Partitioning of Atmospheric $O_2$ into High-pressure Ice in Ocean Worlds

A. Levi © and D. Sasselov ©
Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA; amitlev.planetphys@gmail.com
Received 2021 July 16; revised 2021 December 7; accepted 2021 December 17; published 2022 February 15

Abstract

Planets with a few percent water by mass may have a high-pressure ice mantle separating the rocky interior from both the ocean and atmosphere. Here we examine whether the partitioning of $O_2$ into high-pressure ice can constrain the atmospheric abundance of $O_2$ produced by water photolysis in the atmosphere. We find that the partition coefficient of dissolved $O_2$ between high-pressure ice and liquid water is about unity. We show that the solubility of $O_2$ in high-pressure water ice yields an upper value for the atmospheric abundance of $O_2$ that depends on the ocean surface temperature. The atmospheric pressure of $O_2$ has a maximum of approximately 3000 bars. The latter drops to a few hundred bars as the surface temperature of the ocean approaches supercritical conditions.

1. Introduction

It is known that life maintains $O_2$ in Earth’s atmosphere (Lyons et al. 2014). However, exoplanetary atmospheres may accrue $O_2$ abiotically by oceanic evaporation and water photolysis in the upper atmosphere (Wordsworth & Pierrehumbert 2014). For planets orbiting M dwarf stars, known to be superluminous in their pre-main-sequence phase, abiotic production of $O_2$ may be highly efficient. In this case, planets that spend considerable time inward of the habitable zone may build up thousands of bars of $O_2$ in their atmosphere if their water content is up to approximately 10 times Earth’s ocean (e.g., Luger & Barnes 2015; Lincowski et al. 2018). Likely sinks for atmospheric $O_2$, suggested in the literature, include oxidation and recycling of the planetary rocky surface, for example, oxidation of FeO in the case of a magma ocean (Schaefer et al. 2016). If that is the case, it is highly intriguing to put to the test a common hypothesis that, in water worlds, a high-pressure water-ice layer overlying the rocky interior would render any internal sink of abiogenic atmospheric $O_2$ unlikely. In Figure 1, a cross section of the planetary case examined in this work is presented.

Water worlds may have substantial water mass fractions and are likely very common in our galaxy around Sun-like stars (Zeng et al. 2019). Alibert & Benz (2017) predicted, using planetary formation models, that water worlds should readily form around low-mass stars as well. Possible examples exist within the TRAPPIST-1 system (Gillon et al. 2017). In terms of planetary composition, a water mass fraction of the order of a few percent may suffice, pressure-wise, to form a high-pressure water-ice mantle above a rocky interior (Levi et al. 2014). Therefore, given the high abundance of water beyond the snow line, a high-pressure water-ice mantle may be a very likely internal structural feature in many exoplanets. The multi-component chemical nature of this mantle would dictate the chemical transport between the interior and any overlying ocean and atmosphere. Therefore, in this work, we study the binary solution $H_2O$-$O_2$ in the solid form of filled ice (i.e., $O_2H$-III) and in the fluid phase. The goal is to quantify the partitioning of $O_2$ between the two phases, representing the high-pressure ice mantle and an overlying ocean, respectively. This partitioning can be related to the atmospheric abundance of $O_2$ around water worlds and the role that high-pressure ice may play as a sink for abiogenic atmospheric $O_2$.

Filled ices are a form of multicomponent aqueous solid solution with a very high capacity for storing other volatiles (e.g., CH₄, H₂, N₂, etc.) in addition to the water matrix itself. Therefore, their potential formation is likely to have an effect on the transport of volatiles and the outgassing of secondary atmospheres around water worlds.

Filled ice is a low-pressure water-ice polymorph (based on ice Ic, II, and Ih) stabilized at high pressure by its guest molecules (Bove & Ranieri 2019). Clathrate hydrates tend to form filled ice upon increasing the pressure. The only exception is the Xe–H₂O binary system, where filled ice was not observed (Loveday & Nelmes 2008). The type of clathrate hydrate and filled-ice structure that forms is dependent on the size of the guest molecule. The size of an $O_2$ molecule (1.46 Å) is intermediate to that of Ar (1.42 Å) and N₂ (1.50 Å). The Ar–H₂O system is known to form an sII clathrate hydrate at relatively low pressures and then successively transform into sH, sT, and filled ice based on ice Ih (Manakov et al. 2001; Hirai et al. 2002; Loveday & Nelmes 2008). The $N_2$–H₂O binary follows the same sequence of crystal structure transformation with pressure (Loveday et al. 2003; Loveday & Nelmes 2008). The $H_2O$–$O_2$ system has not been studied thoroughly at high pressure, probably due to the extra risk in dealing with $O_2$ in experiments. However, at low pressure, sII clathrate hydrate is favored (Tse et al. 1986), as predicted by the size argument. Therefore, in this work, we adopt for the filled ice of $O_2$ the same ice Ih-based water lattice stabilized in the $H_2O$–$N_2$ and $H_2O$–Ar systems. This water lattice is that referred to as MH-III in the literature, also known as the filled ice of CH₄ or methane hydrate III. In this work, we will refer to the filled ice of $O_2$ as $O_2H$-III and the filled ice of CH₄ as MH-III.

In Section 2, we describe our computational methods. In Section 3, we discuss the thermodynamics of mixing in the $H_2O$–$O_2$ system. In Section 4, we derive the partitioning coefficient of $O_2$ between high-pressure ice and fluid. In Section 5, we estimate the abundance of atmospheric $O_2$ for water worlds as constrained by the interaction with a high-
atmospheric O₂ in the ocean. The theory developed here depends on there being high-pressure ice at the ocean floor following the solvation of atmospheric O₂ in the ocean. The theory developed here depends on there being high-pressure ice at the ocean floor (starting at ~2 GPa). This condition, pressure-wise, may be attained for various planetary compositions, from as little as 3% water mass fraction around a 2 M⊕ planet to encompassing higher water mass fractions and more massive planets (Levi et al. 2014). The illustration above must therefore not be taken to scale.

