Does detecting water vapors on rocky planets indicate the presence of oceans?:
An insight from self-consistent mantle degassing models

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ABSTRACT

A sufficient amount of water is required at the surface to develop water oceans, but a significant fraction of water remains in the mantle during magma ocean solidification. Also, mantle degassing during the subsequent period is limited for planets operating under stagnant lid convection. The existence of water oceans is therefore not trivial even for exoplanets located in the habitable zone. To discuss the likelihood of ocean formation, we calculate the rate of mantle degassing during magma ocean and in the subsequent solid-state convection stage. We find that the most important criterion for ocean formation is the H/C ratio of the initial mantle composition, and a threshold ratio increases with planetary size and net stellar radiation. Smaller planets are more likely to develop water oceans because a smaller volume of greenhouse gases are emitted to the atmosphere during magma ocean, and hydrogen escape would hinder ocean formation for planets receiving stronger radiation. Volatile concentrations in the bulk silicate Earth are close to the threshold amount for ocean formation, so even with similar volatile compositions to Earth, all surface water could exist as vapor, and water oceans may be absent when exoplanets are larger or receive stronger stellar radiation compared to Earth. Despite its difficulty in detection, smaller exoplanets located further away from the central star may be a better candidate to search for potential life. Our results also provide a plausible explanation for the divergent evolutionary paths of Earth and Venus.

Keywords: habitability, magma ocean, ocean formation

1. INTRODUCTION

The continuing discovery of extrasolar terrestrial planets has increased the prospect of identifying habitable exoplanets. Earth-size exoplanets are starting to be found at a heliocentric distance where liquid water may be stable (Gillon et al. 2017; Gilbert et al. 2020), and one of the super-Earth size exoplanets identified in the habitable zone, K2-18b, has water vapor detected in its atmosphere (Benneke et al. 2019b; Tsiaras et al. 2019). With the upcoming James Webb Space Telescope, more detections of water vapor are expected on potentially habitable exoplanets (Gardner et al. 2006), and the possible presence of surface water makes such exoplanets a leading candidate to search for biosignatures (Schulze-Makuch et al. 2011; Madhusudhan et al. 2020). Given the importance of surface liquid water, one of the key questions is whether water vapor in the atmosphere does indeed indicate the existence of water oceans on such an exoplanet.

The presence of surface water has often been discussed in terms of the habitable zone (Kasting et al. 1993; Kopparapu et al. 2013; Kodama et al. 2019), which is the region where liquid water is stable at the temperature
and pressure conditions of a planetary surface. The premise, however, is that the amount of surface water is large enough to develop oceans. Although a threshold value to form water oceans is $\sim 10^{-5}$ ocean mass (one ocean mass = $1.4 \times 10^{21}$ kg) for the present-day Earth and thus well exceeds the current ocean mass, the threshold changes with the amount of greenhouse gases and net stellar radiation (Abe 1993a; Salvador et al. 2017). For example, during the early Hadean on Earth, an atmosphere of 100 bar CO$_2$ would have increased this threshold to $\sim$0.1 ocean mass, so it is not guaranteed that the threshold amount of water would always exist on the surface of terrestrial planets. A significant fraction of the water inventory can be retained in the planetary interior, precluding the formation of water oceans.

The initial amount of surface water is determined by volatile partitioning during magma ocean solidification, whereas its subsequent evolution is governed by interaction with mantle convection (Ito et al. 1983; Korenaga et al. 2017). Previous studies have often assumed that the mantle entirely degases during magma ocean solidification (Elkins-Tanton 2008; Lebrun et al. 2013; Salvador et al. 2017), but considering the rheological transition of a partially molten medium and its slow compaction velocity, a significant amount of volatiles could be trapped in the mantle (Hier-Majumder and Hirschmann 2017; Miyazaki and Korenaga 2021). Furthermore, if water oceans are initially absent, the lack of surface water may have persisted for a geological timescale. The presence of surface water is critical in reducing the lithospheric strength and thus in triggering plate tectonics (Korenaga 2007, 2020). Without oceans, the mantle may be in the mode of stagnant lid convection, and mantle upwelling would be suppressed by a rigid lid covering the entire surface (Solomatov 1995). Under such a mode of convection, mantle degassing becomes inefficient, and the amount of surface water could be limited over a substantial period of time.

In this paper, we solve for mantle degassing during and after the solidification of a magma ocean to investigate the likelihood of ocean formation on terrestrial planets. Initial conditions necessary for planets to develop water oceans are explored for various sizes and volatile compositions. Previous studies discussing the impact of mantle degassing on habitability have mostly focused on the solid-state convection stage (Noack et al. 2017; Tosi et al. 2017; Vilella and Kaminski 2017; Dorn et al. 2018), but the atmosphere could be dominated by volatiles degassed during the preceding magma ocean. Moreover, volatile concentrations in the mantle affect viscosity and thus the thermal evolution of planets, so it is crucial to solve for the entire history of mantle degassing self-consistently. It is noted that we assume that planets are in an oxidized condition, and the atmospheric components considered here are limited to H$_2$O and CO$_2$. The redox of the early Earth remains controversial, but recent studies suggest that planets larger than Mars-size would have an oxidized atmosphere (Hirschmann 2012; Deng et al. 2020).

2. DEGASSING DURING MAGMA OCEAN: PRIOR TO THE SOLIDIFICATION OF THE MANTLE SURFACE

We first consider mantle degassing during the early stage of magma ocean solidification. Here the focus is on the aftermath of the final magma ocean produced by giant impacts, which are common in N-body simulations of planetary formation (e.g., Rubie et al. 2015; Quintana et al. 2016). The final one was likely energetic enough to melt most of the mantle (Nakajima and Stevenson 2015), so the atmosphere existing prior to the impact would either have been lost (Genda and Abe 2005) or have re-equilibrated with the magma ocean. The same is likely to be true for larger exoplanets because, with an impactor of 10% target mass, a typical impact velocity is high enough to produce substantial melting of the mantle (Stixrude 2014). Therefore, the final atmospheric mass or composition would not be affected by mantle degassing during earlier magma oceans, and we estimate how the volatile budget after the final giant impact would be distributed between the atmosphere and the mantle.

The solidification of a magma ocean can be divided into two stages by its surface melt fraction (Figure 1). With a high melt fraction at the surface, the magma ocean produces a high convective heat flux, resulting in a surface temperature high enough to maintain a molten surface (Lebrun et al. 2013; Salvador et al. 2017). As the mantle cools down and melt fraction becomes lower than the critical value ($\sim$0.4), however, the partially molten mantle would undergo a rheological transition and start to behave as solid (Abe 1993b). Convective heat flux plummets, and the surface temperature would drop to $<$500 K, which is well below the mantle solidus temperature (Lebrun et al. 2013; Miyazaki and Korenaga 2021). Therefore, the surface layer would be completely solidified in a short timescale once the surface melt fraction reaches the critical value, even though the interior may still be partially molten. Chemical equilibrium between the mantle and the hydrosphere is not maintained thereafter, and volatile exchange between the surface and the interior would instead be characterized by solid-state convection (Abe 1997). In this section, we focus on mantle degassing during the early stage while a partially molten surface is sustained.

2.1. Volatile partitioning
When a magma ocean behaves rheologically as liquid, the atmosphere and the magma ocean are equilibrated in a short timescale, and volatile partitioning between the magma and the atmosphere would determine the atmospheric pressure (Elkins-Tanton 2008; Lebrun et al. 2013). Magma at the surface dissolves volatiles up to their solubility limits, and volatiles in excess of saturation would reside in the atmosphere. We solve for volatile partitioning and mass balance at each time step as the magma ocean undergoes the rheological transition from the bottom upward (e.g., Abe 1993b; Solomatov 2007).

