# Early planetary atmospheres and surfaces: Origin of the Earth's water, crust and atmosphere

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Abstract. The origin of the planets atmosphere is a profound question of comparative planetology. There are two competing models, i.e. outgassing from the interior or late delivery from comets or volatiles-rich asteroids after most of the planet has been formed, of which the former is currently preferred. Meteorite compositions as well as radial mixing during accretion derived from accretion models suggest that the building blocks of the terrestrial planets contained some volatiles. Processes like dehydration by hydrous melting, oxidation, impact devolatilization, and in particular degassing during magma ocean solidification will then lead to a significant volatile loss of the interior and to the formation of a dense atmosphere during the early stages of planetary evolution. These processes are also responsible for the oxidation state of this early atmosphere, i.e. whether it was more reduced or oxidized. Although this early volatile loss was very efficient, the interior probably retained some water. This was distributed in the subsequent evolution between interior and atmosphere, as well as on the surface as liquid water in case of favorable temperature and pressure conditions. The main processes responsible for the water distribution are volcanic outgassing driven by partial melting of the silicate mantle and formation of the crust and recycling of water-rich crustal material. Here, an important difference between the terrestrial planets is the tectonic style prevailing on the planet. For the Earth with its plate tectonics, recycling of water is very efficient and can even balance the outgassing. For terrestrial planets in the stagnant lid regime of mantle convection such as Mars, the exchange of water between the interior and the surface/atmosphere is mainly in one direction and results in a continuous depletion of the interior. In this talk, I will briefly review our current knowledge on these interactions between interior and atmosphere and on the problem we are facing to better understand the influence of the interior on the habitability of a planet.

Keywords. Earth, planets and satellites: formation, convection, astrobiology

# 1. Introduction

The initial volatile inventory of a planet is acquired from colliding planetesimals, impacting asteroids and comets (e.g., Lunine *et al.* 2003, Brasser 2013). Based on the knowledge of the composition of these building blocks and the accretion scenarios, the initial volatile content for terrestrial planets can be estimated. Water and  $CO_2$  are among the most important greenhouse gases in the atmospheres of terrestrial planets. We will focus in the following on the origin and outgassing of water, although some of the described processes and effects also apply to  $CO_2$  but some are different.

The assumption about the amount of water that accreted on the terrestrial planets varies from almost 0 wt to 5 wt % (e.g., Lunine *et al.* 2003, Raymond *et al.* 2006). Three possible scenarios for the terrestrial planets are shown in Fig. 1. In the first scenario (upper row), the accreting material originates from the region of the solar nebula in

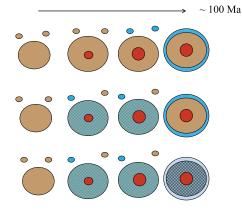


Figure 1. Accretion scenarios which assume a different time of accumulation of volatile-rich material and show the distribution of volatiles between interior and atmosphere. The brownish color represents dry material, bluish color is wet material, red is iron-rich core material, the light blue represents the atmosphere. Further description see in the text.

which the planet is forming. In this region, the inner solar system, the planetsimals are assumed to be dry and form a dry proto-planet. Only after the end of the main accretion phase and core formation, water is brought into the inner solar system by volatile-rich impacting bodies such as carbonaceous chondrites or comets. However, the analysis of the deuterium/hydrogen (D/H) ratio on comets, i.e., water-rich bodies from the Kuiper belt or the Oort cloud, suggests that these objects probably didn't bring water to Earth. Instead, asteroids as the origin for ocean water seem to be more likely (Genda & Ikoma 2008). The late accretion of volatiles after core formation, is also known as the Late Veneer model. The interior of the planets remains mainly 'dry' and an early primordial atmosphere is formed. In the second scenario (middle and lower row), volatilerich bodies accrete much earlier, i.e., while the terrestrial planets are still growing and core formation is not completed. The volatile-rich bodies originate from regions beyond the planets feeding zone, i.e., beyond the snow line where it is cold enough for volatile compounds such as water and carbon dioxide to condense into solid ice grains. Planet formation models show that the exchange between inner and outer solar system is likely but the timing and amount is not well constrained (e.g., Morbidelli et al. 2000).