Figure 1. Cross section of the planetary case examined in this work. A metallic and rocky interior is surrounded by a water-rich mantle divided into a high-pressure ice shell underlying an ocean. Above the ocean lies an atmosphere enriched with O₂ as a result of water photolysis in the atmosphere. Filled ice of O₂ (O₂H-III) may form at the ocean floor following the solvation of atmospheric O₂ in the ocean. The theory developed here depends on there being high-pressure ice at the ocean floor (starting at ~2 GPa). This condition, pressure-wise, may be attained for various planetary compositions, from as little as 3% water mass fraction around a 2 M⊕ planet to encompassing higher water mass fractions and more massive planets (Levi et al. 2014). The illustration above must therefore not be taken to scale.

pressure ice mantle. Sections 6 and 7 are reserved for discussion and summary, respectively.

2. Computational Methods

We studied the structure of O₂H-III and the fluid solution using first-principles electronic structure methods. We performed both static total energy relaxation and molecular dynamics (MD) simulations on various compositions of O₂ within the filled-ice structure and dissolved in the fluid with the CP2K code (Kühne et al. 2020). Simulations were carried out using the CSVR thermostat, which was shown to produce for ice Ih the same vibrational spectrum as that derived with the microcanonical ensemble (Bussi et al. 2007). In addition, we tested this thermostat for our system and checked that it obeys the laws of equipartition.

We use the quick-step framework within CP2K with the Gaussian and plane-wave mixed bases. We adopt the Gaussian basis sets from VandeVondele et al. (2005) and VandeVondele & Hutter (2007), in conjunction with the pseudopotentials (GTH-PBE) of Goedecker et al. (1996), Hartwigsen et al. (1998), and Krack (2005). Our system is converged for a plane-wave cutoff energy of 600 Ry and a REL_CUTOFF of 50 Ry. We use the exchange functional XC_GGA_X_RPW86 from Marques et al. (2012) and a local density approximation (LDA) local correlation functional of Vosko et al. (1980) with the nonlocal van der Waals correlation functional of Lee et al. (2010), requiring a cutoff energy of 200 Ry.

For the initial structure of O₂H-III, we have adopted the structures we have optimized for MH-III (Levi & Cohen 2019) and replaced all CH₄ molecules with O₂ molecules. The initial structures for the aqueous solution were prepared with the insert-molecules code within GROMACS (Abraham et al. 2015), followed by optimization using CELL_OPT in CP2K. The effect of composition was studied by adding or removing O₂ molecules from the structure. The number of H₂O molecules was kept constant throughout this work, set at eight molecules per unit cell.

Our finite-temperature MD was performed on a 2 × 2 × 2 supercell. For both the solid O₂H-III and the fluid, we prepared six supercells with a composition of 64 H₂O molecules and 29, 30, 31, 32, 33, and 34 O₂ molecules. All simulations carried out on the supercell used Γ sampling. The NPT ensemble was used for the MD simulations of the solid phase O₂H-III with a 3 ps thermalization run, followed by 14 ps production. For the MD simulations of the fluid phase, the NVT ensemble was first used in order to equilibrate to the proper temperature with a 2 ps thermalization run, followed by 6 ps weak thermalization. After this, the barostat was introduced and simulated for 15 ps. A time step of 1.0 fs was adopted.

We also simulated the end-members of our studied binary solution in order to calculate the enthalpy of formation. We performed MD simulations of fluid O₂ in the NPT ensemble. First, the unit cell of the solid γ-phase of pure O₂ was built using data reported in Jordan et al. (1964) and Cox et al. (1973). The cubic unit cell consists of eight O₂ molecules and has a density similar to that of the fluid, which is advantageous in the initial setup of the system. The structure was optimized at 3.5 GPa, and a 2 × 2 × 2 supercell was constructed. Smaller supercells were also constructed, but convergence of the energy proved that the larger 2 × 2 × 2 supercell (64 O₂ molecules) was more adequate. Then the temperature of the supercell was raised to 450 K (where the fluid is stable), and the structure melted during a 2 ps run adopting the NVT ensemble. Then a barostat was added, and another 2 ps equilibration was performed in the NPT ensemble, followed by a 12 ps production run. The time step adopted was 1.0 fs, and a short test with a time step of 0.5 fs showed no significant difference.

We simulated water ice VII adopting the NPT ensemble. A thermalization run of 3 ps was followed by a production run of 16 ps. The simulation was carried on a 2 × 2 × 2 supercell with a smaller time step of 0.5 fs, which proved important for convergence. In addition, we also simulated liquid water, adopting a cubic cell of 64 H₂O molecules. The cell was first optimized, followed by the introduction of a thermostat that was strongly thermalized for 2 ps, followed by weak thermalization for 6 ps. Then a barostat was introduced for a run of 15 ps with a time step of 1 fs.

The convergence of all MD runs in this work was tested using block sampling.

3. Thermodynamics of Mixing

In this section, we calculate the solubility of O₂ in high-pressure water ice (in structure O₂H-III) by varying the O₂ composition of filled ice and analyzing the free energy of formation in terms of a temperature–composition phase diagram. We also compare with the free energy of formation of the liquid solution.

The formation of O₂H-III from water and O₂ may be represented by the following reaction:

\[ n\text{O}_2(f) + m\text{H}_2\text{O}(s) \rightleftharpoons (\text{O}_2)_{2n} \cdot (\text{H}_2\text{O})_m(s). \]  

(1)

We note that for our pressure and temperature domain of interest, the pure solute, O₂, is a supercritical fluid (Abramson et al. 1999; Freiman et al. 2018), and pure water is here in the
form of ice VII. The liquid solution may be represented by a
analogous formula where the pure-water end-member is liquid.