Volatile concentration in the surface magma, $x_i$, corresponds to the solubility at its atmospheric partial pressure, $P_i$, for each volatile species $i$. The solubility measurements of CO$_2$ and H$_2$O are parameterized as follows (Blank and Brooker 1994; Lichtenberg et al. 2021):

$$P_{\text{H}_2\text{O}} = \left( \frac{x_{\text{H}_2\text{O}}}{6.8 \times 10^{-8}} \right)^{1.42},$$

$$P_{\text{CO}_2} = \left( \frac{x_{\text{CO}_2}}{4.4 \times 10^{-12}} \right),$$

where pressure is shown in the unit of Pa. Some models indicate higher solubility for both H$_2$O and CO$_2$ (Papale 1997; Gardner et al. 1999), but we adopt the least soluble model to prepare the most optimistic case for ocean formation. The variables $P_i$ and $x_i$ can be solved using the following mass balance (Bower et al. 2019):

$$\phi x_i M_i + \frac{\mu_i 4\pi r_p^2}{\mathcal{P} g} P_i = m_i,$$

where $\phi$ is the melt fraction at the surface, $M_i$ is the mass of the melt-dominated layer, $\mu_i$ is the molar mass of volatile $i$, $\mathcal{P}$ is the mean molar mass of the atmosphere, $r_p$ is the planetary radius, and $m_i$ is the total mass of volatile $i$ in the atmosphere and the melt-dominated layer (Figure 1a). The surface melt fraction $\phi$ is calculated to be consistent with the depth of the melt-dominated layer (Miyazaki and Korenaga 2019), considering that the magma ocean would have an adiabatic temperature profile as a result of rapid convection.

The volatile mass $m_i$ represents those that were not trapped in the solid-dominated layer existing in the deeper region. Taking into account the rheological transition of a partially molten medium, a significant amount of melt could be trapped in the pore space of the solid matrix, together with volatiles dissolved in the melt (Figure 1b). The percolation of pore melt is slower than the speed of magma ocean solidification (Hier-Majumder and Hirschmann 2017), and a newly formed rheologically-solid layer, which includes volatile-rich pore melt, would be quickly delivered to the deeper region by the Rayleigh-Taylor instability (Maurice et al. 2017; Miyazaki and Korenaga 2019). For parameters used in Miyazaki and Korenaga (2019), the entire lower mantle solidifies in ~4000 years, whereas the timescale for the Rayleigh-Taylor instability is less than a year just after the lower mantle undergoes the rheological transition. Volatiles trapped in the pore space of the solid matrix would thus be effectively sequestered in the deep mantle and be segregated from the remaining melt layer (Figure 1b).

During the instability-triggered downwellling, the melt in the pore space would solidify by adiabatic compression, and the melt would be supersaturated and exsolve volatiles. Yet, the saturation limit would be reached only when melt fraction becomes lower than ~0.002. Here we consider an initial H$_2$O content below 0.1 wt%, and in such a case, concentrating volatiles by 500 times would still not result in exceeding saturation limits (Kawamoto and Holloway 1997). Therefore, the melt-solid mixture would be mostly solidified when volatiles in melt pockets finally start to be degassed, and exsolved volatiles would either diffuse into the surrounding solid phase to form nominally anhydrous minerals or be trapped in the solid matrix as bubbles. We thus assume that volatiles incorporated in the pore space of the solid matrix are kept in the solid-dominated layer, and the corresponding amount is subtracted from the volatiles budget of the melt-dominated layer $m_i$ at each time step.

### 2.2. Degassing of the upper mantle by percolation

Once the entire mantle undergoes the rheological transition and the melt-dominated layer disappears, the evolution of a magma ocean is characterized by solid-state convection. Although percolation is slower than the Rayleigh-Taylor instability, it is faster than solid-state convection (Miyazaki and Korenaga 2021), so melt and dissolved volatiles in the pore space would escape towards the surface (Figure 1c). Volatiles included in the partial melt would be degassed to the hydrosphere, and their amount is proportional to the volume of partially molten layer when the melt-dominated
layer disappears. We calculate its thickness from the adiabatic temperature profile with a critical melt fraction of 0.4 at the surface (see Appendix A.1) (Abe 1993b; Solomatov 2007). The depth of the partial melt layer would depend on the mantle composition after magma ocean solidification, which is likely different from the present-day mantle as a result of differentiation during the solidification process (Elkins-Tanton et al. 2003; Maurice et al. 2017; Miyazaki and Korenaga 2019). Here we assume that the mantle had a heterogeneous structure after the solidification, consisted of Mg-enriched materials containing small-scale iron-rich blobs (Miyazaki and Korenaga 2019), and adopt \( \sim 2 \) GPa as the bottom pressure of the partial melt layer (Miyazaki and Korenaga 2021).

### 2.3. Results

Figure 2 shows a typical evolution of the atmospheric pressure for an Earth-size planet at 1 AU. A fraction of volatiles would be degassed from the beginning to maintain equilibrium with volatiles in the mantle, but further degassing is limited during the early stage of solidification because volatiles are trapped in the pore space of the solid-dominated layer and thus volatile concentrations remain mostly unchanged (Figure 2a). Here we assume initial volatile concentrations of 0.04 and 0.1 wt% for both H\(_2\)O and CO\(_2\), and regardless of the initial concentration, >99% of the total H\(_2\)O budget is estimated to be retained in the mantle during the early stage of magma ocean solidification.
On the other hand, because CO$_2$ is less soluble to silicate magma, $\sim$70% of the total CO$_2$ would be released to the atmosphere (Figure 2a; Hier-Majumder and Hirschmann 2017), and such an atmosphere dominated by CO$_2$ would further suppress the degassing of lighter gases, including H$_2$O (Bower et al. 2019). Degassing resumes when the surface magma starts to solidify as volatiles concentrate in the remaining melt phase (Figure 2b) and a higher atmospheric pressure is required to maintain equilibrium between the atmosphere and the magma ocean. Degassing by percolation would also increase the volatile mass in the atmosphere, yet $\sim$95% of H$_2$O would still be retained in the mantle.

We repeat this calculation for a range of initial volatile content and planetary mass. As expected, the pressure of degassed atmosphere increases with higher initial volatile concentrations, but a larger planetary mass does not necessarily result in a thicker atmosphere; the partial pressure for degassed H$_2$O atmosphere, $p_{H_2O}$, shows little dependence on planetary mass (Figure 3a). This is because the majority of H$_2$O is stored in the mantle, and the water concentration in the mantle changes little from the initial value. Therefore, the corresponding atmospheric pressure in equilibrium with the mantle reservoir is mostly the same regardless of planetary mass. In contrast, most of the CO$_2$ inventory is degassed to the atmosphere, and thus $p_{CO_2}$ becomes higher for larger planets (Figure 3b). The partial pressure is related to the mass of volatile i in the atmosphere, $M_i$, through:

$$p_i = \frac{M_i g r_p}{4 \pi r_p^2 \mu_i} \sim M_i,$$

where $g$ is the gravitational acceleration and $r_p$ is the planetary radius, and the relation between $g$ and $r_p$ is calculated from the simplified interior model of Seager et al. (2007). With the same volatile concentrations, $p_{CO_2}$ increases with planetary mass (Figure 3b), whereas $p_{H_2O}$ remains the same for planets of any size (Figure 3a).

The threshold amount of H$_2$O for ocean formation increases for a thicker atmosphere of CO$_2$ (Abe 1993a; Salvador et al. 2017), so larger planets are less likely to develop water oceans immediately after the solidification of the mantle surface (Figure 3a, 3c). For an initial CO$_2$ concentration of 0.01 wt%, the pressure of total degassed CO$_2$ ($p_{CO_2}$) increases from $\sim$11 bar for a Mars-size planet to $\sim$141 bar for a 5$M_E$ super-Earth (Figure 3b), which would raise the amount of surface H$_2$O required to develop water oceans from $\sim$1.3 to $\sim$21 bar in terms of $p_{H_2O}$ (Figures 3a). Conditions necessary to stabilize oceans are estimated using a 1-D radiative-convective model of Nakajima et al. (1992) (Appendix A.2). The amount of surface water $p_{H_2O}$ does not change with planetary size if the volatile concentrations remain the same, so assuming a H/C mass ratio of 1.02 (0.05 wt% H$_2$O when 0.02 wt% CO$_2$), planets smaller than 2$M_E$ would only have a sufficient amount of water to stabilize water oceans (Figure 3a). How the initial volatile concentration of terrestrial planets is characterized is still debated (Li et al. 2021; Hirschmann et al. 2021), but if terrestrial exoplanets have similar volatile concentrations to Earth, super-Earths larger than 2$M_E$ would not develop water oceans when the surface of the mantle solidifies (Figure 3c). It is noted that when $p_{CO_2}$ is larger than 74 bar, CO$_2$ existing near the surface may be in a supercritical state. The temperature and pressure conditions considered here, however, are distant from its critical point, and thus physical properties including opacity are unlikely to differ considerably from the gas state.