Even if the water content and the origin of the building blocks were known, the open question remains of how much is lost from the interior due to oxidation, impact devolatilization, and degassing during magma ocean solidification. The second scenario can therefore be subdivided further which differ in the initial amount of volatiles in the planet's interior after planet formation and magma ocean solidification (Fig. 1, middle and lower row). All these early processes tend to strongly dehydrate the planet, leaving the interior dry and producing an early atmosphere - possibly similar to the one of the first scenario but the atmosphere is already formed during accretion not shown in Fig. 1. Please note that this early atmosphere is not a primary atmosphere defined as gas captured gravitationally from the solar nebula. Such a primary atmosphere is mainly made of hydrogen. In principle small planets like Earth could have captured significant primary atmospheres, depending on how long the nebula lasted (Hayashi et al. 1979). Alternatively to efficient and almost complete early outgassing (Fig. 1, middle row), some volatiles remained in the interior and are released during secondary volcanism (Fig. 1, lower row). The timing of volatile loss from the interior in these first  $\sim 100$ Ma (assumed time for accretion and magma ocean solidification in the case of Earth), however, determines the loss of the volatiles from the atmosphere into space because an early atmosphere was particularly unstable due to a high activity of the young sun. The evolution of the atmospheres and especially of the habitable surface conditions may therefore vary depending on how many volatiles remain in the early planet, and/or can degas later but also whether volatiles can be recycled into the interior depending on the tectonic style of a planet.

## 2. Early volatile loss from the planet's interior

During planetary accretion, the interior temperature progressively increases as a consequence of impact heating and the decay of radioactive elements. Before accretion is completed and core formation starts, the temperature can reach the stability fields of the hydrous silicate phases and the H<sub>2</sub>O saturated solidus of mantle material. The latter is significantly reduced by several hundred degrees with respect to dry mantle material (Medard & Grove 2006). Thus, before complete accretion, hydrous phases can be dehydrated and mantle material starts to melt resulting in efficient H<sub>2</sub>O outgassing. A primordial water-rich atmosphere is formed and as water acts as an efficient greenhouse gas, the surface temperature increases (Abe & Matsui 1986). The latter makes it even more difficult for hydrous phases in the accreting material to retain their water. However, as the temperature of an accreting body increases toward the surface, it has been suggested that  $H_2O$  can be preserved in the interior of a planet (Medard & Grove 2006): Material that accreted before the planet reached 55% its final radius does not dehydrate, assuming the temperature distribution derived from the accretion model by Senshu et al. (2002). Water in this deeper region will become unstable with further heating and hydrous phases may transform to nominally anhydrous minerals. Anhydrous minerals in the transition zone of the Earth and in the deep Martian mantle are typically wadsleyite and ringwoodite (Bertka & Fei 1997) that can store up to 2 wt.% water while in the deeper mantle of the Earth, the water storage is assumed to be much smaller (Bolfan-Casanova 2005).

In addition to early dehydration and hydrous melting, oxidation can be very efficient as long as free iron (and other metallic phases) and water is available, i.e., before complete formation of the core. Water delivered after core formation will not bind with free iron and can be sequestered in the silicate portion of the planet. Dreibus & Wänke (1987) argue that for homogeneous accretion, i.e., the dry and the volatilerich components are delivered almost at the same time and before core formation, almost all of the H<sub>2</sub>O added during accretion is converted on reaction with metallic Fe to FeO and H<sub>2</sub>, of which the former remained in the mantle and the latter escaped. The possibility of significant oxidation has been questioned by Rubie *et al.* (2014) who demonstrate that at high temperatures and pressures in terrestrial magma oceans, iron moves into a metallic phase preferentially to the oxidized phase. Thus, in deep magma oceans metallic iron could be stable and water may remain in the liquid magma ocean. Furthermore, iron may sink quickly through any potentially oxidizing magma ocean and aggregate into a core before oxidation can occur.

Water can also be lost by impact devolatilization during accretion. The efficiency of these processes to dehydrate an accreting planetary body increases with the amount of accretional heating, which on the other hand is related to the size of the growing body and the size of the impactor. As a planet grows, the impact velocities increase owing to the increase in radius until first partial and then, at a larger radius, complete devolatilization occurs. Volatiles in minerals are released because of the resulting high temperatures. At what planetary radius devolatilization becomes effective depends also on the hydrated minerals and estimates for complete volatilization range from 1300 km to 2500 km (e.g., Tyburczy *et al.* 2001). However, recent experiments have shown that up to 30% volatiles can be stored in impact melt and in projectile survivors (Daily & Schulz 2018).