The free energy of formation of O2H-III may be defined as

$$\Delta G_{\text{mix}} = G^\text{I}(P, T, m, n) - m \mu^\text{III}(P, T) - n \mu^\text{O}_2(P, T),$$

(2)

where $G^\text{I}$ is the free energy of O2H-III, and $\mu^\text{III}$ and $\mu^\text{O}_2$ are the free energies per particle of water ice VII and fluid O2, respectively. In the structure filled-ice Ih, adopted here for O2H-III, every unit cell consists of eight water molecules (i.e., $m = 8$; Loveday et al. 2001a, 2001b; Hirai et al. 2003). Therefore, our studied O2H-III supercell has $m = 64$. Replacing the value for filled ice and ice VII with that for the liquid solution and pure liquid water, respectively, would yield the liquid solution free energy of formation.

The free energy of formation may also be written as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}},$$

(3)

where $\Delta H_{\text{mix}}$ and $\Delta S_{\text{mix}}$ are the enthalpy and entropy of formation, respectively.

The results for the six O2H-III compositions studied at $T = 450$ K and $P = 3.5$ GPa are tabulated in Table 1. In Table 2, we give the data for the fluid solution studied at the same temperature and pressure. This temperature-pressure point is adopted here because it sits on the melting curve of ice VII (Datchi et al. 2000; Dubrovinskaia & Dubrovinsky 2003; Frank et al. 2004; Joumaux et al. 2013); the latter is the natural phase transition boundary between the ocean and an internal high-pressure ice layer for a system in which O2 is produced in the atmosphere and eddy diffuses into the ocean to interact with any high-pressure ice.

Supercritical fluid O2 was also simulated, and the results at $T = 450$ K and $P = 3.5$ GPa are tabulated in Table 3. Our derived mass density for supercritical fluid O2 is in agreement with experimental data reported in Abramson et al. (1999). In Table 4, we give our simulation results for water ice VII at $T = 450$ K and $P = 3.5$ GPa. Our derived data for ice VII is in agreement with unit cell data reported in the literature (Bezacier et al. 2014; Klotz et al. 2017). In Table 5, we report our derived data for pure liquid water.

The enthalpy of formation of O2H-III is here defined as

$$\Delta H_{\text{mix}} = H^\text{I}(P, T, m, n) - m \Delta H^\text{III}(P, T) - n \Delta H^\text{O}_2(P, T),$$

(4)

with an analogous formula for the fluid solution. The enthalpies are reported in Tables 1–5. Here the lowercase $h$ is the enthalpy per molecule. In Figure 2, we plot the enthalpies of formation for our studied solid and fluid solutions. These differ in both magnitude and sign. The solid solution has a negative enthalpy of formation, as is reported for clathrate hydrates (see

---

**Table 1**

| $n$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $U$ (Ha) | $H$ (Ha) |
|-----|---------|---------|---------|-------------|----------|----------|
| 29  | 9.550 ± 0.016 | 15.178 ± 0.045 | 15.558 ± 0.067 | 2253.997 ± 1.393 | −2047.773 ± 0.008 | −2045.963 ± 0.009 |
| 30  | 9.479 ± 0.016 | 15.426 ± 0.054 | 15.633 ± 0.086 | 2285.462 ± 1.799 | −2080.018 ± 0.007 | −2078.183 ± 0.007 |
| 31  | 9.477 ± 0.007 | 15.528 ± 0.020 | 15.647 ± 0.028 | 2302.448 ± 0.976 | −2112.222 ± 0.006 | −2110.373 ± 0.006 |
| 32  | 9.515 ± 0.014 | 15.601 ± 0.044 | 15.654 ± 0.052 | 2323.062 ± 2.922 | −2144.441 ± 0.007 | −2142.576 ± 0.007 |
| 33  | 9.531 ± 0.007 | 15.716 ± 0.035 | 15.718 ± 0.026 | 2354.252 ± 4.088 | −2176.611 ± 0.007 | −2174.721 ± 0.008 |
| 34  | 9.581 ± 0.011 | 16.241 ± 0.029 | 15.248 ± 0.048 | 2372.354 ± 4.022 | −2208.792 ± 0.005 | −2206.887 ± 0.006 |

**Table 2**

| $n$ | $V$ (Å$^3$) | $U$ (Ha) | $H$ (Ha) |
|-----|-------------|----------|----------|
| 29  | 2293.041 ± 3.557 | −2047.557 ± 0.004 | −2045.716 ± 0.005 |
| 30  | 2321.130 ± 2.404 | −2079.765 ± 0.007 | −2077.902 ± 0.007 |
| 31  | 2354.369 ± 1.786 | −2111.957 ± 0.005 | −2110.067 ± 0.006 |
| 32  | 2384.721 ± 4.028 | −2144.143 ± 0.007 | −2142.228 ± 0.008 |
| 33  | 2404.364 ± 1.978 | −2176.352 ± 0.008 | −2174.422 ± 0.009 |
| 34  | 2442.351 ± 1.834 | −2208.533 ± 0.004 | −2206.572 ± 0.004 |

**Table 3**

| $V$ (Å$^3$) | $U$ (Ha) | $H$ (Ha) |
|-------------|----------|----------|
| 1956.941 ± 3.594 | −2060.343 ± 0.003 | −2058.772 ± 0.004 |

**Table 4**

| $V$ (Å$^3$) | $U$ (Ha) | $H$ (Ha) |
|-------------|----------|----------|
| 44.878 ± 0.344 | −34.8126 ± 0.0003 | −34.7766 ± 0.0004 |

**Note.** Reported volumetric data are the supercell (2 × 2 × 2) data divided by eight.

**Table 5**

| $V$ (Å$^3$) | $U$ (Ha) | $H$ (Ha) |
|-------------|----------|----------|
| 1433.682 ± 1.866 | −1114.017 ± 0.006 | −1112.866 ± 0.006 |

**Note.** Reported data are for a cubic cell containing 64 H2O molecules.
For the entropy of formation, $\Delta S_{\text{mix}}$, we adopt the ideal mixing model developed in the Appendix. The latter requires the dependence of the unit cell volume for O$_2$H-III on the O$_2$ mole fraction. This dependence is linear to a good approximation, yielding the following relation:

$$V_{\text{unit}} = 416.451X_{O_2} + 152.134 \text{ [Å$^3$]}.$$  \hspace{1cm} (5)

In Figure 3, we plot our calculated entropy of mixing for a wide range of the oxygen mole fraction, including our studied compositions. We find that the main source of error in the entropy of mixing for the O$_2$H-III solid solution is the uncertainty in the packing efficiency of O$_2$ molecules within the filled-ice water framework.

