Anatomy of rocky planets formed by rapid pebble accretion

III. Partitioning of volatiles between core, mantle and atmosphere

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ABSTRACT

Volatile molecules containing hydrogen, carbon and nitrogen atoms are key components of planetary atmospheres. In the pebble accretion model for terrestrial planet formation, these volatile species are accreted during the main planetary formation phase. We model here the partitioning of volatiles within a growing planet and the outgassing to the surface. The core stores more than 90% of the hydrogen and carbon budgets of Earth for realistic values of the partition coefficients of H and C between metal and silicate melts. The magma oceans of Earth and Venus are sufficiently deep to undergo oxidation of ferrous Fe²⁺ to ferric Fe³⁺. This increased oxidation state leads to the outgassing of primarily CO₂ and H₂O from the magma ocean of Earth. In contrast, the oxidation state of Mars’ mantle remains low and the main outgassed hydrogen carrier is H₂. This hydrogen easily escapes the atmosphere due to the XUV irradiation from the young Sun, dragging with it the majority of the CO, CO₂, H₂O and N₂ contents of the atmosphere. A small amount of surface water is maintained on Mars, in agreement with proposed ancient ocean shorelines, assuming a slightly higher mantle oxidation. Nitrogen distributes relatively evenly between the core and the atmosphere due to its extremely low solubility in magma; burial of large reservoirs of nitrogen in the core is thus not possible. The overall low N contents of Earth disagree with the high abundance of N in all chondrite classes and favours volatile delivery by pebble snow. Our model of rapid rocky planet formation by pebble accretion displays broad consistency with the volatile contents of the Sun’s terrestrial planets. The diversity of the terrestrial planets can therefore be used as benchmark cases to calibrate models of extrasolar rocky planets and their atmospheres.

Key words. Earth – meteorites, meteors, meteoroids – planets and satellites: formation – planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: terrestrial planets

1. Introduction

The delivery of volatiles to the terrestrial planets in the Solar System is traditionally ascribed to impacts of primitive, water-rich asteroids that originated beyond the water ice line (Morbidelli et al. 2000, Raymond & Izidoro 2017). In this view, the amounts of volatiles such as carbon, nitrogen and hydrogen are inherently stochastic and could be sourced from a wide range of parent bodies with different isotopic compositions (Marty 2012, Alexander et al. 2012). This gives the possibility to infer the source population of Earth’s volatiles by comparing e.g. the measured D/H ratio of Earth to that of various meteorite groups.

The atmospheres of Venus, Earth and Mars clearly do have very different atmospheric volatile contents today. Venus hosts a dense and massive atmosphere dominated by 86 bar of CO₂ (corresponding to MCO₂ = 4.5 × 10^20 kg or 35% of the total water mass in the Earth’s oceans), likely outgassed from the mantle in periodic, global resurfacing events and subsequently trapped in the atmosphere due to the lack of surface water reservoirs for carbonate formation and reburial of carbon into the mantle (Taylor et al. 2018). The N₂ budget of Venus’ atmosphere is about three times that of Earth’s atmosphere, indicating perhaps the presence of a few ppm of N₂ buried in the mantle of Earth (Marty 2012, Cartigny & Marty 2013, Mysen 2019). Earth, in contrast to Venus, holds much more carbon in the mantle than in the atmosphere (Dasgupta & Hirschmann 2010, Wong et al. 2019), with an estimated range of total carbon mass between M𝑐 ≈ 10^{20} – 10^{21} kg; the lower end corresponds to the Venusian atmosphere reservoir (using the molecular mass ratio mCO₂ ≈ 3.7Mc).

Modern Mars has a very tenuous CO₂ atmosphere with a pressure of just 0.006 bar. Together with the frozen component at the polar ice caps, the total CO₂ reservoir mass of Mars is around MCO₂ ≈ 3 × 10^{16} kg (Kelly et al. 2006), at least three orders of magnitude below the reservoirs inferred for Earth and Venus. Mars likely experienced extensive loss of atmospheric volatiles due to XUV irradiation from the young Sun as well as continuous solar wind stripping (Erkaev et al. 2014, Jakosky et al. 2015, Wordsworth 2016a). The current global equivalent layer of water ice on Mars is estimated to be only 20–40 m in the surface reservoirs, but atmospheric escape calculations (Scheller et al. 2021) and consideration of ancient ocean shore lines (di Achille & Hynes 2010) indicate a primordial reservoir of approximately 500 m of water. This corresponds to a total outgassed water mass in the range MΗ₂Ο = 7 × 10^{19} – 1.6 × 10^{20} kg, or approximately 10% of the Earth’s modern oceans.