2.4. Discussion: early Earth and early Venus

The amount of volatiles in the bulk silicate Earth (BSE) could have been just above the threshold for stabilizing water oceans at the point of magma ocean solidification. Although the volatile content in the terrestrial mantle remains controversial, recent estimates suggest that the mantle and the hydrosphere in total contain 1.2–3 ocean mass of H$_2$O (Hirschmann and Dasgupta 2009; Korenaga et al. 2017) and 4.8–26×10$^{20}$ kg of CO$_2$, which translates to initial concentrations of 0.04–0.1 wt% and 0.01–0.07 wt%, respectively, in the mantle. The estimated volatile concentrations lie on the boundary between the regimes of ocean formation and dry surface (Figure 3c), and if BSE had a lower-bound H$_2$O and an upper-bound CO$_2$ concentration, water oceans may have been absent during the early stage of evolution. As we discuss in Section 3, the rate of mantle degassing decreases substantially after the mantle surface solidifies, and thus the surface would continue to lack water oceans if oceans are absent at the time of surface solidification. The presence of surface water in the Hadean has been suggested from zircon records (e.g., Wilde et al. 2001; Mojzsis et al. 2001), so water oceans were likely present on the surface of Earth from the beginning of its evolution. Therefore, a combination of a low H$_2$O and a high CO$_2$ concentration in BSE (>0.05 wt%) may be ruled out if water oceans indeed existed on the surface of the Hadean Earth.

The early Venus, on the other hand, may have lacked water oceans because a larger amount of surface H$_2$O is required for planets closer to the central star (Figure 4a). Assuming the same albedo, the net solar radiation for the
Figure 2. The evolution of (a) volatiles in the atmosphere and (b) the thermal state as a function of the melt-dominated layer depth. As solidification proceeds, the layer thickness decreases, so the system evolves from left to right. (a) The ratio of degassed volatiles to the total volatiles budget for H$_2$O (solid) and CO$_2$ (dashed). Initial mantle concentrations of 0.04 wt% (red) and 0.1 wt% (yellow) are tested for both volatiles. For H$_2$O, the two values correspond to 1.2 and 3 ocean masses, respectively. (b) The mantle potential temperature (black solid) and the surface temperature (colored solid, left axis) with the melt fraction of magma ocean at the surface (dashed, right axis). The snapshots of the mantle structure are shown in Figure 1, with triangles indicating the corresponding panels.

early Venus was 330 W m$^{-2}$, which is two times higher than the value for the early Earth. To balance stronger solar radiation, the overall thermal structure, including the planetary surface, becomes hotter, thus allowing more H$_2$O to exist as water vapor in the atmosphere (Nakajima et al. 1992). The minimum amount of H$_2$O to form oceans doubles for a $p_{CO_2}$ of 100 bar and increases by an order of magnitude for $p_{CO_2} < 10$ bar. As a result, for a planet receiving 330 W m$^{-2}$ of stellar radiation, water oceans would be absent for a wider range of initial volatile concentrations. If Venus had similar volatile concentrations to Earth, our result suggests that Venus would develop water oceans only when the total amount of CO$_2$ is less than 9.7 $\times$ 10$^{20}$ kg and the mantle is sufficiently wet (Figure 4b). Because the threshold for ocean formation lies within the estimated volatile concentrations in BSE, the location of planets and thus the amount of net solar radiation may have decided the fate of two similar planets (see Section 3.3 for further discussions). Mars, on the other hand, likely developed water oceans immediately after magma ocean solidification because of its small size (Figure 3c) and its distance from the Sun (Figure 4b).

Volatiles, however, would not be efficiently degassed because the compaction of melt-solid mixture is slow (Hier-Majumder and Hirschmann 2017) and because the Rayleigh-Taylor instability efficiently delivers volatile-rich pore melt to the deeper mantle. Therefore, the remaining melt layer near the surface experiences little change in volatile concentrations, and the mantle is likely to remain hydrated (Section 2.1, Figure 2a).

### 3. Degassing during Solid-State Convection: After the Solidification of the Mantle Surface

Once the surface of the mantle solidifies, mantle degassing during the subsequent evolution would be characterized by solid-state convection (Miyazaki and Korenaga 2021). Although partial melt may still exist in the interior, the planetary surface would be covered by a solidified lid, and the mode of volatile exchange would be similar to what is seen on the present-day Venus and Mars (Noack et al. 2017; Dorn et al. 2018). The solid lid prohibits the mantle and the hydrosphere to reach equilibrium, and instead the evolution of the atmosphere becomes controlled by a balance...
Does detecting water vapors indicate the presence of oceans?

![Diagram](image)

**Figure 3.** (a, b) Atmospheric pressures of (a) H$_2$O and (b) CO$_2$ when the surface of the magma ocean solidified, as a function of the initial volatile concentration. The pressure can be translated to the total amount of degassed volatiles through Equation (4), and the pressure is calculated assuming that all volatiles exist as gas. Colors denote different planetary sizes: Mars- (red), Earth-size ($M_E$, yellow), and 2$M_E$ (green), and 5$M_E$ super-Earths (cyan). The value of $p_{H_2O}$ is similar among planets of different size sizes, and all lines are very close to each other. In (a), the minimum amount of H$_2$O necessary to stabilize water oceans is also plotted, assuming that the H/C mass ratio is 1.02. Mars- and Earth-size planets would have sufficient amount of water to form oceans, whereas super-Earths would lack oceans immediately after the solidification of the mantle surface. (c) Conditions necessary for water ocean formation as a function of initial H$_2$O and CO$_2$ concentrations. Colored lines separate the two regimes: the formation (upper left) and absence of water oceans (lower right) when the mantle surface solidified. With the same volatile concentrations, smaller planets are more likely to develop water oceans. Shaded rectangles represent the estimated volatile concentrations in the bulk silicate Earth (BSE) from Hirschmann and Dasgupta (2009) and Korenaga et al. (2017).
between ingassing to and degassing from the mantle. The rate of ingassing and degassing differs appreciably depending on the mode of solid-state convection, so whether the mantle operates under plate tectonics or stagnant lid convection would control the atmospheric evolution of terrestrial planets. Here, plate tectonics refers to a mode that allows the continuous recycling of the uppermost layer, whereas in stagnant lid convection, a rigid immobile shell covers the surface, and convective motion is limited to the interior region beneath the shell (Solomatov 1995).

The key to triggering plate tectonics is the weakening of oceanic lithosphere (Moresi and Solomatov 1998), and several mechanisms have been proposed, including grain-size reduction (e.g., Kameyama et al. 1997; Bercovici and Ricard 2012) and thermal cracking (Korenaga 2007). Comparison between different mechanisms are discussed in several reviews (Bercovici et al. 2015; Korenaga 2020), but the weakening of the strongest part of the lithosphere requires the reduction of friction coefficient by some means, for which thermal cracking is so far the only mechanism that is consistent with our understanding of rock mechanics. Positive feedback between thermal cracking and serpentinization could potentially hydrate the lithosphere deeply (Korenaga 2017), with trapped water reducing lithostatic-hydrostatic pressure difference and thus effective friction coefficient. The presence of surface water is likely the key to lowering the yield strength of the lithosphere, and although the mechanism is different, the importance of surface water in triggering plate tectonics has been suggested in other studies as well (Regenauer-Lieb et al. 2001; Gerya et al. 2008).

**Figure 4.** (a) The minimum amount of surface \( \text{H}_2\text{O} \) required to form water oceans as a function of \( p_{\text{CO}_2} \). The pressure can be converted to mass using Equation (4), and results are calculated for different levels of net stellar radiation: 73 (dotted, early Mars), 165 (solid, early Earth), and 330 W m\(^{-2} \) (dashed, early Venus). Colors denote different planetary sizes: Earth-size \((M_E, \text{yellow})\) and 5\(M_E\) super-Earth (cyan). (b) The same as Figure 3c but with different levels of net stellar radiation. Colored lines separate the two regimes: the formation (upper left) and absence of water oceans (lower right) when the planetary surface solidified. Planets further away from the central star are more likely to develop water oceans, but planetary size plays a larger role in characterizing ocean formation. Shaded rectangles represent the estimated volatile concentrations in the bulk silicate Earth (BSE) from Hirschmann and Dasgupta (2009) and Korenaga et al. (2017).
Indeed, other oceanless planets, including Venus, Mars, and Moon, are generally considered to be operating under the mode of stagnant lid convection.

