The Abundance of Atmospheric CO₂ in Ocean Exoplanets: a Novel CO₂ Deposition Mechanism

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Abstract

We consider super-Earth sized planets which have a water mass fraction large enough to form an external mantle composed of high-pressure water-ice polymorphs and also lack a substantial H/He atmosphere. We consider such planets in their habitable zone, so that their outermost condensed mantle is a global, deep, liquid ocean. For these ocean planets, we investigate potential internal reservoirs of CO₂, the amount of CO₂ dissolved in the ocean for the various saturation conditions encountered, and the ocean-atmosphere exchange flux of CO₂. We find that, in a steady state, the abundance of CO₂ in the atmosphere has two possible states. When wind-driven circulation is the dominant CO₂ exchange mechanism, an atmosphere of tens of bars of CO₂ results, where the exact value depends on the subtropical ocean surface temperature and the deep ocean temperature. When sea-ice formation, acting on these planets as a CO₂ deposition mechanism, is the dominant exchange mechanism, an atmosphere of a few bars of CO₂ is established. The exact value depends on the subpolar surface temperature. Our results suggest the possibility of a negative feedback mechanism, unique to water planets, where a reduction in the subpolar temperature drives more CO₂ into the atmosphere to increase the greenhouse effect.

Key words: atmospheric effects – planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: interiors – planets and satellites: oceans – planets and satellites: surfaces

1. Introduction

Recent observations of exoplanets have shown that super-Earths are common (Batalha 2011; Dressing & Charbonneau 2015), and water is expected to be a major bulk constituent for many of them. Water and CO₂ have been found to be common both in protoplanetary disks (Pontoppidan et al. 2014, p. 363) and in comets in our own solar system (Bockelée-Morvan et al. 2004, pp. 391–423), so it is natural to assume that they will be important components in water planets as well. Geochemically, CO₂ in water planets has largely been treated in the framework of silicate weathering, representing direct analogies to the Earth (e.g., Abbot et al. 2012; Wordsworth & Pierrehumbert 2013; Alibert 2014). However, for a planet to be analogous to the Earth, its water mass fraction must be kept very small. Therefore, the majority of water planets are probably not Earth-like, and the geochemistry of CO₂ needs further study.

We consider water planets with masses similar to the Earth and lacking a substantial hydrogen atmosphere. For such bodies, if the mass fraction of water is greater than ~1%, the pressure at the bottom of the water layer will be high enough that high-pressure ice polymorphs will form (Levi et al. 2014). As a result, there would be no direct contact between the liquid ocean and the silicate interior (as in Type 1 planets discussed by Kaltenegger et al. (2013), for modeling the Kepler-62e, f exoplanets), and the ocean would have very low total alkalinity. This would limit the formation of bicarbonate and carbonate ions (Williams & Follows 2011), making dissolved CO₂ the dominant carbon-bearing molecule in the water planet’s ocean.

In this paper, we consider the case of a secondary atmosphere outgassing, particularly the outgassing of CO₂. In Section 2, we discuss the solubility of freely dissolved CO₂ in water, in the entire pressure–temperature domain expected in water planet oceans. The solubility is derived both outside the SI CO₂ clathrate hydrate thermodynamic stability field, and when in equilibrium with this phase. In Section 3, we model the thermodynamic stability field for the SI clathrate hydrate of CO₂, for the entire parameter space relevant to water planet oceans. We then compare it with the most recent data. In Section 4, we explore the different potential reservoirs for CO₂ at the ocean bottom in water planets. In Section 5, we calculate the power required to maintain an oceanic overturning circulation, and estimate the feasibility of vertical ocean mixing in water planets. In Section 6, we investigate the ocean-atmosphere flux of CO₂, and derive steady-state values for the partial atmospheric pressure of CO₂. The effect of the wind-driven circulation is the subject of Section 6.1, and the effect of sea-ice forming at the poles is quantified in Section 6.2. The results are discussed in Section 7, and a summary is given in Section 8.