In Figure 4, we give the free energy of formation for the solid and fluid solutions. The solid solution shows a deep well with stoichiometric-like behavior around a O$_2$ mole fraction of 0.333. Furthermore, the mixing in the fluid phase is entropically driven.

The standard state for the unmixed materials is chosen to be the stable state of the pure condensed substances at the pressure and temperature of the simulation, i.e., the ice VII and fluid O$_2$ data given above. Figure 5 is the temperature–composition phase diagram for O$_2$H-III. Clearly, the composition of O$_2$H-III is constrained to be around a O$_2$ mole fraction of 0.333, in other words, a H$_2$O:O$_2$ ratio of 2:1. It is interesting to note that this same ratio is reported in the H$_2$O–CH$_4$ system for its associated filled-ice structure (Loveday et al. 2001a).

For this composition for O$_2$H-III, we report a density of $1.555 \pm 0.002$ g cm$^{-3}$, which is denser than ice VI though less dense than ice VII. We also find O$_2$H-III to be denser than liquid water at the same pressure and temperature conditions (Wagner & Pruss 2002). Therefore, if this structure

Figure 2. (Left panel) Molar enthalpy of formation for O$_2$H-III vs. the oxygen (O$_2$) mole fraction dissolved in the crystal structure. The red solid curve is our quadratic polynomial fit to the data, which is used in this work in order to interpolate between our calculated data points. (Right panel) Molar enthalpy of formation for the fluid solution in the H$_2$O–O$_2$ system vs. the oxygen (O$_2$) mole fraction dissolved in the fluid.

Figure 3. (Left panel) Ideal molar entropy of mixing for O$_2$H-III vs. the oxygen (O$_2$) mole fraction dissolved in the crystal structure. The red solid and dashed curves are for assuming a packing efficiency for ellipsoids (see $\phi$ in the Appendix) of 0.64 and 0.77, respectively. (Right panel) Ideal molar entropy of mixing for the fluid solution in the H$_2$O–O$_2$ system vs. the oxygen (O$_2$) mole fraction dissolved in the fluid.

Figure 4. (Left panel) Molar free energy of formation for O$_2$H-III vs. the oxygen (O$_2$) mole fraction dissolved in the crystal structure. (Right panel) Molar free energy of formation for the fluid solution in the H$_2$O–O$_2$ system vs. the oxygen (O$_2$) mole fraction dissolved in the fluid.
forms in water worlds, it is likely gravitationally stable at the ocean floor.

4. The Partitioning Coefficient

In equilibrium, the chemical potential of O$_2$ is equal for both phases, the O$_2$H-III (the high-pressure ice mantle) and the aqueous fluid solution (the oceanic floor),

$$\mu_{o_2}^{\text{fl}}(P, T, m, n') = \mu_{o_2}^{\text{aq}}(P, T, m, n).$$

(6)

Here $P$ and $T$ are the pressure and temperature. The number of H$_2$O molecules in the simulation is $m$. The condition of chemical potential equilibrium between both phases in general requires different mole fractions of O$_2$ for both phases, as represented by a different number of O$_2$ molecules $n'$ and $n$. Therefore, the partitioning coefficient, $C$, which is defined as

$$C = \frac{X_{o_2}^{\text{aq}}}{X_{o_2}^{\text{fl}}}$$

(7)

using molar fractions, is what gives the root for the following relation:

$$0 = \mu_{o_2}^{\text{fl}}(P, T, X_{o_2}^{\text{fl}}) - \mu_{o_2}^{\text{aq}}(P, T, X_{o_2}^{\text{aq}}).$$

(8)

The algorithm for solving the last relation is given in detail in the Appendix.

In the previous section, we have shown that the composition of O$_2$H-III is constrained to $X_{o_2}^{\text{fl}} = 0.334 \pm 0.003$ (see Figure 5). Thus, in conjunction with Equation (8), one can solve for the solubility of O$_2$ at the ocean floor above the filled ice, $X_{o_2}^{\text{aq}}$, if in contact with O$_2$H-III. This is clearly shown in Figure 6, yielding $X_{o_2}^{\text{aq}} = 0.330 \pm 0.013$. The partitioning coefficient is therefore $C = 0.988 \pm 0.030$. It is interesting to note that similar high solubilities in water, induced by pressure, were experimentally derived for CH$_4$ (Pruteau et al. 2017), where again, as seen here, a low-miscibility hydrophobic molecule turns miscible with pressure above about 2 GPa.

5. The Abundance of Atmospheric O$_2$

Here we estimate whether the mixing of O$_2$ into high-pressure ice may serve as a reasonable internal sink for atmospherically produced O$_2$. As shown in the previous section, a oceanic floor with O$_2$H-III would impose a molar fraction, $X_{o_2}^{\text{aq}}$, of about 0.33 of O$_2$ on the oceanic water adjacent to the ocean floor. Assuming the ocean is well mixed, this molar fraction of O$_2$ would become available at the base of the atmosphere and outgas. The resulting O$_2$ fugacity in the atmosphere, $f_{o_2}$, would be, according to Henry’s law,

$$f_{o_2}(P, T) = \hat{H}(T)X_{o_2}^{\text{aq}},$$

(9)

where $\hat{H}$ is the Henry’s law constant for O$_2$ adopted from Fernández-Prini et al. (2003). The fugacity of O$_2$ is estimated using the Soave–Redlich–Kwong equation of state (Soave 1972). Solving for the last relation, we obtain the O$_2$ atmospheric pressure at the base of the atmosphere (see Figure 7).