At face value, the very different volatile inventories of the terrestrial planets could be interpreted as in agreement with the stochastic volatile delivery model discussed above. However, both atmospheric escape as well as the partitioning of volatiles between the atmosphere, the mantle and the core must have played significant roles in shaping the modern atmospheric reservoirs. For example, the oxidation state of the bulk mantle has a decisive effect on the composition of the atmosphere outgassed from the magma oceans of young terrestrial planets. Earth and Venus are massive enough to have undergone oxidation pro-
cesses where ferrous iron Fe\(^{2+}\) is oxidized to ferric iron Fe\(^{3+}\) at the high pressures in their deep magma oceans (Armstrong et al. 2019; Deng et al. 2020a). This leads to the outgassing of an early atmosphere consisting primarily of CO\(_2\) and H\(_2\)O (Sossi et al. 2020), while the lower oxidation state of the martian mantle would have led to outgassing of huge amounts of H\(_2\) that drove an early, hydrodynamic escape of both H- and C-bearing atmospheric species.

The molecular carriers of H, C and N are either moderately (H\(_2\)O) or highly (CO\(_2\) and N\(_2\)) siderophile, meaning that they partition preferentially into the metal melt during the magma ocean phase of terrestrial planet formation (Li et al. 2020; Fischer et al. 2020; Grewal et al. 2019a). The relatively similar reservoirs of N (at the ∼1 ppm level over the full planetary mass) in the atmospheres of Earth and Venus is intriguing. This level is an stark contrast to some of the most commonly assumed source material for Earth, namely the enstatite chondrites containing 100 ppm of (refractory) N, the carbonaceous chondrites containing up to 1,000 ppm of (volatile) N and the ordinary chondrites containing 1–30 ppm of N (Grewal et al. 2019a). Nitrogen does partition into metal melt (Grewal et al. 2021), but its solubility in magma is very low to begin with (Sossi et al. 2020), so the core must compete with atmospheric outgassing (Speelman et al. 2019). The low contents of nitrogen on Earth and Venus could thus be a smoking gun of pebble accretion, since thermal processing of pebbles in the gas envelope of a growing terrestrial planet will limit the accretion of the most volatiles species to the earliest accretion stages (Johansen et al. 2021).

The goal of this paper is to demonstrate that the volatile inventories of Venus, Earth and Mars can be explained within the single framework of pebble accretion and volatile delivery via pebble snow (Ida et al. 2019; Johansen et al. 2021), without invoking delivery by stochastic impacts. This will allow us to make a quantitative and predictive model for terrestrial planet formation and the compositions of the outgassed atmospheres. Hence, we can use the Solar System to understand also the atmospheres of terrestrial planets and potentially habitable planets around other stars.

The origin of life on the planetary surface is a complex and multifaceted problem. The famous Urey-Miller experiments demonstrated how a reducing atmosphere dominated by molecules such as H\(_2\) and CO exposed to energetic lightning discharges is prone to catalysis of organic molecules (Miller & Urey 1959; Miyakawa et al. 2002). However, as discussed above, the early atmosphere of Earth may have been already oxidizing. Neutral or oxidizing atmospheres synthesize far lower amounts of organic molecules in lightning discharge experiments (Schlesinger & Miller 1983; Cleaves et al. 2008). In contrast, the reducing atmosphere on early Mars could have been more conducive to the origin of life (Deng et al. 2020b; Liu et al. 2021). However, the rapid loss of the martian atmosphere is a challenge to Mars as a cradle of life (Wordsworth 2016a). Nevertheless, impacts of metal-rich asteroids could have created temporary reducing atmospheres on both Earth and Mars until hydrogen escape (Zahnle et al. 2020).

On our own Earth, it has been proposed that life arose in warm little surface ponds that experienced periodic wet-dry cycles leading to the assembly of complex organic molecules and protocells (Da Silva et al. 2015; Hassenkam et al. 2020). In this view, the feedstock organic molecules were delivered to Earth by comets and meteorites (Pearce et al. 2017), with the massive early atmosphere helping to reduce the impact speed and hence the survival of the organic molecules (Chyba & Sagan 1992). Alternatively, life on Earth may have originated in underwater hydrothermal vent systems near mid-ocean ridges (Shock & Schulte 1998; Martin & Russell 2003; Kelley et al. 2005). Understanding the composition and evolution of the early atmospheres of terrestrial planets and their water oceans is under all circumstances a key astrophysical/geochemical deliverable that provides the initial conditions for the prebiotic chemistry that led to the origin of life.

The paper is organized as follows. In Section 2 we describe the modules of the ADAP code dedicated to calculating the escape of the atmospheric constituents after the dissipation of the protoplanetary disc. In Section 3 we discuss the fate of H-bearing and C-bearing molecules and how their carriers depend on the oxidation state of the mantle. In Section 4 we focus instead on nitrogen, since this element is both siderophile (enters the core) and atmophile (outgasses easily from the magma ocean). We show that the thermal processing of nitrogen accreted with pebble snow yields final concentrations that are consistent with Earth and Venus. In Section 5 we summarize the pebble accretion model for planetary accretion and differentiation put forward in Paper I, II and III. Figure 1 shows an overview of the core, mantle, atmosphere and envelope of a rocky planet that grows by our proposed model of rapid pebble accretion.