2. High-Pressure CO₂ Solubility

A warm water planet represents a planetary case where the outermost layer is mostly liquid water, i.e., an ocean. For a 2 Mare super-Earth whose water mass fraction exceeds a few percent, this ocean may have a bottom made of high-pressure water-ice polymorphs (see Table 1 in Levi et al. 2014, for water-rock boundary pressures). Because the ocean will be separated from the silicate interior, its alkalinity will be low. Therefore, even for a low oceanic carbon abundance, the freely dissolved CO₂ would represent the dominant dissolved inorganic carbon species. For lower planetary water mass fractions, the ocean may be shallower and have a rocky bottom. In this case, the ocean may have a higher alkalinity, which may turn a larger fraction of the oceanic carbon abundance to carbonate and bicarbonate. For example, in Earth’s ocean, the latter are the dominant dissolved inorganic carbon species. In this work, we
Concentrate on the first water planet composition case. Therefore, investigating carbon dioxide deposition in our studied planets’ deep oceans requires an estimation of the solubility of CO₂ in water at both low and high pressures (from ocean surface pressures to approximately 1 GPa). As a preliminary to solving the solubility problem in the presence of CO₂ SI clathrate hydrate, we shall first solve for the solubility outside of the stability field of this phase.

2.1. CO₂ Solubility Outside Its Clathrate Hydrate Stability Field

Study of the H₂O–CO₂ mixture is very important to our understanding of Earth’s geochemistry. Therefore, much effort has been made to derive equations of state for the mixture (e.g., Duan & Zhang 2006). However, the parameter space occupied by Earth’s crust and upper mantle spans temperatures much higher than those expected for a water planet’s oceans in the habitable zone, leaving our parameter space of interest largely unexplored. Up until very recently, the highest-pressure CO₂ solubility experiments at temperatures more relevant to our case of study were those of Tödheide & Franck (1963), reaching pressures up to 0.35 GPa and a minimal isotherm of 323.15 K. Diamond & Akinfiev (2003) listed the experimental solubility data known up to that time in the temperature range of 271.6–373 K, and evaluated the level of confidence that ought to be given to any one of the data sets. Diamond & Akinfiev (2003) further showed that Henry’s law can accurately describe these experimental data sets in the pressure range up to 100 MPa.

More recently, Bollengier et al. (2013) researched water-rich systems at CO₂ saturation conditions in the temperature range of 250–330 K, and pressures up to the melting pressure of water ice VI. They found that the melting temperature of water ice VI is depressed by a few degrees when saturated with CO₂. Converting melt depression data into solubility requires some acknowledgement of the mixture’s deviations from ideality. For the H₂O–CO₂ system, an ideal solution is a good first approximation as long as the solubility does not exceed about 2 mol% (Diamond & Akinfiev 2003). Bollengier et al. (2013) assumed an ideal solution and the model of Choukroun & Grasset (2007), and reported that their melt depression data suggests the solubility of CO₂ along the melt curve of ice VI is a mole fraction of only a few percent (≈4%). This find is consistent with an earlier experiment by Qin et al. (2010) that found an upper bound of 5% for the solubility of CO₂ at 293 K and 1.26 GPa. A small depression of the melt curve of water ice VI, when in saturation with CO₂, contradicts the findings of Manakov et al. (2009), who argued for much higher melt depressions (30–60 K). We refer the reader to Bollengier et al. (2013) for a consideration of this discrepancy.

If T_{VI}^{m}(P) is the melt curve of water ice VI for a pure water system, and ΔT is the melt depression due to saturation with CO₂, the solubility of carbon dioxide in mole fraction X_{CO₂} may be arrived at using the relation:

\[
\Delta T \left[ -S_{VI}(T_{m}^{VI}(P)) + S_{liq}(T_{m}^{VI}(P)) \right] = k(T_{m}^{VI}(P) + \Delta T)\ln \left( \gamma_{H,O}(1 - X_{CO₂}) \right),
\]

where \( k \) is Boltzmann’s constant and \( \gamma_{H,O} \) is the activity coefficient for water in the liquid phase. Below, we will discuss the activity coefficient used in this work.