The resulting atmospheric pressure of O$_2$ decreases toward the supercritical temperature for water because solubility increases substantially toward that point. This is due to breaking of the hydrogen-bonded water network at supercritical conditions (Postorino et al. 1993). In other words, less overlying pressure is required in order to maintain a given dissolved mole fraction.

Finally, we wish to note that the values stated in Figure 7 are upper bound values for the atmospheric pressure. For example, one may suggest a 1 bar atmospheric pressure of O$_2$ in an ocean world’s atmosphere. Solving Equation (9) for ambient temperature gives a O$_2$ solubility of $X_{o_2}^{\text{aq}} \approx 10^{-5}$. For such a low solubility, the chemical potential of O$_2$ is higher in filled ice than dissolved in the ocean (see Figure 6). Therefore, there would be no thermodynamic incentive to deposit any O$_2$ in the high-pressure ice at the ocean floor. If O$_2$ continues to build up in the atmosphere to levels higher than those in Figure 7, then the solubility of O$_2$ in the ocean increases above about 0.33, which results in the chemical potential of O$_2$ in the ice (in O$_2$H-III) becoming lower than that in the ocean (see Figure 6). Therefore, any attempt to further increase the atmospheric abundance of O$_2$
would result in its deposit into the high-pressure ice at the ocean floor.

6. Discussion

In this work, we find that the equilibrium partitioning of dissolved O$_2$ between high-pressure liquid water and ice results in an upper bound value for the possible atmospheric pressure of O$_2$. Naturally, this result is relevant for planets where a high-pressure water-dominated ice layer survives the process of water evaporation and loss during the period of high stellar activity. This is not unreasonable, considering that water mass loss is estimated at a few to tens of Earth’s oceans (Luger & Barnes 2015; Lincowski et al. 2018), whereas a high-pressure ice layer requires much larger water inventories to begin with (a few percent of the planetary mass).

Since the upper bound value on the atmospheric pressure of O$_2$ is a direct consequence of equilibrium thermodynamics between the outer hydrosphere and the high-pressure ice interior, it has the advantage of representing a universal criterion. For example, it is independent of planetary mass, the tectonic mode of the surface, and the initial assumption of the water inventory as long as there is a high-pressure ice layer.

In addition, there is a clear trend (see Figure 7) where, for higher oceanic upper surface temperatures (i.e., higher proximity to the star), the upper bound value predicts less O$_2$ in the atmosphere. This may seem counterintuitive because a higher proximity to the star would likely result in more water evaporation and photolysis into O$_2$. However, this is a result of the behavior of solubility with temperature and is independent of the type of star.

The possibility of partitioning atmospheric O$_2$ into high-pressure ice suggests a mechanism that may oxidize, to some extent, the interior of a planet. This increased oxygen fugacity may remain superficial at the oceanic floor if the high-pressure ice mantle is deep. This is because the density of O$_2$H-III is less than that of ice VII, so it may not be carried into the interior with convection flows within ocean worlds. However, it may still act as an oxidizing agent for reduced material making its way from the rocky core to be outgassed into the ocean followed by the atmosphere.

As we show above, the abiotic O$_2$ atmospheric fugacity renders O$_2$H-III (the filled ice of O$_2$) a plausible structure in a real geophysical setting (unlike pure fluid O$_2$), where the magnetic effect of triplet O$_2$ may be of interest when embedded within the magnetic field of an exoplanet. Such magnetic estimations, however, are beyond the scope of this work.

Further work on multicomponent filled ices is required to help better constrain the atmospheres of water worlds and mini-Neptunes.

The robustness of the mechanism described here opens it up for potential observational scrutiny with upcoming telescopes and instruments. For a sample of planets with precise bulk densities (from transit radii and dynamic masses) implying more than a few percent of bulk water, one can envision atmospheric transmission O$_2$ and H$_2$O measurements (López-Morales et al. 2019). The exoplanet GJ 1132b could be such an example (Schaefer et al. 2016). Such measurements would be complemented by thermal phase-curve observations with the James Webb Space Telescope, for example. With an estimate of the total atmospheric mass derived that way, one could perhaps attempt detection of O$_2$–O$_2$ collisionally induced absorption features (Schwieterman et al. 2015) for further constraining O$_2$ pressure. The O$_2$ has a range of viable transitions with different pressure dependencies, though most of the information we have is derived at low pressure, while the high-pressure work has not yet been done (Greenblatt et al. 1990; Richard et al. 2012; Karman et al. 2018, 2019). However, transmission spectroscopy probing the top of the atmosphere, where pressures are relatively low, may perhaps be used together with atmospheric modeling to integrate inward and obtain the pressure at the base of the atmosphere. Assessing the viability of this procedure or another to observationally detect atmospheric O$_2$ and determine its partial pressure in the atmosphere of an exoplanet clearly requires thorough modeling of the atmosphere in conjunction with spectroscopic modeling, which is beyond the scope of this work.

7. Summary

In this work, we studied the solubility of O$_2$ in water in the solid phase of filled ice (i.e., O$_2$H-III) and an aqueous liquid solution on the melting curve of ice VII. The purpose was to estimate whether atmospherically produced O$_2$ may be deposited into high-pressure ice composing the ocean floor, which is relevant to ocean worlds.

We find that O$_2$H-III is denser than liquid water and ice VI, though less dense than ice VII. Therefore, it is likely gravitationally stable on the ocean floor, where it may form as the ocean is enriched with dissolved O$_2$ originating from photolysis in the atmosphere.