The absence of surface water thus leads to stagnant lid convection, which limits both ingassing and outgassing compared to plate tectonics (Kite et al. 2009). Under solid-state convection, the degassing of the mantle is triggered when the mantle material undergoes partial melting during its upwelling (Fraeman and Korenaga 2010; O’Rourke and Korenaga 2012), but a rigid immobile shell would limit the extent of such upwelling motion. With the same convective velocity, the processing of the mantle would be significantly slower for stagnant lid convection than plate tectonics, under which the mantle material is brought up all the way to the surface. Oceanless planets would therefore have a smaller supply of H$_2$O from the mantle than those with oceans, implying that an oceanless state may persist for the geological time.

The lack of surface recycling also prevents the transport of volatiles from the hydrosphere to the mantle, whereas the sequestration of volatiles is possible under plate tectonics (Sleep and Zahnle 2001; Miyazaki and Korenaga 2021). Volatiles, in particular CO$_2$, can be stored in oceanic crust as carbonate minerals (e.g., Alt and Teagle 1999), which could then be delivered to the interior by subduction. The majority of atmospheric CO$_2$ existed after magma ocean solidification on Earth should have been transported to the mantle by the end of Hadean (Catling and Zahnle 2020), and a rapid removal of atmospheric CO$_2$ is also expected for other terrestrial planets with plate tectonics. On the other hand, the removal of atmospheric CO$_2$ would be prohibited for stagnant lid convection, and rather CO$_2$ would continue to accumulate in the atmosphere by mantle degassing. The threshold amount of H$_2$O to develop water oceans thus continues to increase with time for such planets, which would be another factor that further delays the formation of water oceans.

Here, we estimate how long it takes for initially oceanless dry planets to develop water oceans after solid-state convection starts, by modeling the thermal evolution of terrestrial planets. Previous studies discussing habitability in the context of stagnant lid convection have focused on the degassing of CO$_2$ because the availability of greenhouse gas on the surface was considered to regulate the outer edge of the habitable zone (Noack et al. 2017; Tosi et al. 2017; Vilella and Kaminski 2017; Dorn et al. 2018). However, they have not taken into account the massive CO$_2$ atmosphere released during magma ocean (Figure 2a), and with its effect included, the amount of greenhouse effect should not be a limiting factor for habitability for planets with stagnant lid convection. Because the focus of this paper is the formation of water oceans on terrestrial planets, we do not model the evolution after water oceans form, but its impact on habitability is discussed in Section 4.1.

### 3.1. Methods: Mantle degassing under stagnant lid convection

The degassing rate of terrestrial planets that initially lack water oceans is calculated based on a heat flow scaling of stagnant lid convection (Korenaga 2009). This scaling has been applied to the evolution of Mars, Venus, and super-Venus planets (Fraeman and Korenaga 2010; O’Rourke and Korenaga 2012), where they modeled the thermal evolution of crust, mantle, and core self-consistently by incorporating the influence of mantle processing on rheology and radiogenic heating. Our theoretical formulation follows Fraeman and Korenaga (2010) and O’Rourke and Korenaga (2012), and readers are referred to these studies for details. We summarize the key equations of our model in the following, focusing on the difference from previous models.

Our primary goal is to estimate the processing rate of the mantle to track the atmospheric evolution over time: melting by adiabatic decompression generates new crust and depleted mantle lithosphere (DML), and volatiles are degassed during crust formation. A wide range of initial conditions were explored in O’Rourke and Korenaga (2012), but sub-solidus convection likely starts immediately after the surface of the mantle solidifies and degassing by percolation takes place (Section 2.2). We thus adopt the thermal structure and volatile concentrations predicted in Section 2 as initial conditions to model the history of mantle degassing in a self-consistent manner.

#### 3.1.1. Scaling of stagnant lid convection

The vigor of convection is characterized by the Nusselt number: convective heat flux normalized by conductive heat flux. The Nusselt number, $Nu$, is calculated through a local stability analysis of the top thermal boundary layer (Korenaga 2009), and it depends on the following variables: the mantle potential temperature, $T_m$, the temperature difference across the thermal boundary layer, $\Delta T$, the mantle viscosity, $\eta_m$, viscosity increase by dehydration, $\Delta \eta_w$, and the thickness of the depleted lithospheric mantle, $h_{\text{DML}}$. The temperatures $T_m$ and $\Delta T$ are solved from the energy balance of the mantle, and $\eta_m$ is calculated as a function of potential temperature $T_m$ and volatile concentrations in
the mantle (Section 3.1.3). The evolution of $h_{\text{DML}}$ is controlled by the combination of mantle processing, delamination, and rewetting (Section 3.1.2).

DML lacks volatiles, so the layer is more viscous than the source mantle. Thermal convection is suppressed with such effect of dehydration stiffening (van Thienen 2007), and its effect is stronger for a higher mantle potential temperature because of a thicker DML. For a potential temperature of 1600 °C, the thermal boundary layer becomes thicker by a factor of $\sim 5$ than what is predicted in a scaling without dehydration (Korenaga 2009). Therefore, hotter mantle does not indicate more efficient thermal convection, and considering the effect of dehydration stiffening is crucial for estimating $Nu$. The thickness of the thermal boundary layer (TBL) can be calculated as $h_{\text{TBL}} = h_m/Nu$, where $h_m$ is the depth of the convective mantle.

3.1.2. Mantle processing and crust formation

The processing of the mantle is assumed to start at a depth where the temperature exceeds a dry solidus. A wet mantle has a lower solidus temperature (e.g., Kawamoto and Holloway 1997), but the mantle would not be completely dehydrated until the melt fraction becomes sufficiently large, which becomes possible after crossing the dry solidus (e.g., Hirth and Kohlstedt 1996). The initial depth of mantle processing can thus be approximated by the dry solidus, and we parameterize the initial pressure of melting, $P_i$ [GPa], as

$$
P_i = \frac{T_m - 1623 + 200 \times \max(t/500 \text{ Myr}, 1)}{100},
$$

(5)

where the time-dependent term describes a decrease in the solidus temperature as the mantle becomes homogenized. The mixing timescale could be longer than 500 Myr, but it would not have a significant effect on the long-term evolution of surface water. As discussed in Section 2.2, the mantle after magma ocean solidification likely has a heterogeneous structure including mostly consisted of high-Mg# materials (Elkins-Tanton 2008), embedding Fe-rich blobs (Miyazaki and Korenaga 2019). An initially high-Mg# mantle has a higher solidus than a pyrolitic mantle (Miyazaki and Korenaga 2021), but as the two components become homogenized by mantle mixing, the solidus temperature would decrease and approach that of the present day. The melting is assumed to stop where it reaches the base of the thermal boundary layer at $P_f = \rho_L g (h_{\text{TBL}} + h_c)$, where $\rho_L$ is the lithosphere density and $h_c$ is crustal thickness. The thickness of melting zone, $h_p$, can be described as

$$
h_p = \frac{P_i - P_f}{\rho_L g},
$$

(6)

and assuming that downwelling is much more localized than upwelling, the volumetric rate of mantle processing is given by

$$
\dot{V}_{\text{proc}} = \frac{2h_p u_{\text{conv}}}{h_m} 4\pi r_p^2,
$$

(7)

We adopt the scaling of Solomatov and Moresi (2000) for the average convective velocity beneath the stagnant lid:

$$
u_{\text{conv}} = 0.38 \frac{\kappa}{h_m} \left( \frac{Ra}{\theta} \right)^{1/2},
$$

(8)

where $\kappa$ is the thermal diffusivity, $Ra$ is the internal Rayleigh number, and $\theta$ is the Frank-Kamenetskii parameter. Finally, we can calculate the volumetric melt productivity by multiplying $\dot{V}_{\text{proc}}$ by the average melt fraction in the partial melt layer, $\overline{\phi}$, which is estimated based on the melt productivity by adiabatic decompression ($d\phi/dP=0.1$ GPa$^{-1}$). The growth of crust is equivalent to the volumetric melt productivity, and the volume of DML increases by

$$
\dot{V}_{\text{DML}} = (1 - \overline{\phi}) \dot{V}_{\text{proc}}.
$$

(9)

Volatiles included in the processed mantle are released to the mantle, and the rate of degassing is proportional to $\dot{V}_{\text{proc}}$ as well. Volatiles are highly incompatible at the depths where melting occurs, so we consider that the processed mantle becomes entirely dry after melting. It is noted that, in previous studies, some large fraction of volatiles (90 % of volatiles with 10 % melting) was assumed to remain in the depleted mantle after melting (Noack et al. 2017; Dorn et al. 2018), which could underestimate the efficiency of degassing a factor of $\sim 10$. 