In the brackets on the left, we have the entropy difference between pure water ice VI and liquid water along the melt curve. The solubility of CO₂ depends exponentially on this entropy of fusion. There are various values reported for the latter in the literature. Calorimetric measurements of the entropy or enthalpy of fusion of ice VI along its melt curve are scarce. One may derive the entropy of fusion from the gradient of the Clausius–Clapeyron equation, in cases where the volume difference at the phase transition is known. Because the latter involves the difference of two numbers that are similar, the volumes of the two phases must be known to high precision. Recent results show that the enthalpy of fusion of D₂O differs substantially from that of H₂O, which may explain part of the scatter in the literature (Fortes et al. 2012).

In Figure 1, we plot the entropy of fusion of ice VI along its melt curve. The data points from Bridgman (1912, 1937) give an entropy of fusion that is relatively constant along the melt curve of ice VI. The model of Dunaeva et al. (2010) yields the highest values for the entropy of fusion at high temperature. We further plot two models of our own. We use the melt curve equation suggested by the IAPWS for ice VI to derive its gradient. We further adopt the IAPWS equation of state for liquid water (Wagner & Pruss 2002) in order to derive its volume. In model I (see solid green curve), the volume for ice VI is taken from Choukroun & Grasset (2007). In model II (see solid red curve), the volume for ice VI is from the equation of state given by Bezacier et al. (2014). Clearly, model I deviates substantially from all other results. Model II coincides with the data reported in Bridgman (1912) and is derived with the most up-to-date equation of state for ice VI. We therefore use the

![Figure 1. Entropy of fusion of ice VI along its melt curve. Blue circles are data points from Bridgman (1912). Red squares are data points from Bridgman (1937). Solid magenta curve is the model of Dunaeva et al. (2010). The solid green curve is our model I, and the solid red curve is our model II. Refer to the text for model explanation. The dashed blue curve is our linear fit.](image-url)
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Figure 2: Solubility (mole fraction) of carbon dioxide in liquid water along the depressed melt curve of water ice VI. The green-shaded area is the solubility, assuming the binary H₂O–CO₂ is an ideal solution, whereas the red-shaded area accounts for the non-ideal behavior of the solution. To the left of the vertical dashed red line, the conditions along the ice VI melt curve coincide with the thermodynamic stability field of SI clathrates of CO₂. Therefore, to the left of this vertical separator, these clathrates govern the solubility of CO₂ in the water. To the right of the vertical dashed red line, the melt curve of ice VI is outside the thermodynamic stability field of CO₂ SI clathrates. The thick solid black curve is our prediction for the solubility of CO₂ in water, as governed by the presence of SI CO₂ clathrates (see Section 2.2), for the P-T conditions along the ice VI melt curve.

Data from Bridgman and our model II to create a linear fit:

\[
S_{\text{liq}}(T_m^{VI}(P)) - S_{VI}(T_m^{VI}(P)) = 2.4775 \times 10^{-19}T + 2.604 \\
\times 10^{-16} \left[ \frac{\text{erg}}{\text{molec} \times \text{deg}} \right],
\]  

(2)

where \( T \) is the temperature in K.

Using the melt depression data for ice VI from Bollengier et al. (2013) we derive the solubility of CO₂ in conditions along the depressed melt curve with the aid of Equation (1). In Figure 2, we present the resulting solubility for two cases. In the first case (green-shaded area), the mixture H₂O–CO₂ is assumed ideal. In the second case (red-shaded area), we model the non-ideal behavior with activity coefficients from Abrams & Prausnitz (1975). The shaded area is a result of the error in the measurement of the temperature in the experiment of Bollengier et al. (2013). The vertical dashed red line separates the melt curve of ice VI between the segment that is inside and the segment that is outside of the CO₂ SI clathrate hydrate stability field. In this subsection, we are solely interested in the part of the figure to the right of this vertical line. We note here that, if an ideal solution is assumed, the much higher melt depression suggested by Manakov et al. (2009) would have resulted in a solubility along the same melt curve in the range of 20%–35%, which is incorrect for such a high solubility.