We find that mixing O$_2$ with H$_2$O in the solid phase of O$_2$H-III (filled ice of O$_2$) is stoichiometric-like around a 2:1 ratio for H$_2$O:O$_2$, similar to the ratio reported for the H$_2$O–CH$_4$ system and its associated filled ice. We derive an equilibrium partition coefficient of 0.988 ± 0.030 for O$_2$ between liquid water and high-pressure ice in the form of O$_2$H-III. This yields an imposed O$_2$ solubility of about 0.330 in molar fraction at the ocean floor if in equilibrium with deposits of O$_2$H-III. If ocean enrichment in dissolved O$_2$ is driven to higher values due to excess buildup of atmospheric O$_2$, then deposition of O$_2$ into
the ocean floor in the form of O$_2$H-III becomes thermodynamically favored.

Therefore, an upper bound value for the atmospheric abundance of O$_2$ is imposed in ocean worlds. This upper bound value depends on the temperature at the boundary between the atmosphere and ocean (see Figure 7), varying from 3000 bars to a few hundred bars as the boundary temperature approaches supercritical conditions. Translated to heliocentric distance, the closer the ocean world is to its host star, the less O$_2$ pressure is allowed in the atmosphere, which is a consequence of how solubility responds to temperature and the deposition of dissolved O$_2$ into high-pressure ice.

A.L. is supported by a grant from the Simons Foundation (SCOL No. 290360 to D.S.). The computations for this paper were run on the Odyssey cluster supported by the FAS Division of Science, Research Computing Group at Harvard University. A.L. is grateful to the administrative staff for their technical support.

Appendix

A.1. Mixing Entropy

Filled ices resemble another type of aqueous solid solution known as clathrate hydrate, since both have a water matrix supported by guest molecules. One can think of filled ices and clathrates as a open water lattice hosting guest molecules within the spaces of the microporous water structure. With that picture in mind, the mixing is among the guest molecules and "empty" particles. This model has been shown to be very effective in characterizing the thermodynamics of clathrate hydrates (Waals & Platteeuw 1958; Sloan & Koh 2007).

Waals & Platteeuw (1958) derived the following partition function for describing clathrate hydrates composed of $n$-type spaces that are occupied by $M$-type guest molecules,

$$Z = e^{-\beta F^\beta} \sum_{N_{empty}^i \text{ empty}} \left[ \frac{N_{space}!}{N_{empty}^i! \prod_{i=1} N_{i}!} \prod_{i=1}^{M} \lambda_{i}^{N_{i}} h_{i}^{N_{i}} \right],$$  

(10)

where $F^\beta$ is the free energy of the empty clathrate hydrate, $\tau = kT$, $N_{i}$ is the number of $J$-type guest molecules occupying $i$-type spaces, $N_{space}^i$ is the total number of $i$-type spaces in the crystal structure that may be occupied by a guest molecule, and $N_{empty}^i$ is the number of $i$-type spaces remaining empty after the guest molecules occupy their appropriate spaces. The absolute activity of the particle reservoir of type $J$, $\lambda_{i}$, is, by definition, exp($\mu_{J}/\tau$), where $\mu_{J}$ is its chemical potential. Finally, $h_{J}$ is the single cage canonical partition function,

$$h_{J} = \sum e^{-\epsilon_{J}/\tau},$$  

(11)

where the sum is over all of the microscopic states of a molecule of type $J$ in its water matrix position, and $\epsilon_{J}$ is its binding energy with the surrounding matrix.

The water lattice of clathrate hydrates has distinct spaces, which are approximately spherical cages, of various types. It is in these cages that hydrophobic molecules are entrapped. This is not the case for filled ice. However, for simplicity, let us assume that a single type of space, i.e., a cage, may suffice to approximate the structure of filled ice. In addition, let us consider a structure of a given composition, $N_{i}$, and a single type of guest molecule. The partition function thus reduces to this simpler form,

$$Z = e^{-\beta \sum_{\lambda_{i}^{j} \text{ empty}} \left[ \frac{N_{space}!}{(N_{space} - N_{i})!N_{i}!} \lambda_{i}^{N_{i}} h_{i}^{N_{i}} \right]}.$$  

(12)

The entropy is

$$\sigma = \left( \frac{\partial \tau \log Z}{\partial \tau} \right)_{V,N_{w},\beta},$$  

(13)

where $V$ is the volume, and $N_{w}$ is the number of water molecules. Inserting Equation (12) into the last equation yields

$$\sigma = \sigma^{\beta} + \log \frac{N_{space}!}{(N_{space} - N_{i})!N_{i}!} + N_{i} \left( \frac{\partial \log \lambda_{i} h_{i}}{\partial \tau} \right)_{V,N_{w},\beta} - \sigma_{w},$$  

(14)

where $\sigma^{\beta}$ is the independent contribution of the empty hydrate to the total entropy. In addition, we identify $\lambda_{i} h_{i}$ as the grand canonical partition function for a single particle of type $J$ in the water matrix. Therefore, the last term on the right of the last equation is the contribution of the $N_{i}$ entrapped molecules to the entropy.

Therefore, the entropy of mixing is

$$\Delta \sigma_{mix} = \sigma^{\beta} - \sigma_{w} + \log \frac{N_{space}!}{(N_{space} - N_{i})!N_{i}!} + N_{i} \left( \frac{\partial \log \lambda_{i} h_{i}}{\partial \tau} \right)_{V,N_{w},\beta} - \sigma_{w},$$  

(15)

where $\sigma_{w}$ is the entropy of water in its stable pure state, and $\sigma_{J}$ is the entropy per molecule of $J$ in its pure stable phase. In an ideal solution, the contribution to the entropy by the water and the guest species is unaffected by their mixing, yielding

$$\Delta s_{mix} = k \log \frac{N_{space}!}{(N_{space} - N_{i})!N_{i}!}.$$  

(16)