Does detecting water vapors indicate the presence of oceans?

Crustal thickness continues to grow by mantle processing, but the thickness of the depleted lithospheric mantle is reduced by delamination or rehydration from the underlying mantle. When the thermal boundary layer is thinner than DML ($h_{DML} > h_{TBL}$), DML would be eroded by convection (Figure 5), so we assume that such a delaminated fraction of DML becomes mixed with the source mantle. Volatile concentrations in the mantle would be diluted as a result of mixing, and we adjust the concentrations accordingly (Fraeman and Korenaga 2010). Also, DML is continuously rewetted by hydrogen diffusion from the underlying mantle. At each time step, a diffusion length $\Delta h_{DML} = \sqrt{D_{diff} \Delta t}$ is calculated, and we assume that the lower $\Delta h_{DML}$ of DML is reincorporated into the source mantle reservoir. The diffusion coefficient is taken from a parameterization given in Korenaga (2009):

$$D_{diff} = 6 \times 10^{-5} \text{m}^2 \text{s}^{-1} \times (-0.0027 + 2.19 \times 10^{-6} (T_m - 273)) .$$

(10)

It is noted that diffusive rewetting is not considered when DML thickness is reduced by delamination.

The initial thicknesses of crust $h_c$ and depleted lithospheric mantle $h_{DML}$ are inherited from the last stage of magma ocean solidification. As discussed in Section 2.2, the uppermost partially molten layer becomes depleted in volatiles through melt escape by percolation when the surface of the mantle solidifies (Figure 1d). The bottom pressure of the initially processed mantle is set to $\sim 2$ GPa, which is equivalent to 65 km for Earth-size planets and 90 km for 5$M_E$ super-Earths.

3.1.3. Mantle rheology

Viscosity, $\eta$, is described as a function of mantle potential temperature, $T_m$, and water content, $c_w$:

$$\eta = \begin{cases} 
A \exp \left( -\frac{E}{RT} \right) \left( \Delta \eta_w \right)^{1-c_w/c_0} & (c_w \leq c_0), \\
A \exp \left( -\frac{E}{RT} \right) \left( \frac{c_0}{c_w} \right) & (c_w > c_0)
\end{cases}$$

(11)

where $E$ is an activation energy (300 kJ mol$^{-1}$) and $R$ is the universal gas constant. Viscosity is assumed to decrease linearly with the water concentration $c_w$ (Mei and Kohlstedt 2000; Jain et al. 2019), but an exponential relation is adopted below a cutoff value, $c_0 = 50$ ppm, to prevent viscosity from reaching infinity. CO$_2$ might also reduce mantle viscosity, but because it is mostly degassed before the solidification of the mantle surface (Figure 2a), its effect is not considered. Viscosity contrast between dry and wet mantle of $c_w = c_0$ is assumed to be $\Delta \eta_w = 125$ (Hirth and Kohlstedt 1996; Mei and Kohlstedt 2000), and we adjust the preexponential constant, $A$, so that viscosity is $10^{19}$ Pa s at 1350 °C and $c_w = 0.04$ wt%. Initial volatile concentrations in the mantle are chosen from Figures 3c and 4b so that water oceans are absent at the beginning of solid-state convection stage.
3.1.4. Thermal evolution of the mantle

The thermal evolution of the convecting mantle is controlled by a balance of radiogenic heating, heating from the core, convective heat flux of the mantle, and latent heat of mantle melting:

$$\rho_m C_m V_{cm} \gamma_m \frac{dT_m}{dt} = \frac{4}{3} \pi (r_m^3 - r_c^3) Q_m + 4\pi \left( r_c^2 F_c - r_m^2 F_m \right) - \rho_L f_m L_m,$$

(12)

where $\rho_m$ is the average density of mantle, $C_m$ is the specific heat of mantle, $V_{cm}$ is the volume of convective mantle, $r_m$ and $r_c$ are the radii of the mantle and core, $Q_m$ is radiogenic heat production per unit volume, and $L_m$ is the latent heat of mantle melting per unit mass. The constant $\gamma_m$ is adopted to convert potential temperature to the average temperature of the mantle. The convective heat flux of the mantle, $F_m$, can be calculated from $Nu$ (Section 3.1.1), and heat flux from the core, $F_c$, is derived using the scaling of Stevenson et al. (1983).

The convecting mantle represents the whole mantle for planets smaller than Earth-size, but the deeper region of super-Earths may be too viscous for convection because its major constituent mineral, post-perovskite, is expected to have viscosity higher by a few orders of magnitude than the terrestrial mantle (Tackley et al. 2013). We thus assume that only the region shallower than $P_{pr}=200$ GPa participates in thermal convection, and the value of $V_{cm}$ is adjusted accordingly. Also, the cooling of the deeper mantle would be inefficient, and heat flux supplied to the convecting mantle would be limited to those derived from core cooling and radiogenic decay (Tackley et al. 2013; Dorn et al. 2018), although core cooling would be much less efficient than the terrestrial mantle. With a viscosity of $10^{24}$ Pa s assumed for the deep mantle, which is $\sim 10^5$ higher than the terrestrial mantle, a local stability analysis of the bottom boundary layer (Stevenson et al. 1983) suggests that core cooling would be suppressed by $\sim 50$ times for super-Earths.

3.2. Results

3.2.1. Evolution of Earth-size planets

Figure 6 shows the thermal evolution and degassing history of a typical Earth-size planet, which illustrates that mantle degassing continues throughout its evolution (Figure 6a). The rate of mantle degassing can be understood from change in the thickness of the depleted lithospheric mantle $h_{DML}$ because mantle processing is reflected in the growth of DML. During the first $\sim 1$ Gyr, the depth where mantle melting starts becomes deeper with time (Figure 6b) as mantle temperature increases by radioactive elements, and also as the solidus temperature decreases as mantle mixing homogenizes heterogeneity created during magma ocean solidification (Equation 5). Therefore, the net growth of DML is observed, resulting in rapid degassing during this period (Figure 6c). In the subsequent stage, however, mantle temperature decreases with time, and the mantle is newly processed only as DML delaminates or is rewetted by hydrogen diffusion. The growth of DML by mantle melting and its delamination by convective erosion are occurring concurrently, and the two competing processes maintain $h_{DML}$ comparable to $h_{TBL}$ (Figure 6a). As a result, degassing is less efficient than in the first 1 Gyr, and its rate further slows down as the mantle cools down and convective velocity decreases (Figure 6c, 6d).

We ran the model for different initial water concentrations, and the results show that, under the same H/C ratio, the timing of water ocean formation is nearly independent of the H$_2$O content ($x_{H_2O}$: Figure 6a). This is a result of two competing processes. Because of a lower viscosity, convective velocity and thus the rate of mantle processing are higher for a wetter mantle: A mantle with a $\times 10$ higher H$_2$O concentration has a $\times 10$ times higher H$_2$O degassing rate. Yet, the amount of surface H$_2$O necessary to stabilize oceans also becomes increasingly larger: An order of magnitude larger CO$_2$ concentration would require a surface H$_2$O amount larger by 40 times (Figure 6c). These two effects nearly cancel out, and thus an oceanless world persists for a similar duration as long as the H/C ratio remains the same. Plate tectonics would operate once the threshold is reached (Korenaga 2020), and mantle degassing would become more efficient afterwards. A wet surface is thus expected to be maintained during the subsequent evolution.

For an Earth-size planet, the atmosphere contains $\sim 3$–$4\%$ of the total H$_2$O budget immediately after the solidification of the mantle surface (Figures 2a), and an additional $\sim 6$–$10\%$ would be degassed in the next 1 Gyr during solid-state convection (Figure 6a). The lower and upper bounds of these estimates, respectively, correspond to initial H$_2$O concentrations of 0.01 and 0.1 wt%. For an H/C mass ratio of 0.45, equivalent to the H$_2$O/CO$_2$ ratio of 1.11, $\sim 8$–$13\%$ of the total H$_2$O budget needs to reside at the surface to stabilize water oceans, and such a condition is satisfied only after 0.5–1 Gyr of evolution (Figure 6a). The threshold ratio increases to $\sim 15$–$24\%$ when the H/C ratio is lowered to 0.27, and the formation of water would be further delayed to $\sim 2.5$–3 Gyr. Because degassing slows down with time,
a planet with a smaller H/C ratio requires a longer duration to form water oceans. The H/C ratio therefore largely characterizes when oceans emerge on terrestrial planets.