An interesting feature present in Figure 2 is the existence of a minimum in the solubility along the melt curve of ice VI, at about 1100 MPa. Neither the pressure nor the temperature are constants along the melt curve of water ice VI; however, it is interesting to note here a high-pressure phenomenon found for isobaric solubilities. It is common knowledge that solubility decreases with increasing temperature. However, this behavior is pressure-dependent. It is experimentally known that, outside of the clathrate stability field, at high pressures, the isobaric solubility versus temperature has a minimum (e.g., Wiebe & Gaddy 1940). This phenomenon may be partly responsible for the minimum in solubility found by Bollengier et al. (2013) along the melt curve.

Extrapolating beyond the experimental data using Henry’s law for the solubility is risky due to it having several free parameters, the exponential term (i.e., Poynting correction), and most of all due to the ill-constrained behavior of the volume of infinite dilution at extreme conditions. However, the recent experimental data of Bollengier et al. (2013) and abundant low-pressure experimental data (e.g., Diamond & Akinfiev 2003) confine the solubility of CO₂ in liquid water at both the high- and low-pressure ends of interest for water planet oceans in the appropriate temperature range. In this work, we can therefore use Henry’s model for the solubility with relative confidence because it is used only to perform interpolations over the experimental data.

The classic thermodynamic approach, using Henry’s law, gives the following form for the mole fraction of CO₂ (\( X_{CO₂} \)) in solution with water (Carroll & Mather 1992):

\[
X_{CO₂} = \frac{f_{CO₂}}{H^{CO₂}} \exp \left\{- \int_{P_{vap}}^P \frac{v_{CO₂} dP}{kT} \right\},
\]  

(3)

where \( f_{CO₂} \) is the fugacity of fluid carbon-dioxide in mixture, derived using the Soave–Redlich–Kwong equation of state (Soave 1972), or of solid CO₂ above its melt curve (see Appendix A.1). \( H \) is Henry’s constant, derived from a fit to experimental data in the limit of a very dilute solution of CO₂.

We fitted all the tabulated data from Dhima et al. (1999) to the following polynomial:

\[
H(T) = -6.589x^5 + 46.67x^4 - 73.37x^3 - 145x^2 \\
+ 320.4x + 417.4,
\]  

(4)

where

\[
x = \frac{T - 354[\text{K}]}{80.63}.
\]  

(5)

This polynomial can explain 96.6% of the total variation in the data about the average, and is good between 278 and 643 K. Here, \( P_{vap} \) is the vapor pressure of water, taken from the NIST Chemistry WebBook (see Bridgeman & Aldrich 1964; Gubkov & Fermor 1964; Liu & Lindsay 1970); \( P \) is the total pressure; \( T \) is the temperature; and \( k \) is Boltzmann’s constant. The volume of infinite dilution, \( v_{CO₂}^{\infty} \), is not theoretically well-constrained. Based on the similarity between hydration shells and clathrate cages (Glew 1962), we model the volume of infinite dilution with an equation of state for the SI clathrate hydrate of CO₂ (see Equation (15)) using a volume of 34 cm³ mol⁻¹ at 273.15 K and 1 bar. This value was found by Carroll & Mather (1992) to be appropriate for temperatures below 100°C, Moore et al. (1982) also reported a value of 33.9 ± 0.4 cm³ mol⁻¹. See Figure 3 for the variation of the volume of infinite dilution with pressure and temperature, as modeled in this work.
The activity coefficient for carbon dioxide in water is $\gamma_{CO_2}$. In a thorough investigation, one should not approximate ideality for the solution, i.e., $\gamma_{CO_2} = 1$, as is assumed in the Krichevsky–Kasarnovsky equation. In order to account for the non-ideality of the $CO_2-H_2O$ system, we adopt the universal quasi-chemical (UNIQUAC) formalism for the activity coefficients (Abrams & Prausnitz 1975). Care is taken to insure that $\gamma_{CO_2}$ approaches unity in the limit $X_{CO_2} \rightarrow 0$, i.e., infinite dilution. Both the UNIQUAC and Functional-group activity coefficients (UNIFAC) of Fredenslund et al. (1975) describe the activity coefficient dependency on temperature and composition, although its dependency on pressure is still not known. The activity coefficient we adopt introduces a free parameter. Activity coefficients require, among other things, an estimation for the solute–solvent energy of interaction. In the theory of Abrams & Prausnitz (1975), the interaction between molecules of types A and B in a binary mixture is modeled by taking the geometric mean of the pure components’ enthalpy of sublimation:

$$U_{AB} = \hat{\alpha}\sqrt{U_{AA}U_{BB}},$$

where $\hat{\alpha}$ is an adjustable free parameter. The geometric mean is often used to estimate the interaction energy between unlike molecules from data derived for homogeneous systems (Hirschfelder et al. 1966). To the zeroth approximation, $\hat{\alpha} = 1$ (Abrams & Prausnitz 1975). Empirical potential energy functions take no account of the electronic structure of matter. Therefore, they are non-transferable. Their free parameters need to be adjusted so as to fit experimental data. As is often the case, the value of these free parameters has to be changed for different $P-T-x$ regimes; therefore, it is reasonable to expect that $\hat{\alpha}$ depends on the pressure. Up to a pressure of 825 MPa, we fit $\hat{\alpha}$ using a combined fit to both high-pressure solubility data and the dissociation curve of the CO$_2$ SI clathrate hydrate, thus maintaining consistency. In this pressure regime, we find it has the following form:

$$\hat{\alpha} = -5.961 \times 10^{-10}P^3 + 5.027 \times 10^{-7}P^2 - 0.0001757P + 1.071,$$

where $P$ is pressure in MPa. For even higher pressures, we use $\hat{\alpha}$ to somewhat improve the fit between Henry’s solubility model and the experimentally inferred solubility along the melt curve of ice VI. We find that, above 825 MPa, it has the following form:

$$\hat{\alpha} = \frac{T_{mVI}(P)}{288.18[K]}(1.271 - 0.00021337P[MPa]).$$

We find that, for the entire pressure range of interest to water planet oceans, $\hat{\alpha}$ falls between 1 and 1.1. Because Equation (6) is invariant to the exchange between components A and B, it would appear the same in the activity coefficient for water and for CO$_2$ in the solution. Therefore, this form for $\hat{\alpha}$ gives the pressure correction for both the activity coefficients of water and CO$_2$ in the binary solution.

In Figure 4, we show theoretical solubility interpolations for four isotherms: 50°C, 40°C, 25°C, and 15°C as a function of pressure, truncated at the transition to the depressed melt curve for water ice VI. From the experimental data for the 50°C isotherm, it is clear that the isothermal solubility has a maximum; the solubility measurements of Tödheide & Franck (1963) at lower pressures exceed the solubility estimates inferred at higher pressures from the Bollengier et al. (2013) data set. A maximum in solubility may be understood in the context of Equation (3), if the influence of the fugacity is dominant at low pressure, thus increasing the solubility with pressure, whereas the exponential factor (i.e., the Poynting correction) gains dominance at higher pressures, therefore decreasing the solubility. For example, the solubility of diatomic nitrogen in liquid water exhibits a maximum at around 0.27 GPa (see Prausnitz et al. 1999, and references therein), and such is the case for several aromatic hydrocarbons, as was shown by Sawamura (2007), reaching maximum solubilities around a pressure of 0.1 GPa. For the case of the $H_2O$–$CO_2$ system, we find that the sharp maximum is a result of the sharp change in the CO$_2$ fugacity gradient with pressure during the phase transition from fluid to solid CO$_2$.