## 2. ADAP code modules on atmospheric escape

The interior structure and outgassing modules of the ADAP code are described in Paper I and Paper II. Here we describe our approach to atmospheric mass loss after the dissipation of the protoplanetary disc.

### 2.1. Atmospheric escape

We follow Erkaev et al. (2007) and Salz et al. (2016) and define the mass loss rate of the atmosphere as

\[
\dot{M} = \frac{3\beta^2 \mu F_{\text{XUV}}}{4KG\rho_{\text{pla}}}.
\]

(1)

Here \(\beta = R_{\text{XUV}}/R_{\text{pla}}\) parameterizes the effective capture radius of XUV photons \(R_{\text{XUV}}\) relative to the planetary radius \(R_{\text{pla}}\); \(\eta\) is the efficiency of mass loss relative to the energy-limited expression (defined as \(\eta = 1\)), \(F_{\text{XUV}}\) is the energy flux in the XUV range by the young Sun, \(K\) is a parameter of order unity that parameterizes the effect of the stellar gravity on the planetary loss rate and \(\rho_{\text{pla}}\) is the internal mass density of the planet.

We assume for simplicity that the mass loss occurs only through direct acceleration of H atoms and the associated drag by the escaping H on the heavier species C, O and N. The intense radiation environment at the base of the thermosphere is assumed to dissociate all molecules into their constituent atoms (Erkaev et al. 2014). We define from equation (1) an equivalent number loss rate of hydrogen atoms with of mass \(m_{\text{H}}\) as

\[
N_{\text{H}}^+ = \frac{3\beta^2 \eta F_{\text{XUV}}}{4KG\rho_{\text{pla}} m_{\text{H}}} X_{\text{H}}.
\]

(2)

Here \(N_{\text{H}}\) is the total number of atoms of species \(i\) (where \(i\) denotes the atomic species H, C, O and N), \(X_i = n_i/n\) is the mixing ratio of species \(i\) in the thermosphere, with \(n = \sum n_i\) denoting the sum of the number density of all species \(n_i\), taking into account that the water mixing ratio may fall with height due to water cloud condensation (see Paper II). The multiplication by the hydrogen mixing ratio \(X_{\text{H}}\) into the number loss rate in equation (2) reflect the energy lost to heating of species other than H.

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Fig. 1. The figure shows an overview of the core, mantle, atmosphere and envelope of a rocky planet growing by rapid pebble accretion. The protoplanetary disc flows penetrate through the recycled part of the envelope, carrying along water vapour released at the ice line at $T \approx 170$ K back to the protoplanetary disc. The radiative-convective boundary at $T \approx 200$ K marks the transition to a bound, convective envelope. The desiccated pebbles sediment through the convective gas down to the outgassed atmosphere. The atmosphere is in vapour equilibrium with the silicate magma ocean and pebbles therefore survive until they plunge into the magma ocean. Here the metal separates from the silicates and metal blobs coalesce and sediment to the core. There is an equilibrium between the concentration of volatiles H, C and N in the magma ocean and the outgassed atmosphere. The speciation of the volatiles in the atmosphere depends on the oxygen fugacity of the magma ocean, which is set by the iron-wüstite buffer $\text{Fe} + (1/2) \text{O}_2 \rightleftharpoons \text{FeO}$. The lower regions of the magma ocean undergoes additional oxidation by the process $\text{FeO} + (1/4) \text{O}_2 \rightleftharpoons \text{FeO}_{1.5}$. Finally, the volatiles H, C and N are all siderophile and partition primarily into metallic melt over silicate melt. This results in a core that holds the main reservoirs of H and C, while N has so low solubility in magma that the atmosphere is the dominant reservoir of nitrogen.

We thus assume that the absorption of XUV radiation (a) has a similar cross section for H, C, O and N atoms and (b) only leads to escape of H while the heavier species remain bound even after absorption of an XUV photon. These assumptions allow us to make relatively simple calculations of the escape of primordial atmosphere dominated by hydrogen.

All the atmospheric components escape together, driven by drag from the hydrogen atoms but maintaining their initial mixing ratio. We assume that the mixing ratio in the thermosphere is the same as in the bulk atmosphere, neglecting any scale-height differences due to the mean molecular weight. This gives a number loss rate of the mixed species as

$$\dot{N} = \frac{N^*_H}{X_H + X_C(\mu_C/\mu_H) + X_O(\mu_O/\mu_H) + X_N(\mu_N/\mu_H)}.$$  \hspace{1cm} (3)

Here $\mu_i$ is the atomic weight of species $i$. The individual number loss rates can then be written as

$$\dot{N}_i = X_i \dot{N}.$$  \hspace{1cm} (4)

which maintains the mixing ratio $N_i/N = N_i/N_{\text{all}}$ for H, C, O and N. We furthermore need to ensure that the drag from the escaping H atoms is sufficient to accelerate the heavier species to the escape speed. This is seen by calculating the escape parameter

$$\Phi_i = \frac{N_i k_B T_{\text{photo}}}{3 \pi G M_{\text{pl}} \mu_i b_{HI,i}}.$$  \hspace{1cm} (5)