With growing size of the planet and of the impactor in the last stage of accretion, the amount of melting increases. In case of large scale melting and the formation of a magma ocean, a substantial part of the water inventory can be outgassed as a consequence of magma ocean solidification (Elkins-Tanton 2008, Lebrun *et al.* 2013). Water enters solidifying minerals in only small quantities and is enriched in magma ocean liquids as solidification proceeds. Water in excess of the saturation capacity of the magma will then degas into the atmosphere when convection transports liquid close enough to the surface as the consequence of the pressure dependent  $H_2O$  solubility in silicate melts (e.g., Burnham 1994). Therefore, the efficiency of outgassing depends on the process of magma ocean crystallization, i.e. how much of the silicate melt was effectively transported toward the surface, how much of the melt was retained in the solidified mantle and when and whether a floating or stable conductive lid formed on top the magma ocean preventing melt to rises to the surface. If magma is transported close to the surface, water will then partition between the atmosphere and the magma ocean liquids according to their equilibrium partial pressures.

A magma ocean would freeze from the bottom (i.e., from the core-mantle boundary, if it comprises the entire mantle) to the surface because of the steeper slope of the mantle adiabat compared to the slope of the solidus (e.g.; Solomatov 2000, Elkins-Tanton et al. 2003). For larger planets like Earth, the situation can be different and crystallization begins in the middle of the mantle, which can also lead to a basal magma ocean that may still exist today (e.g., Labrosse *et al.* 2007). Typically, the forming crystals are denser than the liquid and sink to the bottom of the magma ocean, i.e. fractional crystallization. Water and  $CO_2$  as incompatible elements are continuously enriched in the liquid and degases into the atmosphere. Whether the water contained in the melts is outgassed into the atmosphere or retained in the solidifying melt depends on its solubility in surface lavas at the evolving pressure and temperature conditions of the atmosphere (Gaillard &Scallet 2014), whereby the effect of pressure dominates. The solubility of  $H_2O$  is much larger than that of  $CO_2$  (by more than two orders of magnitude at atmosphere-relevant pressures below 100 bar). Therefore, the outgassing of water can be significantly limited by its high solubility in the melts, while all extracted  $CO_2$  is easily released into the atmosphere. As a result,  $CO_2$  is first outgassed and  $H_2O$  only at the end of magma ocean crystallization when the melt is increasingly enriched. It should be noted though that for a low oxygen fugacity (IW4 to IW+1) in the magma ocean, the equilibria of C-O-H fluids predicts degassing of  $CH_4$ , CO, and  $H_2$  rather than  $CO_2$  and  $H_2O$  (e.g., Holloway & Jakobsson 1986).

In any case, degassing is efficient and most volatiles got lost from the interior (e.g., Elkins-Tanton 2008, Lebrun et al. 2013). Although the formation of an insulating atmosphere can increase substantially the lifetime of a magma ocean (Abe 1997), the entire process of solidification is rapid (Solomatov 2000) and may occur within a few million years (Elkins-Tanton 2008). However, this degassing efficiency may limit the assumptions of the initial magma ocean water inventory. It has been speculated that 0.1 wt%was unlikely because this would imply initial atmosphere pressures of thousands of bars and times related to cooling of clement surface conditions may have lasted hundreds of Myr (Elkins-Tanton 2008). But old zircons in Earth rocks provide compelling evidence that liquid water was in place before 4.2 Ga and probably before 4.3 Ga (Valley et al. 2005). In addition to interior outgassing, magma ocean solidification influences strongly the initial distribution of water and the initial density stratification. As a certain amount is partitioned into the solidifying minerals, an exponential increase of water toward the surface can be expected. In the process of fractional crystallization, the evolving magma ocean liquid is also continuously enriched in iron and therefore Mg-rich cumulates can be found at the CMB and Fe-rich cumulates close to the surface (Elkins-Tanton et al.

#### D. Breuer

2003). This leads to a non-monotonic density increase toward the surface, resulting in a gravitationally unstable configuration and initiating early mantle convection.

As described above, fractional crystallization suggests efficient degassing. A depletion of more than 90% of the initial amount of volatiles has been assumed and even small initial volatile contents (0.05 wt.% H<sub>2</sub>O, 0.01 wt.% CO<sub>2</sub>) can produce atmospheres in excess of 100 bars (Elkins-Tanton 2008). However, fractional crystallization and degassing is disturbed among others by inefficient crystal-melt segregation, i.e., melt in which incompatible elements are enriched can be sequestered in the solid cumulates. The faster the cooling and the slower the compaction, the less efficient is the crystal-melt separation (e.g., Solomatov 2000, Hier-Majumder & Hirschmann 2017). The melt fractions that are trapped in the cumulate pile have been estimated to values of between 1 and 10% (Elkins-Tanton 2008, Hier-Majumder & Hirschmann 2017). Furthermore, if the magma ocean did not comprise the entire mantle, the lower mantle remains primordial and thus more water-rich in comparison to the dehydrated upper mantle due to magma ocean solidification. This means that a substantial amount of volatiles may still be present within planets after this early accretion and differentiation process.