We note that a thick depleted lithospheric mantle acts as a limiting factor for heat transport and thus mantle degassing (Figure 7). In a conventional scaling of stagnant lid convection, which does not consider dehydration stiffening, a higher mantle temperature leads to a thinner thermal boundary layer and thus a higher convective heat flux to promote cooling (the case of $\Delta \eta = 1$; Solomatov and Moresi 2000). Assuming such a scaling, the mantle is predicted to be efficiently processed from the beginning, crustal thickness would rapidly grow (Figure 7b), and water oceans would form within the first 100 Myr (Figure 7a). Neglecting dehydration stiffening thus severely overestimates the rate of mantle degassing. In reality, the presence of a dry DML impedes convection, and the thermal boundary layer becomes thicker at higher mantle potential temperatures (Figure 6a, 6c). The Nusselt number $N u$ is inversely proportional to $h_{TBL}$, so a hotter mantle actually results in lower convective heat flux (Korenaga 2009). Because of inefficient cooling, excess radiogenic heat production heats up the mantle during the first $\sim 1.5$ Gyr (Figure 6c), and mantle temperature starts to decrease only after this period. The depth where mantle melting starts then becomes shallower with time, DML thins, and with a weaker influence of dehydration stiffening, $h_{TBL}$ starts to decrease (Figure 6a). A larger viscosity contrast between dry and wet mantle $\Delta \eta_w$ further delays the rate of cooling and degassing (Figure 7c), and thus better constraining the dependence of viscosity on water content would be important to accurately predict the timing of ocean formation. Some experimental studies suggest that the water dependence of mantle viscosity can be more drastic than assumed here (Faul and Jackson 2007).

3.2.2. Evolution of super-Earths

For larger planets, the formation of water oceans is predicted only under a restricted range of initial conditions, and even when oceans are expected to emerge, the formation would take longer than Earth-size planets (Figure 8a). As discussed in Section 2.3, more CO$_2$ is released during the magma ocean stage on larger planets (Figure 3b), so a greater amount of surface H$_2$O is required to stabilize oceans (Figure 3a). Yet, the amount of water residing at the surface is nearly independent of planetary mass at the beginning of the evolution (Figure 3a), and the amount of degassed volatiles during solid-state convection increases little with planetary size (Figure 9). Under the same initial volatile concentrations, larger planets thus may not have a sufficient amount of surface H$_2$O to stabilize oceans.

Larger planets have a higher rate of degassing, but mantle processing ceases earlier during solid-state convection. This is seen in Figure 9a, which compares the evolution of surface water for Earth-size and 5$M_E$ super-Earth planets: the total amount of degassed water increases faster during the first 1–2 Gyr for a 5$M_E$ super-Earth, yet no degassing is observed during the subsequent period. The scaling for mantle processing can be derived from Equation (7):

$$V_{proc} \sim f_m \Delta t \sim \frac{h_p u_{conv} R_a}{h_{cm}} \Delta t,$$

(13)

where $h_{cm}$ is the depth of convecting mantle. The scaling for whole mantle convection ($h_{cm}=h_m$) has been provided in O’Rourke and Korenaga (2012) as $V_{proc} \sim M_p^{0.24} \Delta t$, and a similar scaling for super-Earths can be derived considering the effect of viscous post-perovskite in the deeper mantle: $h_{cm}$ decreases to $P_{ppr}/(\rho_m g)$, and $u_{conv}$ to $R_a^{1/2}/h_{cm} \sim (h_{cm} g)^{1/2} \sim 1$. Using the interior model of Valencia et al. (2006) ($r_p \sim M_p^{0.26}$), $V_{proc}$ follows $r_p^2 \Delta t \sim M_p^{0.52} \Delta t$, and degassing is in general more efficient for larger planets during the first 1 Gyr of continuous degassing (Figure 9). The duration of degassing, $\Delta t$, however, shortens with increasing planetary size. Mantle processing is triggered when the initial depth of melting, $h_i=P_i/(\rho_L g)$, is greater than the base of the thermal boundary layer $h_{TBL}$, but larger planets are less likely to meet such a condition. When super-Earths of different sizes under the same thermal state are considered, the initial depth of melting scales with $g^{-1}$, whereas the thickness of the thermal boundary layer is scaled as

$$h_{TBL} = \frac{h_{cm}}{N u} \sim \frac{h_{cm}}{R_a^{1/3}} \sim g^{-1/3}.$$  (14)

With increasing planetary mass, the initial melting depth becomes shallower at a faster rate than TBL, and triggering mantle processing becomes more difficult. Consequently, mantle processing ceases earlier for larger planets, and even though the rate of mantle degassing is higher during the early stage, the total amount of degassed volatiles throughout their evolution does not change appreciably with planetary size (Figure 9b). We note that the limited processing of the mantle for larger planets is in a broad agreement with previous studies of 2-D mantle convection models (Dorn et al. 2018). A larger fraction of the water budget is thus expected to remain in the mantle for super-Earths without degassing to the surface, precluding the formation of water oceans.

Does detecting water vapors indicate the presence of oceans?
3.3. Discussion: Hydrogen escape and long-term habitability

Hydrogen escape can be important for the timing of ocean formation when the initial H$_2$O concentration in the mantle ($x_{H_2O}$) is small and the planet is close to the star. The efficiency of hydrogen escape depends on the mixing ratio of water vapor at the top of the atmosphere, and diffusion is the rate-controlling process when the mixing ratio is below $\sim 2$–$3\%$, assuming a similar EUV flux to the present-day Sun and a heating efficiency of 30% (Watson et al. 1981). Although the luminosity of younger stars may be higher than the present-day Sun, hydrogen escape from a planet without a significant H/He envelope would continue to be limited by diffusion. A larger EUV flux is thus not expected to enhance the rate of water loss. The 1-D radiative-convective model (Appendix A.2; Nakajima et al. 1992) predicts that the mixing ratio is smaller than 1% for conditions considered in this study (Figure 10), and thus hydrogen escape would be limited by diffusion (e.g., Catling and Kasting 2017, chapter 5). For a $5M_E$ super-Earth with a water vapor mixing ratio of 0.003, the total amount of hydrogen escape during a 1 Gyr period is estimated to be $4.3 \times 10^{19}$ kg,
Figure 7. The same as Figure 6 but for an initial H$_2$O concentration of 0.1 wt% with three different values for viscosity contrast between dry and wet mantle: $\Delta \eta_w = 1$ (green), 12.5 (cyan) and 125 (yellow). A larger viscosity contrast results in slower degassing, and thus an oceanless surface would be maintained for a longer time. The case with $\Delta \eta_w = 1$ does not exhibit any dehydration stiffening, and thus convection and mantle degassing are more efficient than the other two cases, although it is an unrealistic assumption. While depleted lithospheric mantle is actively eroded by thermal convection and its thickness is kept thin, crust grows rapidly to the point that, after 700 Myr, it becomes thick enough to halt mantle processing (shown in (c)). Markers in (a) show the time when a threshold amount of surface H$_2$O is degassed to stabilize water oceans.

which is equivalent to $3.8 \times 10^{20}$ kg of H$_2$O. This amount is comparable to the total amount of degassed water for $x_{H_2O} < 0.04$ wt% (Figure 9a), and thus ocean formation would be delayed, or in some case precluded, compared to what is predicted in Figures 6a and 8a. Diffusion-limited flux is linearly proportional to the mixing ratio, so under a weaker net stellar radiation, the amount of water lost by hydrogen escape is negligible because the atmosphere contains a smaller amount of water vapor (Figure 10b).

We calculate mantle degassing under solid-state convection and estimate the likelihood and timing of ocean formation for various initial volatile concentrations, considering the loss of water by hydrogen escape. With a stronger net stellar radiation and thus a higher water mixing ratio, hydrogen escape becomes significant and prohibits the formation of ocean formation at a small initial H$_2$O concentration ($x_{H_2O}$). On early Venus, for example, if oceans are absent at the time of magma ocean solidification, degassing during solid-state convection does not supply a sufficient amount of water to stabilize oceans, and the surface would lack oceans throughout its evolution under $x_{H_2O} < 0.08$ wt%, equivalent to a total water inventory of $\sim 2.4$ ocean mass (Figure 11a). Although the threshold $x_{H_2O}$ is higher for larger planets (Figure 11d), the general trend remains the same. On the other hand, if $x_{CO_2}$ is small and thus water oceans are formed
from the beginning, the mantle would operate under plate tectonics, and efficient mantle degassing would maintain oceans during the subsequent period. Therefore, for planets receiving $>240 \, \text{W m}^{-2}$ of radiation with a small initial H$_2$O content, whether water oceans exist immediately after magma ocean solidification characterizes the long-term existence of water oceans and thus the habitability of planets (Figure 11).