Our interpolations fit the experimental data for the 50°C, 40°C, 25°C, and 15°C isotherms with absolute average deviations (AADs) of: 3.3%, 2.2%, 2.5%, and 3.4%, respectively. For the 50°C isotherm, the maximum solubility is 7.8 mol%, reached at a pressure of 0.75 GPa. For the 40°C isotherm, the maximum solubility is 7.2 mol%, reached at a pressure of 0.66 GPa. For the 25°C isotherm, the maximum solubility is 6.6 mol%, reached at a pressure of 0.53 GPa. For the 15°C isotherm, the maximum solubility is 6.5 mol%, reached at a pressure of 0.45 GPa.

When pressures are high, packing efficiency becomes a consideration. As long as carbon dioxide is a fluid, the volume occupied by a CO$_2$ molecule in its fluid-rich phase is $\approx$65 Å$^3$ (from liquid CO$_2$ bulk density). The volume added to the solution due to the expansion associated with the formation of hydration shells can be estimated from the partial molar volume at infinite dilution. Values from the literature suggest an added volume that could be as high as 63 Å$^3$ per added CO$_2$ molecule (Anderson 2002). However, the bulk density of solid CO$_2$ is much higher than that of the fluid of CO$_2$. In other words, the
volume occupied by a CO$_2$ molecule in its solid ($\approx 45$ Å$^3$) is much smaller than the volume added due to the formation of a hydration shell. This means that, beyond the CO$_2$ melt condition, the packing of the molecules under pressure would drive a rapid reduction in the solubility.

It is of interest to qualitatively examine the reasons why the solubility of carbon dioxide behaves as described in Figure 4, from a molecular point of view. In the process of dissolution of hydrophobic molecules, they become encapsulated in cavities made by water molecules, i.e., hydration shells. Let us first consider a CO$_2$ molecule that is part of a CO$_2$ rich environment, for example a CO$_2$ gas or a condensed particle. This CO$_2$ molecule may reach a boundary surface with a water-rich environment on the other side. With some probability, an opening may form in the water hydrogen bonds forming this boundary surface, through which the CO$_2$ molecule can thermally jump. Thus, when the hydrophobic solute molecule is in the water bulk, a water hydration shell should form around it to finalize the solvation. Each such step in the process happens with some probability that is governed by an activation energy.

Activation energies for the first steps of the process of dissolution may be estimated using simulations of SI CO$_2$ clathrate. This is based on the clathrate cage-like geometry of hydration shells encapsulating dissolved hydrophobic molecules (Glew 1962). Using molecular dynamics and Monte Carlo simulations, Demurov et al. (2002) found that an opening in the water rings forming clathrate cages must exist if CO$_2$ diffusion between cages via thermal hopping is to be enabled. The activation energy for forming such an opening in the

Figure 4. Carbon-dioxide solubility (mole fraction) in solution with liquid water, outside the clathrate stability field, for the isotherms 50°C (upper left panel), 40°C (upper right panel), 25°C (lower left panel), and 15°C (lower right panel). The solid (blue) curve is Henry’s model (see Equation (3)), used in this work to make interpolations. Solid (black) squares are data points generated from the software of Diamond & Akinfiev (2003). Green circles are experimental data from Wiebe & Gaddy (1939, 1940). Red circles are experimental data from Tödheide & Franck (1963). The magenta rhombus represents inferred solubility from the melt depression data of Bollengier et al. (2013), with its associated error. Theoretical interpolations are truncated at high pressure due to the transition to high-pressure water-ice polymorphs (i.e., bottom of the ocean).
hydrogen bond network of water molecules was found to be 1.31 eV.