### 3. Secondary volatile loss from the planet's interior

In the subsequent evolution after accretion, core formation and magma ocean crystallization, the amount and distribution of water in the terrestrial mantle is significantly influenced by mantle convection and partial melting of the mantle. Vice versa, water influences the mantle dynamics and melting as the rheology (viscosity) and solidus of mantle rocks strongly depend on water content.

<u>Effect of water on solidus and viscosity</u> The viscosity of mantle rocks is strongly temperature, pressure and water dependent and it is usually assumed that the flow behavior in terrestrial mantles is dominated by olivine. Thus, typically values of activation energy, activation volume and the stress exponent for olivine (e.g., Karato & Wu 1993, Hirth & Kohlstedt 1995) are used to calculate the viscosity. Olivine like the other mantle minerals is a nominally anhydrous minerals and can not store a lot of water. However, the critical water content above which viscosity is significantly reduced is only a few ppm wt.% (Mei & Kohlstedt 2000) and for a water content close to 100 ppm, the viscosity is reduced by a factor of 100 in comparison to a completely dry mantle. Therefore, a few tens of ppm water can be rheologically significant, but the exact value depends on the operating deformation mechanism (e.g., Mei & Kohlstedt 2000). As limiting cases, viscosities of  $10^{19}$  and  $10^{21}$  Pa s at a temperature of 1600 K and a pressure of 3 GPa are generally assumed to represent wet and dry mantle rheologies, respectively. In general, low viscosity suggests vigorous convection and a strong planetary cooling while a high viscosity suggests a more sluggish convection and a slower cooling.

In addition to the influence of water on the rheology, water can significantly reduce the solidus of mantle materials (e.g., Hirschmann 2006). The solidus depression is approximately linear with dissolved water and for instance a bulk water content of 250 ppm (0.025 wt.%) can lower the peridotite solidus by 100 K. It is important to note that in contrast to the effect of water on rheology for which a few tens of ppm water can significantly reduce the viscosity, a water content above 100 ppm is required to notably reduce the mantle solidus (e.g., Green *et al.* 2014).

<u>Interaction between volatiles, partial melting and convection</u> To understand the evolution of volatiles in the planetary interior and its relation to the thermo-chemical and atmospheric evolution of a planet, it is therefore important to study the interaction between volatiles, partial melting, convection and outgassing. It should be noted, however, that in addition to the unknown initial water content, the present content of water in the interior of the planets is also not well known although this knowledge may help constraining potential evolution scenarios. For the Earth, the surface ocean corresponds to  $\sim 300$  ppm water in the interior but the estimates of the present interior water vary between 0.5 and 10 ocean masses (i.e., 150 ppm - 3000 ppm water). We have even less evidence about the amount and distribution of water in other terrestrial planets although there's more and more evidence that planets like Mars and even Mercury aren't completely dry.

Volatiles present in the mantle minerals are transported and mixed by mantle convection. During melting, volatiles are preferentially enriched in the liquid phase. The enrichment depends on the partition coefficient, which is for water about 0.01. Modelling of  $CO_2$  extraction is more complicated by the fact that carbon is not directly soluble in silicate minerals, but occurs in separate phases depending on pressure, temperature, and oxygen fugacity (e.g. Dasgupta & Hirschmann 2010). The partial melt, typically having a lower density than the remaining solid mantle, rises toward the surface and redistributes the volatiles: Erupting material will release essentially all dissolved volatiles into the atmosphere as the solubility of volatiles in magmas at surface pressure is low (Burnham 1994). Volatiles in intrusive material will mostly remain in the crust, although dissolved volatiles may outgas and reach the atmosphere when some crustal porosity is present at the depth of the intrusion (Hirschmann & Withers 2008). In any case, the mantle water concentration decreases due to dehydration by melting, resulting in an increase of the mantle viscosity by several orders of magnitude (e.g., Hirth & Kohlstedt 1995). This effect of dehydration stiffening tends to thicken the upper thermal boundary layer, which then limits melt production, crustal growth, and mantle degassing (Morschhauser et al. 2011).