Here $T_{\text{photo}}$ is the temperature at the photosphere and $b_{HI,i}$ is the binary diffusion coefficient of species $i$ dragged by H [Zahnle & Kasting 1986; Erkaev et al. 2014]. We then set $\dot{N}_i = 0$ when $\Phi_i < (\mu_i - \mu_H)/\mu_i$, assuming that the energy transferred from H to the heavier species in that case goes to heating but does not
The terrestrial magma ocean expels approximately one modern ocean mass of water after crystallisation of the magma. The oxidized atmosphere dominant molecule in the atmosphere at the end of the accretion stage; this oxygen is nevertheless dissolved back into the magma ocean as it cools. The oxygen fugacity of the magma ocean rises with increasing temperature and hence $O_2$ partitions within the magma ocean strongly into the metal melt. The core of Earth incorporates after the termination of accretion more than 90% of the total hydrogen and carbon budgets. The onset of the run-away greenhouse effect after 3.5 Myr heats the surface to form a global magma ocean. The water dissolves in the magma and partitions within the magma ocean strongly into the metal melt. The core of Earth incorporates after the termination of accretion more than 90% of the total hydrogen and carbon budgets. The oxygen fugacity of the magma ocean rises with increasing temperature and hence $O_2$ becomes the dominant molecule in the atmosphere at the end of the accretion stage; this oxygen is nevertheless dissolved back into the magma ocean as it cools. The terrestrial magma ocean expels approximately one modern ocean mass of water after crystallisation of the magma. The oxidized atmosphere of Earth avoids any extensive mass loss by XUV irradiation and maintains an atmosphere consisting mainly of $CO_2$ with a mass similar to modern Venus' atmosphere.

lead to escape. This way the H escape flux drives the escape of the heavier species only when the flux is high, while the heavy species ($C$, $N$, $O$) eventually decouple from the H drag for lower flux values. The H flux decreases both because the H mixing ratio of the atmosphere decreases and because the XUV luminosity of the young Sun falls with time. For the capture radius $\beta$ and the efficiency relative to energy-limited escape $\eta$ in equation (2), we follow the parameterizations fitted to computer simulations by Salz et al. (2016). The efficiency flattens out to a relatively constant value of around 30% for the low-mass planets considered here, while the capture radius increases with decreasing planetary mass as the gravitational acceleration decreases, increasing the scale-height of the atmosphere. For the first 100 Myr of solar evolution, we read off a fit to the data of Tu et al. (2015) of

$$L_{XUV} = L_1 (t/\text{Myr})^{-0.75},$$

with the luminosity at 1 Myr set for simplicity to a nominal value of $L_1 = 10^{24}$ J s$^{-1}$. The XUV flux is then calculated as $F_{XUV} = L_{XUV}/(4\pi r^2)$ where $r$ is the distance from the star. The decrease of the luminosity with time becomes steeper after a few hundred 100 Myr of stellar rotation evolution, but we do not include these later stages of atmospheric evolution here.

2.2. Stellar irradiation

The radiative heating of the young planets by the Sun also becomes relevant once the protoplanetary disc has vanished. We assume that the stellar luminosity was 70% of the luminosity of the modern Sun and that the planets had the same albedo as modern-day Venus ($A = 0.77$). This high value of the albedo combined with the faint, young Sun implies that both Earth and Venus condense their water vapour atmospheres into oceans. More complex atmospheric circulation models and realistic albedo values are needed to understand whether Venus started off with a runaway greenhouse atmosphere or whether surface oceans condensed out on early Venus (Way et al. 2016 Turbet et al. 2021).

Fig. 2. The evolution of H-bearing (left panels, including $O_2$) and C-bearing volatiles (right panels) in the atmosphere and surface (top panels) and interior (bottom panels) of our Earth analogue. Hydrogen resides initially in a massive surface layer of ice and water and an interior layer of clay. The water dissolves in the magma and partitions within the magma ocean strongly into the metal melt. The core of Earth incorporates after the termination of accretion more than 90% of the total hydrogen and carbon budgets. The oxygen fugacity of the magma ocean rises with increasing temperature and hence $O_2$ becomes the dominant molecule in the atmosphere at the end of the accretion stage; this oxygen is nevertheless dissolved back into the magma ocean as it cools. The terrestrial magma ocean expels approximately one modern ocean mass of water after crystallisation of the magma. The oxidized atmosphere of Earth avoids any extensive mass loss by XUV irradiation and maintains an atmosphere consisting mainly of $CO_2$ with a mass similar to modern Venus' atmosphere.
Fig. 3. The evolution of the H-bearing and C-bearing volatiles in our Mars analogue. The smaller martian core can only hold 50% of the water, resulting in the outgassing of a massive H$_2$-dominated atmosphere (we show for H$_2$ its equivalent water mass). The dominant H$_2$ component of Mars’ atmosphere undergoes hydrodynamical escape within 70 Myr and drags along with it the entire atmospheric CO, CO$_2$ and H$_2$O contents.

