H<sub>2</sub>O dissolved in the "magma ocean" was then driven out by the giant Moon-forming impact. If supercritical H<sub>2</sub>O and CO<sub>2</sub> were totally inert to each other, dense supercritical H<sub>2</sub>O would precipitate on early Earth along the path a → b, then supercritical CO<sub>2</sub> would condense on early Earth at c. Otherwise, dense supercritical H<sub>2</sub>O-CO<sub>2</sub> mixture would precipitate on Earth along the path a → b' → c', or liquid H<sub>2</sub>O-CO<sub>2</sub> mixture along the path a' → b' → c'.

dissociate into oxygen and hydrogen, and the latter would be lost to outer-space (Liu 2004).

When carbonization reactions (transfer of atmospheric CO<sub>2</sub> to carbonates via the ocean) took place, the ocean was no longer pure water and the CO<sub>2</sub> solubility in aqueous NaCl solution must also be taken into consideration. On the basis of both experimental data and theoretical calculations shown by Duan and Sun (2003), the CO<sub>2</sub> solubility in aqueous NaCl solution decreases with increasing NaCl concentration. In other words, once carbonization reactions occurred in Earth's early life, the rate of carbonization would gradually start to slow down when Na<sup>+</sup> concentration in the ocean started to increase. This effect on CO<sub>2</sub> solubility, however, is relatively small as compared with that of pressure. If the pressure on the surface of the indigenous ocean was around 600 bar, as in Liu's (2004) model, the pressure at the bottom of the ocean may be assumed to be 2000 bar. The calculations of Duan and Sun (2003) showed that the CO<sub>2</sub> solubility in aqueous NaCl solution at the bottom of the indigenous ocean was about double of that on the surface at high temperatures.

The interactions among atmosphere, ocean and crust would exchange not only materials but heat between the different bodies. In addition to heat exchange, the near-complete removal of CO<sub>2</sub> from the Earth's early atmosphere would greatly reduce the greenhouse effect. All these might in turn have helped Earth cool down more rapidly than its neighbor Venus, even if the distances from the Sun of these planets were taken into consideration. No giant-impact ever had happened on Venus and most of its H<sub>2</sub>O is still preserved in the "magma ocean" that was entrapped beneath the solid crust. Venus is deficient in water as observed.

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