Demurov et al. (2002) further suggested four possible thermal jumping routes for the carbon dioxide molecule in the SI clathrate hydrate. Two of them go through a pentagonal water ring, once from the small cage (51262, made of twelve pentagons) to the large cage (51262, made of twelve pentagons and two hexagons), and once the other way around. Two other routes represent jumps between two adjacent large cages, once via a pentagonal water ring and once via a hexagonal water ring. Each of the four different routes has a unique activation energy. Sato et al. (2000) have shown that CO2 is more soluble than CO in water, in contradiction to the rule of thumb that “like dissolves like,” due to the ability of CO2 to form two weak hydrogen bonds with water. Therefore, during the process of dissolution, the CO2 molecule passes from a non-hydrogen-bonded state to a weak hydrogen-bonded state. Khan (2003) has shown that, in the SI small cage, a CO2 molecule forms no hydrogen bonds with its enclathrating water molecules while forming two weak hydrogen bonds with its water surroundings in the large cage. The thermal jumping of CO2 from the small to large cages in the SI clathrate hydrate, with an activation energy of 0.1 eV, thus bears the strongest resemblance to CO2 transitioning from a CO2-rich phase into a water liquid cavity.

A crucial part is played by the activation energy associated with the CO2 encapsulation in a liquid water hydration shell. It is the sum of the work required to create the water hydration shell and the solute–solvent potential of interaction. For a solid sphere molecular model, the work necessary for creating a cavity in liquid water depends linearly on the pressure (Graziano 1998). We note that this linear dependence on the pressure is greatly enhanced because the activation energy sets the thermal probability of the process in an exponential manner via the Boltzmann factor. Therefore, at low pressures, the work required to create a hydration shell is relatively low, making the probability of cavity creation high, and the solubility simply increases with increasing fugacity. For high pressure, on the other hand, the work required is large and may cause the solubility to decrease. The CO2 potential of interaction with its liquid water surrounding is $-0.31$ eV (Sato et al. 2000).

We now turn to consider the solubility of carbon dioxide in water in the presence of carbon dioxide clathrates.

2.2. CO2 Solubility Inside Its Clathrate Hydrate Stability Field

We now wish to address the solubility of CO2 in liquid water while in equilibrium with CO2 clathrate grains. In particular, we are interested in the solubility value at the bottom of the wind-driven circulation, where pressures are on the order of 100 bar, and at the bottom of the ocean, where the pressure is approximately 10 kbar. Due to the importance of this issue, we will deal with it at length.

From a thermodynamic perspective, calculating solubilities is straightforward. One has to equate the chemical potentials of the different solution constituents between the various phases they occupy. This leads to some formulation that relates the solubility to the exponential of the constituents’ partial volumes. This line of reasoning was adequately executed by various authors in order to derive the solubility of CH4 and CO2 while in equilibrium with their respective clathrate hydrate phase (e.g., Handa 1990; Bergeron et al. 2010; Tsimpanganiamis et al. 2014). Implementation of this approach, however, relies on the availability of an equation of state that can accurately describe the mixture. When clathrate hydrates are a part of the modeled system, there is an additional complication where the equation of state of the empty clathrate hydrate (a metastable phase) is also required. Therefore, thus far models for the solubility in equilibrium with clathrate hydrate have only been implemented for pressures up to a few hundred bars.

A considerable effort was made to formulate the equation of state of the H2O–CO2 binary mixture. Such an equation of state for the temperature range of 273–533 K and up to 2 kbar was formulated by Duan & Sun (2003) and Duan et al. (2006). Mao et al. (2010) developed an equation of state for the system CO2–CH4–C2H6–H2–H2O–NaCl for the temperature range from 273 to 1273 K and for pressures up to 5 kbar. This is somewhat lower than the pressures prevailing at the bottom of our studied oceans. In addition, the equation of state parameters were obtained using a regression to experimental data. However, the data used to perform this fit does not extend above 350 bar for our temperature range of interest, 270–300 K. These elaborate equations of state are very important. However, they have a complex and non-intuitive form and they require a large number of parameters obtained by fitting to experimental data. Therefore, it is hard to assess their performance outside of the parameter space where experimental data exists. Below, we try to overcome this problem by adopting a semi-microscopic approach to estimate the solubility.