3. Partitioning and loss of H-bearing and C-bearing molecules

We run simulations for model analogues of Earth, Mars and Venus using simple exponential growth rates as in Paper II. Mars and Venus are evolved to their current masses, while Earth grows to only 0.6 $M_E$ within the adopted 5 Myr life-time of the protoplanetary disc. This is because of the later collision with the additional planet Theia, assumed here to have a mass of 0.4 $M_E$, to form the Moon. In Paper II we demonstrated that Theia must have had a mass of at least 0.3 $M_E$ to satisfy the low $^{182}$W abundance in the Earth’s mantle after the collision.

We are particularly interested in understanding the effect of the partition coefficients of H, C and N between metal melt and silicate melt, $D = C_{\text{met}}/C_{\text{sil}}$ with $C_{\text{met}}$ denoting the equilibrium mass concentration in metal melt and $C_{\text{sil}}$ the equilibrium mass concentration in silicate melt. The measured partition coefficients intrinsically depend on both temperature and pressure; additionally they come with large experimental uncertainties. We therefore vary the partition coefficients around a set of chosen nominal values. We choose nominal values $D_H = 5$ (Li et al. 2020), $D_C = 300$ (Fischer et al. 2020) and $D_N = 10$ (Grewal et al. 2019a) and examine how the results depend on varying the partition coefficients around those values, with $D_H$ in the range from 1 to 10, $D_C$ in the range from 1 to 10,000 and $D_N$ in the range from 1 to 100. We study a very large variation in the carbon partition coefficient since the partition coefficient has been determined experimentally to display a parabolic dependence on the pressure, with high partition coefficients at both low ($\sim$Mars) and high ($\sim$Earth) magma ocean pressures (Fischer et al. 2020).

The outgassing of O$_2$ from the magma ocean is key to determining the speciation between H$_2$/H$_2$O and CO/CO$_2$ in the outgassed atmosphere. We choose nominal oxidation states of the mantles of Earth and Venus as IW-2 (where IW denotes the iron-wüstite buffer $\text{Fe} + (1/2) \text{O}_2 \rightleftharpoons \text{FeO}$, see Paper II), while we assume a much more reduced mantle two log-units below the buffer (IW-2) for Mars (Armstrong et al. 2019; Ortenzi et al. 2020). The loss of O by atmospheric escape should lead to a reduction of the oxygen fugacity. We proposed in Paper I that this reduction could be significant for a small body like Vesta. However, planetary-mass bodies have enormous oxygen reservoirs bound as FeO in their mantles. We calculate that Mars would have to lose on the order of 10 Earth oceans and Earth and Venus would have to lose order 100 Earth oceans to affect the total oxygen budget of mantle plus atmosphere. We therefore do not change the oxygen fugacity due to atmospheric loss.

In Figures 2 and 3 we show the evolution of H-bearing, C-bearing species as well as O$_2$ for our Earth and Mars analogues. During the earliest accretion stages, hydrogen resides mainly as water in a massive surface ocean and bound as OH
Mars initially undergoes a similar evolution to Earth, but its lower mantle oxidation state results in the outgassing of large amounts of H₂. The hydrodynamical escape of H drives a catastrophic atmospheric mass loss during the first 70 Myr of stellar activity evolution, leading to the escape of the entire atmosphere (Erkaev et al. 2014). The mantle of Mars stores $(2 \pm 3) \times 10^{16}$ of CO₂, which is approximately equal to the modern CO₂ reservoirs of Mars. The martian mantle also stores H₂ equivalent of approximately 0.1 terrestrial ocean mass if oxidized. However, this hydrogen storage would be degassed as 10% H₂O and 90% H₂ in volcanism and impacts, due to the low oxygen fugacity of the martian mantle. In this picture of early loss of the primordial CO₂ atmosphere followed by a gradual resupply from the mantle, the inferred flow of liquid water on Mars likely took place during short-lived heating events caused by impacts that released large amounts of gases such as H₂ that acted as temporary thermal blanketing (Wordsworth et al. 2017; Deng et al. 2020b).

The partial pressure of oxygen is fixed in our model by the assumption that the magma ocean works as an oxygen buffer with a fixed fugacity (Ortenzi et al. 2020). Hirschmann (2020) proposed that the outgassing and escape of H₂ (or correspondingly, the ingassing of O₂ from thermal destruction of H₂O in the atmosphere) could increase the oxidation state in the martian

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1 The solubility of carbon actually first increases with depth in the magma ocean and then decreases at the pressures below 500 km where diamonds crystallize [Hirschmann 2012; Armstrong et al. 2019]. The overall concentration of carbon (in CO₂ or diamond) is nevertheless dictated at the surface interface and maintained throughout the magma ocean by convection.
mantle and lead to outgassing of more oxidized species. This view nevertheless does not take into account that the oxygen released in the atmosphere could instead undergo atmospheric escape together with the hydrogen and hence maintain the mean planetary oxidation state if the escape occurs at a relative rate of O/H = 0.5.