In this work, we estimate the number of available spaces for guest molecules by the integer division,

$$N_{space} = \left[ \frac{V_{unit} - V_{w}}{v_{J}} \right],$$  

(17)

where $V_{unit}$ is the volume of a unit cell, and $V_{w}$ is the volume occupied by the water molecules in the unit cell. The difference between the latter two volumes yields the empty space. The volume per entrapped molecule of type $J$ is $v_{J}$. In this work, we adopt effective diameters of 2.74 Å for H$_2$O and 2.80 Å for O$_2$ (Zhang & Xu 1995), giving volumes of 10.771 and 11.494 Å$^3$, respectively. We correct for the packing efficiency by introducing the factor $\phi$. The packing efficiency of guest molecules in filled ice has never been studied. The packing depends on the exact shape of the guest molecule and the degree of randomness of the packing. Such an analysis is beyond the scope of this work. For the case of O$_2$, we adopt simulation results for the packing efficiency of ellipsoids giving values in the range 0.64–0.77 for $\phi$ (Donev et al. 2004a, 2004b). The uncertainty in the value of $\phi$ would result in an error for the entropy of mixing.
For the ideal entropy of mixing in the fluid solution, we adopt the more common form,
\[
\Delta_{\text{mix}}^{\text{ideal}} = k \log \left( \frac{(N_w + N_j)!}{N_w!N_j!} \right),
\]
where \( N_w \) is the number of water molecules in the simulated fluid cell. The reason for the different model adopted for the fluid is that here the water molecules do not form a crystal structure stabilized by guest and "empty" particles entrapped in various locations of the structure but rather an intimate mixture of water molecules and another dissolved chemical species of type \( J \).

### A.2. Partitioning Coefficient Algorithm

We equate the chemical potential of \( O_2 \) between the \( O_2 \)H-III (the filled ice, \( FI \)) and the aqueous fluid solution,
\[
\mu_{O_2}^{FI}(P, T, m, n') = \mu_{O_2}^{aq}(P, T, m, n).
\]
(19)

Here \( P \) and \( T \) are the pressure and temperature. The number of \( H_2O \) molecules in the simulation is \( m \). The condition of chemical potential equilibrium between both phases may require different mole fractions of \( O_2 \), as represented by a different number of \( O_2 \) molecules \( n' \) and \( n \). The partitioning coefficient, \( C \), would thus be the ratio
\[
C = \frac{X_{O_2}^{aq}}{X_{O_2}^{FI}} = \frac{n' + m}{n' + n + m}
\]
for which Equation (19) is satisfied.

We can define the needed chemical potentials of \( O_2 \) using a central difference scheme,
\[
\mu_{O_2}^{FI}(P, T, m, n') = \frac{G^{FI}(P, T, m, n' + 1) - G^{FI}(P, T, m, n' - 1)}{2}
\]
\[
\mu_{O_2}^{aq}(P, T, m, n) = \frac{G^{aq}(P, T, m, n + 1) - G^{aq}(P, T, m, n - 1)}{2},
\]
(21)

where \( G^{FI} \) and \( G^{aq} \) are the free energies of \( O_2 \)H-III and the fluid solution, respectively. Those are related to the free energy of formation,
\[
\Delta G^{\text{mix}}_{\text{aq}}(P, T, m, n') = G^{\text{aq}}(P, T, m, n') - m \mu_{\text{H}}^{\text{aq}}(P, T) - n' \mu_{O_2}^{aq}(P, T)
\]
\[
\Delta G^{\text{mix}}_{\text{aq}}(P, T, m, n) = G^{\text{aq}}(P, T, m, n) - m \mu_{\text{H}}^{\text{aq}}(P, T) - n \mu_{O_2}^{aq}(P, T),
\]
(22)

where the different terms are defined in Equation (2), though we also require \( \mu_{\text{H}}^{\text{aq}} \), the free energy per molecule in pure liquid water. We can now write the chemical potentials in terms of the free energy of formation:
\[
\mu_{O_2}^{FI}(P, T, m, n') = \Delta G_{\text{mix}}^{FI}(P, T, m, n' + 1) - \Delta G_{\text{mix}}^{FI}(P, T, m, n' - 1) + \mu_{O_2}^{aq}(P, T, m, n)
\]
\[
\mu_{O_2}^{aq}(P, T, m, n) = \Delta G_{\text{mix}}^{aq}(P, T, m, n + 1) - \Delta G_{\text{mix}}^{aq}(P, T, m, n - 1) + \mu_{O_2}^{aq}(P, T).
\]
(23)

Finally, the equilibrium condition of Equation (19) may be written as
\[
\Delta G_{\text{mix}}^{FI}(P, T, m, n' + 1) - \Delta G_{\text{mix}}^{FI}(P, T, m, n' - 1)
\]
\[
\Delta G_{\text{mix}}^{aq}(P, T, m, n + 1) - \Delta G_{\text{mix}}^{aq}(P, T, m, n - 1) - \mu_{O_2}^{aq}(P, T).
\]
(24)

Our simulations have specific compositions \( m, n' \), and \( n \); however, by converting to the oxygen mole fraction (i.e., \( n'/[n' + m] \) and \( n/[n + m] \)) and interpolating, we are able to solve the last relation as a smooth function of the composition in order to obtain the partitioning coefficient.