In general, the water concentration in the interior decreases and the atmospheric pressure increases with time - neglecting volatile loss of the atmosphere. This effect is strongest in the early evolution of stagnant lid planets like Mars, Mercury and possibly Venus, while volcanism is strongest. Furthermore, this effect is strengthen with an increasing water content due to lower melting temperatures and a lower mantle viscosity. The situation is different for Earth with its plate tectonics because crust formation and degassing is longstanding until present at the diverging plate boundaries (mid-ocean ridges) and, most importantly, volatiles can be efficiently recycled into the mantle. Water and  $CO_2$  stored in the subducting plates either in the sediments or in the basaltic oceanic crust can be transported back into the mantle. It has been even speculated that the interior has become volatile-rich over time due to recycling by plate tectonics (Korenaga et al. 2017) - in contrast to the stagnant lid planets. However, this depends on the time of the onset of plate tectonics, which is controversially discussed. It may have started just after magma ocean crystallization or only 2.5 Ga ago (Korenaga 2013). For a late onset of plate tectonics and with an initially dry mantle, the interior would have remained dry for a longer time of the planet's evolution while for an initially wet mantle, the interior would have been dehydrated first. The implication for the early atmosphere and surface conditions is however unclear. Thus, the initial amount of interior water and the onset of plate tectonics seem to be crucial in our understanding of the habitable condition on Earth.

Recycling of volatiles also requires low enough surface temperatures for precipitation (fluid water) and weathering to occur. The evidence for liquid  $H_2O$  on Earth's surface from zircons indicates that these conditions occurred already during the fist few hundred million years (Valley *et al.* 2005). Precipitation will remove  $CO_2$  from the atmosphere, which is then stored due to weathering into carbonates. The interplay between weathering and plate tectonics, known as silicate-carbon cycle, allows stable clement surface conditions in the long-term evolution. This is particularly important in view of the increase in solar flux over time (faint young sun problem) (e.g., Kasting & Catling 2003). For a late

start of plate tectonics, stable surface temperatures must be ensured without recycling of the volatiles.

## 4. Summary and conclusions

According to the discussion above, volatile loss from the interior and earlyatmosphere formation was efficient and took place in several phases. Nevertheless, it is to be expected that terrestrial planets likely started with some amount of water in its interior after its accretion, core differentiation and magma ocean crystallization - although the amount is unknown and can vary from dry to a few hundred ppm of water, it is crucial for the subsequent evolution. The efficient early degassing created a dense primordial,  $H_2O$  and  $CO_2$  rich or a more reducing  $CH_4$ , CO, and  $H_2$  atmosphere. This should not to be confused with a nebular-based proto-atmosphere, which, if existent, has likely been removed by a high EUV flux of the young sun. But also the primordial atmosphere could be lost to space. How much got lost depends on the early sun activity and the planetary mass, i.e. smaller planets such as Mars lost most of not all of their early atmosphere while Earth and Venus may have kept a substantial part (e.g., Tian *et al.* 2009, Lammer *et al.* 2013). Efficient precipitation and weathering has significantly changed the Earth's primordial atmosphere in contrast to Venus with its higher surface temperatures due to its closer proximity to the sun.

Degassing by secondary volcanism helps then to form (Mars) or maintain (Earth) the atmosphere. The atmosphere would otherwise disappear slowly into space due to continuous loss processes by solar activity or by silicate weathering. It is to be speculated that the less efficient the early degassing (i.e. in case of wet initial conditions in the interior) and the more pronounced the secondary volcanism and degassing, the better the habitable conditions of a planet. This is in particular true for a small planet like Mars that loses rapidly its early atmosphere and requires a sufficiently thick atmosphere for clement surface conditions. This probably not the case for planets with a dense primordial atmosphere like Venus' that did not get lost and for which surface temperatures are too high for precipitation due to the greenhouse effect. In the case of the Earth, however, the question arises as to whether an initially volatile-rich mantle was necessary for its habitability, since plate tectonics could have provided the interior with water for later volcanic degassing. But is it possible to initiate plate tectonics with a dry interior or is a wet interior necessary? What if plate tectonics started much later (Korenaga 2013)? Can the mantle have stayed 'dry' for so long and thus contributed little to the atmosphere and surface water and is this consistent with the observations of clement conditions? If this is not the case, it would support the assumption that secondary volcanism and degassing from an initially more volatile-rich interior is important for habitability. Thus, processes that influence the distribution of volatiles between interior and atmosphere - especially in the early planetary phase of accretion and differentiation - need to be investigated more in the future.

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