The adopted value of the partition coefficient of carbon between metal and silicate melt, $D_C$, has key influence on the outgassed atmosphere. In Figure 4, we show the reservoirs of water CO$_2$, H$_2$O and CO in the core, mantle, ocean and atmosphere after 100 Myr of atmospheric evolution. The carbon reservoirs on Earth and Mars are compared directly in Figure 5 as a function of the partition coefficient $D_C$. We show the results for a range of $D_C$ values between 1 and 10,000. The atmosphere of Mars is not much affected by this choice, since the atmosphere is lost under all circumstances. The amount of carbon trapped in the core becomes significant above $D_C = 300$, but 90% of the carbon is lost to atmospheric escape even for large values of $D_C$. The cores of Earth and Venus, in contrast, hold much larger reservoirs of C, unless the $D_C$ value is 10 or lower. Very low values of $D_C$ result in an extremely massive CO$_2$ atmosphere of more than 10 times the modern Venus atmospheric mass.

The surface water reservoir of Mars (in the form of a global ice layer) is only maintained in Figure 4 for the highest value of $D_C = 10000$. This assumption stores the most C in the core and therefore the atmosphere is colder. Some water is thus maintained during atmospheric escape as the thinning atmosphere cools to condense out a global ice layer of approximately 100 m depth. Venus and Earth instead hold approximately one modulus of the dissolved C in the core and the mantle. We mark the accreted CO$_2$ for Earth and Mars as well as the modern CO$_2$ reservoir in Venus’ atmosphere. Lowering the partition coefficient leads to a decreased carbon storage in the core and more outgassing to the surface. The mantle holds negligible carbon in all cases. The escape of the reduced martian atmosphere removes any outgassed CO or CO$_2$ reservoirs from Mars.

The results are shown in Figure 5. The mass of CO$_2$ in the surface, mantle and core reservoirs after 100 Myr of evolution for Earth (filled circles) and Mars (asterisks) as a function of the partition coefficient of carbon between metal melt and silicate melt. The measurement is given for C + O$_2$ to reflect the CO$_2$ equivalent mass of the dissolved C in the core and the mantle. We mark the accreted CO$_2$ for Earth and Mars as well as the modern CO$_2$ reservoir in Venus’ atmosphere. Lowering the partition coefficient leads to a decreased carbon storage in the core and more outgassing to the surface. The mantle holds negligible carbon in all cases. The escape of the reduced martian atmosphere removes any outgassed CO or CO$_2$ reservoirs from Mars.
from the magma ocean as H$_2$O and the total amount of water in the surface reservoir saturates. The best match to Mars’ estimated primordial surface water reservoir comes at an oxygen fugacity slightly above IW − 1. This increase over the nominal value could indicate that Mars’ magma ocean FeO was slightly decoupled from the core material when the atmosphere was outgassed.

4. Nitrogen partitioning

The distribution of nitrogen between the atmosphere and the core is of particular interest for understanding the source material of Earth. The atmosphere of Earth contains approximately 0.5 ppm of nitrogen, normalized by the full mass of the planet. This is in stark contrast to several hundred ppm found in enstatite chondrites and even higher values in the carbonaceous chondrites (Grewal et al. 2019a). Grewal et al. (2021) proposed that large amounts of N are sequestered in the core of Earth. Transport of nitrogen from the mantle to the core is expected due to the strong partitioning of N into the metal melt over the silicate melt. The partition coefficient could be as high as $D_N = 10$ or even $D_N = 100$ for relatively oxidized magma compositions (Grewal et al. 2019a). However, the transport of N from mantle to core has to compete with strong tendency for outgassing of nitrogen into the atmosphere (Speelmanns et al. 2019).

In addressing the nitrogen problem, we first calculate the relative distribution of nitrogen between atmosphere, mantle and core. We assume here that nitrogen constitutes a constant fraction of the accreted material at an (arbitrary) total amount corresponding to the atmospheric inventory of the modern Earth. In Figure 8 we show the fraction of N$_2$ in the different mass reservoirs for our Earth analogue as a function of time for partition coefficients $D_N = 1, 10, 100$. For low values of $D_N$, the majority of the nitrogen ends in the atmosphere, with only a small amount distributed to the core. Even for $D_N = 100$ the core and atmosphere inventories only become about equal; this is due to the low dissolution of N in the magma melt. Hence even large values of $D_N$ do not lead to a substantially higher core reservoir than mantle reservoir. This implies then that no chondrites class, except perhaps the ordinary chondrites, provides the right amount of nitrogen to be reservoirs for Earth formation. This leaves differentiated bodies that experienced extensive N outgassing and loss as a possible source planetesimals for Earth formation (Grewal et al. 2019b). Samples of planetesimals that formed early enough to melt (e.g., Vesta meteorites, ureilites, angrites) nevertheless have isotopic compositions of lithophile elements such as Cr and Ca that disagree with Earth (Schiller et al. 2018; Zhu et al. 2021). In contrast, if Earth formed mainly by accreting pebbles, then the nitrogen depletion can be well understood from the same thermal processing that filtered away water and carbon.