This could provide an explanation for why Venus and Earth had divergent evolutionary paths: Venus may have continued to lack oceans throughout its history because of the comparable rates of mantle degassing and hydrogen escape, whereas Earth has had water oceans and plate tectonics since the solidification of the mantle surface. The net solar radiation received by early Venus is considered to be close to the tropospheric radiation limit (Hamano et al. 2013), but even if Venus was not in a runaway greenhouse state, water oceans are not guaranteed on early Venus. Limited mantle degassing under stagnant lid convection also implies that the Venusian mantle could still be wet, and that the amount of hydrogen escape and thus its by-product oxygen could be smaller than previously predicted.
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![Graph showing total amount of degassed water over time for different planetary masses with varying initial H$_2$O concentrations.](image)

**Figure 9.** (a) The total amount of degassed water for Earth-size (solid) and $5M_E$ super-Earth planets (dotted) with three different initial H$_2$O concentrations in the mantle $x_{\text{H}_2\text{O}}$: 0.01 (red), 0.04 (yellow), and 0.1 wt% (green). Mantle degassing is faster during the first 1 Gyr but ceases after $\sim$2 Gyr for a $5M_E$ super-Earth. (b) The amount of degassed water for different planetary sizes with H$_2$O concentrations of 0.01 (red) and 0.04 wt% (yellow). The bars show the amount of degassed water during three different periods: before the solidification of a magma ocean (gray), before 1 Gyr (light red/yellow) and 5 Gyr of solid-state convection (dark red/yellow). The minimum amount of surface H$_2$O for ocean formation is also plotted for initial CO$_2$ concentrations $x_{\text{CO}_2}$ of 0.02 (black), 0.04 (dark gray), and 0.07 wt% (light gray).

Such a small amount of oxygen could be consumed by the oxidation of surface rocks without invoking other removal mechanisms (e.g., Kurosawa 2015).

Hydrogen escape has little influence on ocean formation when the stellar radiation is weaker and/or a mantle contains a greater amount of H$_2$O (Figure 11c, 11f). In such cases, planets with the same H/C ratio would develop water oceans on a similar timescale regardless of the absolute value of initial H$_2$O concentrations as discussed in Section 3.2.1. For planets resembling early-Earth, oceans would exist from the beginning for H/C > 0.69, and the formation timescale becomes increasingly longer as the H/C ratio decreases because degassing slows down as the mantle cools (Figures 6c, 8c; Section 3.2.2). Degassing eventually discontinues, and thus the surface would never acquire a sufficient amount of water to stabilize oceans for H/C ratios lower than 0.16. Such threshold H/C ratios for ocean formation increase.
Figure 10. The mixing ratio of H$_2$O vapor at the top of the atmosphere as a function of (a) the initial CO$_2$ concentration in the mantle and (b) as of net stellar radiation. A planet with water oceans is assumed, and an oceanless one would have a smaller mixing ratio than shown here. Colors indicate planetary mass: Earth-size (red), 2$M_E$ (yellow), and 5$M_E$ super-Earth (green). (a) Solid and dashed lines represent net stellar radiation of 330 and 165 W m$^{-2}$, respectively. Dotted gray line describes a critical ratio above which hydrogen escape is limited by the magnitude of EUV flux, and for the range of stellar radiation considered here, hydrogen escape is limited by diffusion. (b) An atmosphere containing 1 bar of N$_2$ and 100 bar of CO$_2$ is assumed here. Water loss by diffusion-limited hydrogen escape is estimated for an Earth-size planet using a binary diffusion coefficient of $b_{H_2}=1.46 \times 10^{21}$ m$^{-1}$ s$^{-1}$ (Catling and Kasting 2017, chapter 5).

with planetary mass and net stellar radiation. A 5$M_E$ super-Earth receiving the same radiation as early Earth would not develop oceans for H/C<0.37 (Figure 11f), and its threshold increases to ~0.7 if the planet is located at the orbit of early Venus (Figure 11d). These values are within the estimate for the bulk silicate Earth (0.99 ± 0.42; Hirschmann and Dasgupta 2009), so if terrestrial exoplanets have similar volatile concentrations to Earth, the presence of water oceans is not guaranteed, especially for super-Earths. Planets may have a different fate with a slight difference in their volatile concentrations, and the habitability of planets would depend largely on their size and the H/C ratio of the mantle, in addition to the distance from the central star.

4. DISCUSSION AND CONCLUSIONS

4.1. Plate tectonics and the removal of thick CO$_2$ atmosphere
Does detecting water vapors indicate the presence of oceans?

Plate tectonics maintains a habitable atmospheric composition over geological time (Berner 2004), so the presence of surface water, a key to plate tectonics, is crucial for the long-term habitability of the planet. Its role is particularly important during the early stage of evolution because the majority of the CO₂ budget is degassed during magma ocean solidification. When $p_{\text{CO}_2} > 100$ bar, its greenhouse effect would maintain a surface temperature over 100 °C (Abe and Matsui 1988; Abe 1993a), which may prevent life forms similar to those existed on Earth from evolving. The removal of such a thick CO₂ atmosphere likely requires rapid plate motion (Sleep and Zahnle 2001; Miyazaki and Korenaga 2021), so although this study has focused on the formation of water oceans, stabilizing water oceans is only one of the requirements for creating a habitable environment.

The efficiency of CO₂ removal from the atmosphere depends on plate velocity, and when the mantle has a pyrolitic composition, plate velocity could be slower for a hotter mantle than in the present-day (Korenaga 2006, 2010). Miyazaki and Korenaga (2021) suggests that a chemically heterogeneous mantle resulting from magma oceans solidification would develop a thinner depleted lithospheric mantle and thus allows faster plate velocity than a pyrolitic mantle. Whether such chemical differentiation occurs in a magma ocean can be a critical factor in developing a habitable environment, although it depends on several unconstrained physical properties and is subjected to debate (Solomatov and Stevenson 1993; Solomatov et al. 1993; Xie et al. 2020).

Plate velocity also depends strongly on the degree of mantle hydration (Korenaga 2010), and the idea of a wet mantle after magma ocean solidification is also consistent with the removal of the thick CO₂ atmosphere. The previous models of magma ocean degassing have often assumed that the mantle would be entirely dehydrated during solidification (Elkins-Tanton 2008; Hamano et al. 2013; Lebrun et al. 2013; Salvador et al. 2017), but a dry mantle would have a slower plate motion than in the present-day, despite the hotter mantle temperature in the past (Korenaga 2006). If so, the removal of CO₂ over $>100$ bar would become highly inefficient (Miyazaki and Korenaga 2021), which fails to explain the emergence of the moderate climate by the early Archean. The wet mantle and thus rapid plate motion also agree with recent geochemical modeling, which suggests the efficient recycling of the surface material in the Hadean (Rosas and Korenaga 2018; Hyung and Jacobsen 2020). Studies on magma ocean have often suffered from a lack of

![Figure 11](image-url) Contours showing the timing of ocean formation for Earth-size (top) and 5$M_E$ super-Earth planets (bottom). Results are calculated for three different levels of net stellar radiation: 330 (left), 240 (middle), and 165 W m⁻² (right). Water oceans form immediately after magma ocean solidification and exist throughout the evolution of planets in regions left of black lines, whereas oceans would be absent for longer than 10 Gyr under conditions shaded in light gray. Rectangles represent the estimated volatile concentrations in the bulk silicate Earth (BSE) from Hirschmann and Dasgupta (2009) and Korenaga et al. (2017). Lines indicating a H/C ratio of 0.16 and 0.69 are shown as a reference in (c) and (d), respectively.
observational constraints, but we may be able to obtain new insights into this period by taking into account the aftermath of a magma ocean.