### ORCID iDs

A. Levi @ https://orcid.org/0000-0003-1080-1007
D. Sassellov @ https://orcid.org/0000-0001-7014-1771

### References

Abraham, M. J., Murtola, T., Schulz, R., et al. 2015, SoftX, 1, 19
Abramson, E. H., Slutsky, L. J., Harrell, M. D., & Brown, J. M. 1999, IChPh, 110, 10493
Aliberti, Y., & Benz, W. 2017, A&A, 598, L5
Bezacier, L., Journaux, B., Perrillat, J.-P., et al. 2014, IChPh, 141, 104505
Bove, L. E., & Ranieri, U. 2019, RSPTA, 377, 20180262
Bussi, G., Donadio, D., & Parrinello, M. 2007, IChPh, 126, 014101
Cox, D. E., Samuelsen, E. J., & Beckurts, K. H. 1993, PhRvB, 7, 3102
Datchi, F., Loubeyre, P., & LeToullec, R. 2000, PhRvB, 61, 6535
Donev, A., Cisse, I., Sachs, D., et al. 2004a, Sci, 303, 990
Donev, A., Stillinger, F. H., Chaikin, P. M., & Torquato, S. 2004b, PhRvL, 92, 255506
Dubrovinskaia, N., & Dubrovinsky, L. 2003, HPR, 23, 307
Fernández-Prini, R., Alvarez, J. L., & Harvey, A. H. 2003, IJCRD, 32, 903
Frank, M. R., Fei, Y., & Hu, J. 2004, GeCoA, 68, 2781
Freiman, Y., Jodl, H., & Crespo, Y. 2018, PhR, 743, 1
Gillson, M., Triaud, A. H. M., J., Demory, B.-O., et al. 2017, Natur, 542, 456
Goedecker, S., Teter, M., & Hutter, J. 1996, PhRvB, 54, 1703
Greenblatt, G. D., Orlando, J. J., Burkholder, J. B., & Ravishankara, A. R. 1990, IGR, 95, 18,577
Hartwigsen, C., Goedecker, S., & Hutter, J. 1998, PhRvB, 58, 3641
Hirai, H., Tanaka, T., Kawamura, T., Yamamoto, Y., & Yagi, T. 2003, PhRvB, 68, 172102
Hirai, H., Uchihara, Y., Kawamura, T., Yamamoto, Y., & Yagi, T. 2002, PJA, 78, 39
Jordan, T. H., Streib, W. D., Smith, H. W., & Lipscomb, W. N. 1964, Acta Crystallogr., 17, 777
Journaux, B., Daniel, I., Caracas, R., Montagnac, G., & Cardon, H. 2013, Icar, 226, 355
Karpman, T., Gordon, I. E., van der Avoird, A., et al. 2019, Icar, 328, 160
Karmen, T., Koenis, M. A. J., Banerjee, A., et al. 2018, NatCh, 10, 549
Klotz, S., Komatsu, K., Kagi, H., et al. 2017, PhRvB, 95, 174111
Krack, M. 2005, Theor. Chem. Acc., 114, 145
Kühne, T. D., Iannuzzi, M., Del Ben, M., et al. 2020, IChPh, 152, 194103
Kvanme, B. 2019, Energies, 12, 1039
Lee, K., Murray, E. D., Kong, L., Lundqvist, B. I., & Langreth, D. C. 2010, PhRvB, 82, 081101
Levi, A., & Cohen, R. E. 2019, ApJ, 882, 71
Levi, A., Sassselov, D., & Podolak, M. 2014, ApJ, 792, 125
Lincowski, A. P., Meadows, V. S., Crisp, D., et al. 2018, ApJ, 867, 76
López-Morales, M., Ben-Ami, S., Gonzalez-Abad, G., et al. 2019, AJ, 158, 24
Loveday, J. S., & Nemes, R. J. 2008, PCCP, 10, 937
Loveday, J. S., Nemes, R. J., Guthrie, M., et al. 2001a, Natur, 410, 661
Loveday, J. S., Nemes, R. J., Guthrie, M., Klug, D. D., & Tse, J. S. 2001b, PhRvL, 87, 215501
Loveday, J. S., Nemes, R. J., Klug, D. D., Tse, J. S., & Desgreniers, S. 2003, CaPh, 81, 539
Luger, R., & Barnes, R. 2015, AsBio, 15, 119
Lyons, T. W., Reinhard, C. T., & Planavsky, N. J. 2014, Natur, 506, 307
Manakov, A. Y., Voronin, V. I., Kurnosov, A. V., et al. 2001, Dokl. Phys. Chem, 378, 148
Marques, M., Oliveira, M., & Burnus, T. 2012, CoPhC, 183, 2272
Postorino, P., Tromp, R. H., Ricci, M. A., Soper, A. K., & Neilson, G. W. 1993, Natur, 366, 668
Pruteanu, C. G., Ackland, G. J., Poon, W. C. K., & Loveday, J. S. 2017, SciA, 3
Richard, C., Gordon, I., Rothman, L., et al. 2012, JQSRT, 113, 1276
Schaefer, L., Wordsworth, R. D., Berta-Thompson, Z., & Sassselov, D. 2016, ApJ, 829, 63
Schwieterman, E. W., Robinson, T. D., Meadows, V. S., Misra, A., & Domagal-Goldman, S. 2015, ApJ, 810, 57
Shock, E. L., Helgeson, H. C., & Sverjensky, D. A. 1989, GeCoA, 53, 2157
Sloan, E., & Koh, C. 2007, Clathrate Hydrates of Natural Gases, Chemical Industries (3rd ed.; Boca Raton, FL: CRC Press)
Savage, G. 1972, ChEnS, 27, 1197
Tse, J. S., Handa, Y. P., Ratcliffe, C. L., & Powell, B. M. 1986, J. Incl. Phenom., 4, 235
VandeVondele, J., & Hutter, J. 2007, JChPh, 127, 114105
VandeVondele, J., Krack, M., Mohamed, F., et al. 2005, CoPhC, 167, 103
Vosko, S. H., Wilk, L., & Nusair, M. 1980, CaPh, 58, 1200
Waals, J. H. V. D., & Platteeuw, J. C. 1958, Clathrate Solutions (New York: Wiley), 1
Wagner, W., & Pruss, A. 2002, JPCRD, 31, 387
Wordsworth, R., & Pierrehumbert, R. 2014, ApJL, 785, L20
Zeng, L., Jacobsen, S. B., Sassselov, D. D., et al. 2019, PNAS, 116, 9723
Zhang, Y., & Xu, Z. 1995, AmMin, 80, 670