In Johansen et al. (2021) we calculated the final mass fraction of water and carbon for Earth, using source material where the early accretion phase consists of 35% mass of water and 3,000 ppm mass of carbon, while the late-accreted outer Solar System material carries 5% carbon (Alexander et al. 1998). This material is then processed in the hydrostatic hydrogen envelope of the planet, with the accreted water fraction dropping to zero when the envelope acquires a temperature above 160 K and carbon sublimated and pyrolyzed in successive steps from 325 K to 1,100 K (Gail & Trieloff 2017). Here we extend this analysis to nitrogen. We assume that the N contents of the NC reservoir (characteristic of inner Solar System material) is 10 ppm, while the N contents of the CC reservoir (characteristic of outer Solar System material) is 500 ppm. We also plot estimated values of these total reservoirs.

In Figure 9 we show the mass fraction (in ppm) of water, carbon and nitrogen for our Earth analogue as a function of its accreted mass. We overplot the water ocean reservoir on Earth, the carbon atmospheric reservoir of Venus and the nitrogen atmospheric reservoirs of Venus and Earth. Mysen (2019) estimated the mantle reservoir of N on Earth to be twice the atmospheric value. This way the total N contents of Earth correspond well to the total mass of atmospheric N on Venus. The release of the bulk N contents of Venus to its atmosphere could be due to oxidation of the mantle by oxygen left over from the loss of water in the upper atmosphere (Wordsworth 2016b). Since significant amounts of water and carbon may be stored in the cores of Venus and Earth, we also plot estimated values of these total reservoirs.

Figure 9 confirms that the water and carbon reservoirs of Earth fit well with the pebble accretion model. The nitrogen gives an equally good fit. The low nitrogen contents of the NC reservoir (at 10 ppm) combined with thermal processing in the envelope at elevated planetary masses gives a final mass fraction of nitrogen of around 2 ppm. This is in stark contrast to the nitrogen contents of the enstatite chondrites, often considered the source material of Earth (Dauphas 2017). With a little help from the ocean of Earth, the nitrogen contents of the NC reservoir could be raised to 1,100 K (Gail & Trieloff 2017).

In Figure 10 we show the mass fraction of nitrogen for our Earth analogue as a function of its accreted mass. Since significant amounts of water and carbon may be stored in the cores of Venus and Earth, we also plot estimated values of these total reservoirs.

In Johansen et al. (2021) we calculated the final mass fraction of water and carbon for Earth, using source material where the early accretion phase consists of 35% mass of water and 3,000 ppm mass of carbon, while the late-accreted outer Solar System material carries 5% carbon (Alexander et al. 1998). This material is then processed in the hydrostatic hydrogen envelope of the planet, with the accreted water fraction dropping to zero when the envelope acquires a temperature above 160 K and carbon sublimated and pyrolyzed in successive steps from 325 K to 1,100 K (Gail & Trieloff 2017). Here we extend this analysis to nitrogen. We assume that the N contents of the NC reservoir (characteristic of inner Solar System material) is 10 ppm, while the N contents of the CC reservoir (characteristic of outer Solar System material) is 500 ppm. We also plot estimated values of these total reservoirs.

In Figure 9 we show the mass fraction (in ppm) of water, carbon and nitrogen for our Earth analogue as a function of its accreted mass. We overplot the water ocean reservoir on Earth, the carbon atmospheric reservoir of Venus and the nitrogen atmospheric reservoirs of Venus and Earth. Mysen (2019) estimated the mantle reservoir of N on Earth to be twice the atmospheric value. This way the total N contents of Earth correspond well to the total mass of atmospheric N on Venus. The release of the bulk N contents of Venus to its atmosphere could be due to oxidation of the mantle by oxygen left over from the loss of water in the upper atmosphere (Wordsworth 2016b). Since significant amounts of water and carbon may be stored in the cores of Venus and Earth, we also plot estimated values of these total reservoirs.

In addressing the nitrogen problem, we first calculate the relative distribution of nitrogen between atmosphere, mantle and core. We assume here that nitrogen constitutes a constant fraction of the accreted material at an (arbitrary) total amount corresponding to the atmospheric inventory of the modern Earth. In Figure 8 we show the fraction of N$_2$ in the different mass reservoirs for our Earth analogue as a function of time for partition coefficients $D_N = 1, 10, 100$. For low values of $D_N$, the majority of the nitrogen ends in the atmosphere, with only a small amount distributed to the core. Even for $D_N = 100$ the core and atm...
fraction

in the core. Hence it is hard to store significant amounts of N in the core of Earth.