4.2. Conclusions

We estimated the likelihood of ocean formation and its timing for planets with various volatile concentrations by solving for the evolution of mantle degassing during and after magma ocean solidification. Considering the rheological transition of a partially molten medium, magma ocean is predicted to retain a significant fraction of the H$_2$O inventory, whereas CO$_2$, which is less soluble to magma, would mostly reside in the atmosphere after the solidification. When the H/C ratio is lower than a threshold, surface water exists entirely as water vapor as a result of a strong greenhouse effect, and water oceans would be absent on the surface. Larger planets are less likely to develop water oceans because more greenhouse gases are emitted to the atmosphere during the solidification process.

If water oceans do not form at the beginning of solid-state convection, planets would operate under stagnant lid convection, severely limiting mantle degassing during the subsequent evolution. The rate of mantle degassing decreases and eventually reaches zero as the mantle cools and the thermal boundary layer grows, so the majority of H$_2$O is expected to be retained in the mantle throughout its evolution. The total amount of degassed water is nearly independent of planetary mass under the same volatile concentrations, but because a CO$_2$ atmosphere is thicker and thus a larger amount of surface water is necessary to form oceans for larger planets, the threshold H/C ratio for ocean formation increases with planetary size. The threshold also increases with net stellar radiation as a larger amount of water vapor is contained in the atmosphere. In addition, water loss by hydrogen escape may preclude ocean formation for planets receiving strong radiation and containing a small amount of H$_2$O. These would not be the case once water oceans form at the surface because the mode of mantle convection would likely change to plate tectonics, promoting mantle degassing during the subsequent evolution.

If the volatile contents of rocky exoplanets are similar to those of the bulk silicate Earth, mantle degassing during magma ocean would not supply a sufficient amount of H$_2$O when planets are larger and/or receive stronger radiation than Earth. Exoplanets could be richer in volatiles than Earth, and indeed, exoplanets of larger size are known to have an atmosphere of smaller metallicity (Benneke et al. 2019a). Yet, the redox evolution of rocky planets is not well understood, and if hydrogen existed in a reduced form, a high H/C ratio may not necessarily result in the formation of water oceans. An increasing number of observations for the exoplanet atmosphere is expected with upcoming missions, but the detection of water vapor does not necessarily indicate the presence of water oceans. In addition to the habitable zone, planetary mass and the H$_2$O/CO$_2$ ratio are also important parameters in predicting the likelihood of oceans on exoplanets. Because the threshold H/C ratio for ocean formation is lower for smaller planets receiving weaker radiation, such planets are a more promising candidate to search for potential life, although they may be more difficult to detect and observe the atmosphere.

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APPENDIX

A. METHOD DETAILS

A.1. The initial thickness of depleted lithospheric mantle

The initial thickness of depleted lithospheric mantle (Figure 5) is calculated by drawing an adiabatic temperature profile with a temperature that creates melt fraction of 0.4 at the surface. This is because the timescale for the Rayleigh-Taylor instability is predicted to be faster than the rate of solidification (Maurice et al. 2017; Miyazaki and Korenaga
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2019), and thus the upper mantle likely has an adiabatic thermal gradient when the surface of the mantle solidifies. The adiabatic gradient is expressed as (Mckenzie 1984):

$$ \left( \frac{dT}{dP} \right)_S = \phi \frac{\alpha T}{\rho l c_p, l} + (1 - \phi) \frac{\alpha_s T}{\rho_s c_p, s} - \frac{T \Delta S}{c_p} \left( \frac{d\phi}{dP} \right)_S, \quad (A1) $$

where $\alpha$ is thermal expansivity, $\rho$ is density, $c_p$ is specific heat per unit mass, and $\Delta S$ is entropy change upon melting. Subscripts $l$ and $s$ denote the melt and liquid phases, respectively. Values adopted for thermal expansivity are $3.0$ and $4.6 \times 10^{-5} \text{K}^{-1}$ for $\alpha_s$ and $\alpha_l$, and, for density, $\rho_l$ and $\rho_s$ are taken to be $2900$ and $3300 \text{kg m}^{-3}$, respectively. We adopt $1000 \text{J kg}^{-1} \text{K}^{-1}$ for $c_p$ and $300 \text{J kg}^{-1} \text{K}^{-1}$ for $\Delta S$. Melt fraction at a given temperature and pressure is calculated using a thermodynamic model of Katz et al. (2003), and the term $d\phi/dP$ in Equation (A1) is calculated so that changes in $T$ and $\phi$ are consistent with thermodynamics (see Supplementary of Miyazaki and Korenaga (2021) for details).

A.2. Atmospheric model

The surface temperature and the total amount water vapor in the atmosphere are estimated using a 1-D radiative-convective model by Nakajima et al. (1992). We consider two layers within the atmosphere: stratosphere and troposphere, where the temperature is controlled by different heat transport mechanisms. Whereas radiative equilibrium governs the stratosphere, the thermal structure in the troposphere is characterized by convective heat transport from the bottom. The atmosphere is assumed to be plane-parallel and is transparent to stellar radiation, but opaque to infrared radiation regardless of the wavelength. Although this assumption of gray atmosphere may underestimate the surface temperature during the earlier stage of magma ocean, the calculated temperatures are similar for the gray and nongray cases for surface temperatures below $200 \text{ °C}$ (Salvador et al. 2017). For simplicity, the effects of clouds are neglected in our model.

The thermal profile of the stratosphere can be written as a function of optical thickness, $\tau$:

$$ \sigma_B T(\tau)^4 = \frac{1}{2} F_{net} \left( \frac{3}{2} \tau + 1 \right), \quad (A2) $$

where $\sigma_B$ is the Stefan-Boltzmann constant and $F_{net}$ is the net infrared flux emitted from the top of the atmosphere. Upward, $F_\uparrow$, and downward radiation fluxes, $F_\downarrow$, are also calculated as

$$ F_\uparrow(\tau) = \frac{1}{2} F_{net} \left( \frac{3}{2} \tau + 2 \right), \quad (A3) $$
$$ F_\downarrow(\tau) = \frac{1}{2} F_{net} \left( \frac{3}{2} \tau \right). \quad (A4) $$

Optical thickness $\tau$ is defined so that it increases towards the Earth’s surface:

$$ \tau(z) = - \int_{\infty}^{z} \kappa \rho_g dz, \quad (A5) $$

where $\kappa$ denotes the Rosseland mean opacity. Opacity $\kappa$ depends on the atmospheric concentrations of greenhouse gases, and for the atmosphere which has a molar fraction of $x_i$ of gas species $i$, $\kappa$ is given by

$$ \kappa = \frac{1}{\mu} \sum_i \kappa_i x_i \mu_i, \quad (A6) $$

where $\mu$ is the mean molar mass of gas, $\kappa_i$ and $\mu_i$ are the Rosseland mean opacity and molar mass, respectively, of species $i$. For opacity, we use $10^{-2}$ for $\text{H}_2\text{O}$, $1.3 \times 10^{-4}$ for $\text{CO}_2$ (Abe and Matsui 1985), and 0 for $\text{N}_2$, assuming $\text{N}_2$ is transparent to infrared radiation. The composition of the atmosphere is assumed to be uniform in the stratosphere.

In the troposphere, the thermal structure is controlled by the moist adiabatic lapse rate, which is described as

$$ \left( \frac{dT}{dP} \right) = \frac{\mu}{\rho_g C_p} \frac{1 + qL}{1 + qL^2}, \quad (A7) $$
where $\rho_g$ is the mean gas density, $C_p$ is heat capacity, $q$ is water mixing ratio, and $L$ is the latent heat of the water. Water mixing ratio $q$ is set to be saturated, which is likely in a CO$_2$ dominated atmosphere, and is obtained from the water phase diagram.

The tropopause, a boundary between the stratosphere and troposphere, is determined as a height that the radiation energy is balanced. The upward radiation flux emitted from the troposphere can be calculated as

$$F_{\uparrow}(\tau) = -\sigma B T^4 + \int_{\tau_b}^{\tau} e^{-(\tau' - \tau)} \frac{d}{d\tau'} \left( \sigma B T(\tau')^4 \right) d\tau',$$

where $\tau_b$ is the optical depth at the bottom of the atmosphere. We assume that the upward flux at the ground is the blackbody radiation of the ground temperature ($F_{\uparrow,\text{surf}} = -\sigma B T_{\text{surf}}^4$). At the optical depth of the tropopause, $\tau_p$, the values of $F_{\uparrow}(\tau_p)$ calculated from Equations (A3) and (A8) should be identical to satisfy the energy balance. We search for the profiles of temperature and water vapor content that agree with energy conservation. The temperature and the water vapor mixing ratio are smoothly connected at the tropopause.

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