levels (a few percent CC or up to 10% OC) would also deliver

terrestrial planets is a monotonously decreasing function of the

to liquid water. This in turn implies that the core mass fraction of

The mass fraction of water, carbon and nitrogen for the Earth

material instead to ordinary chondrites, using the abundances from

reasonable fits to the noble gas abundance of our planet (Marty

5. Summary of pebble accretion model for terrestrial planet formation

In our three “Anatomy of rocky planets” papers, we have explored a novel model for the formation of terrestrial planets where the solid mass of the planets as well as the volatiles are delivered mainly via pebble accretion (see our overview of the model in Figure[1]). This idea is attractive to explore for three major reasons: (i) observations of protoplanetary discs reveal large populations of mm-cm-sized pebbles – planetary building blocks in the pebble accretion model – around young stars (Zhu et al. 2019), (ii) measurements of the isotopic composition of Earth and the known meteorite classes show that our planet incorporated a large fraction (~40%) mass with the composition of material from the outer Solar System that was likely delivered to our planet via drifting pebbles (Schiller et al. 2018), and (iii) while the pebble accretion was developed in order to explain the rapid formation of the cores of gas giants in the outer Solar System (Ormel & Klahr 2010; Lambrechts & Johansen 2012), the large flux of pebbles drifting through the terrestrial planet region must by extension have played a role in the assembly of terrestrial planets as well (Johansen et al. 2021).

In Paper I we identified the core mass fraction and FeO mantle fraction of terrestrial planets and planetesimals as a direct consequence of the formation of the terrestrial planets by pebble accretion exterior of the water ice line. Water is accreted as ice as long as the envelope is not yet hot enough to sublimate the ice into water vapour that is recycled with hydrodynamical flows back to the protoplanetary disc. Upon melting by the accretion heat, the water oxidizes metallic iron to form magnetite. This oxidized iron in turn becomes unavailable to contribute to the core. We could therefore show that the increasing core mass fraction and decreasing FeO mantle fraction of the Vesta, Mars, Earth triplet is consistent with iron oxidation by early exposure to liquid water. This in turn implies that the core mass fraction of terrestrial planets is a monotonously decreasing function of the
planetary mass, with the extrapolated expectation that massive super-Earths should have a very high core mass fraction if they formed by pebble accretion near the water ice line.

The differentiation of such rapidly formed planets occurs via the continuous release of accretion energy rather than via giant impacts that melt the mantle, as we demonstrated in Paper II. The retention of the pebble accretion heat requires a thermally blanketing atmosphere and here the accreted volatiles play an important role in outgassing an early atmosphere of H₂O and CO₂ that traps the accretion heat. The core of Earth thus forms within the life-time of the protoplanetary disc and this would seem at first glance to be in conflict with the Hf-W dating of core formation, which yields ages in excess of 35 Myr (Kleine & Walker 2017). However, we demonstrated in Paper II that a moon-forming giant impact occurring after 40–60 Myr resets the Hf-W clock and makes the Earth appear younger than its actual bulk core formation time of only 5 Myr after the formation of the Sun.

Thermal processing of pebbles in the envelope of the growing planets is a key difference between the pebble accretion model and the traditional view that volatiles are delivered via planetesimal impacts. Particularly, the terrestrial planets can grow exterior of the ice line without accreting excessive amounts of volatiles (Johansen et al. 2021). Nitrogen appears to be a decisive volatile in this connection. In solid substances, this atom resides mainly in organic molecules in the inner regions of the protoplanetary disc and is hence released successively as the organics sublimate and pyrolyze at increasing temperatures. This way we demonstrated in Paper III that the 10 ppm concentration of nitrogen typical of ordinary chondrite meteorites that formed in the asteroid belt region is reduced to a few ppm by thermal processing, in agreement with the nitrogen reservoirs residing in the atmospheres of Earth and Venus. This contrasts strongly to the several hundred ppm of refractory nitrogen found in enstatite chondrites (Grewal et al. 2019a), often considered a potential source material for Earth (Dauphas 2017).

We demonstrated here in Paper III that the surface water reservoir of Earth as well as the CO₂ contents of Venus' atmosphere are reproduced well in the pebble accretion model using nominal values for the partition coefficients of these volatiles between metal melt and silicate melt. Preventing complete loss of the martian surface water requires a slight increase in the oxygen fugacity of the mantle over the nominal value of IW - 2, indicating perhaps a gradual decoupling of the magma ocean from the metal in the core. The mantles of our model Venus, Earth and Mars also store significant hydrogen that can later be outgassed as H₂ and H₂O, depending on the evolution of the mantle oxygen fugacity with time. The cores of the terrestrial planets hold under all circumstances large reservoirs of H and C that were trapped in the ascending metal droplets during the core-formation stage.

In summary, we believe that we have demonstrated that our pebble accretion model for terrestrial planet formation displays several key consistencies with the observed properties of the terrestrial planets in the Solar System. This in turn implies that these well-studied terrestrial planets can be used as benchmark cases for the testing of a self-consistent planet formation model that can subsequently be applied to predict the properties of the interiors and atmospheres of extrasolar rocky planets as well as the early conditions on the surface when prebiotic chemistry strives towards ever increasing complexity.

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