If the concentration of CO2 molecules in the clathrate grain and the surrounding liquid water differs, the system will tend to balance this difference. However, this tendency will be restrained by the different potential well depths the CO2 molecule occupies in the liquid water and in the clathrate hydrate structure. The transfer of a carbon dioxide molecule between the clathrate grain and the surrounding liquid water requires a strong enough thermal agitation to overcome the potential barrier characterizing this process. Thermal agitation or coupling to a heat bath may also be described as the action of Brownian forces. In other words, the migration of a CO2 molecule between the clathrate and the liquid water may be described using the Kramers theory of a Brownian particle escaping a potential well (Kramers 1940).

The flux of particles under a concentration gradient and the action of an external force is, in one dimension (Kramers 1940):

$$j = -D \frac{dU}{dT} n - D \frac{\partial n}{\partial x},$$

where $D$ is the molecular diffusion coefficient, $k$ is Boltzmann’s constant, $T$ is the temperature, $U$ is the external potential, and $n$ is the number density of the Brownian particles. When a dissolved carbon dioxide molecule joins the clathrate grain it experiences an energetic change as do the water molecules that compose its hydration shell in the liquid. Those must reorganize in order to form a clathrate cage from the liquid cavity. Therefore, the Brownian particle we are considering is a combination of the CO2 molecule and its surrounding water molecules. We shall return to this point later.

Assuming an equilibrium between the clathrate grains and the surrounding liquid, the net flux of CO2 between the two environments ought vanish, $j = 0$. Further integrating the last equation between the two states of entrapment for the CO2, we
obtain:

\[
\frac{n_{\text{CO}_2}^{\text{CO}_2}}{n_{\text{Clath}}} = e^{-\frac{1}{B}(U_{\text{liq}}-U_{\text{Clath}})},
\]

where \(n_{\text{CO}_2}^{\text{CO}_2}\) and \(n_{\text{Clath}}^{\text{CO}_2}\) are the number densities of CO\(_2\) dissolved in the liquid water and clathrate, respectively; \(U_{\text{liq}}\) and \(U_{\text{Clath}}\) represent the potential wells trapping the Brownian particle in the liquid water and clathrate, respectively.

The solubility of carbon dioxide in water in terms of abundance, in both the liquid water and clathrate may be written as:

\[
X_{\text{CO}_2}^{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{CO}_2}}{n_{\text{H}_2\text{O}}^{\text{liq}} + n_{\text{H}_2\text{O}}^{\text{clath}}},
\]

\[
X_{\text{Clath}}^{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{Clath}}}{n_{\text{Clath}}^{\text{Clath}} + n_{\text{H}_2\text{O}}^{\text{Clath}}},
\]

where \(n_{\text{H}_2\text{O}}^{\text{liq}}\) and \(n_{\text{H}_2\text{O}}^{\text{clath}}\) are the number densities of water molecules in the liquid and clathrate structure, respectively. With the definitions of Equation (11), Equation (10) may be written as:

\[
\frac{n_{\text{CO}_2}^{\text{CO}_2}}{n_{\text{CO}_2}^{\text{Clath}}} = \frac{n_{\text{H}_2\text{O}}^{\text{liq}} X_{\text{CO}_2}^{\text{CO}_2} 1 - X_{\text{CO}_2}^{\text{Clath}}}{n_{\text{H}_2\text{O}}^{\text{Clath}} X_{\text{CO}_2}^{\text{Clath}} 1 - X_{\text{CO}_2}^{\text{liq}}} = e^{-\frac{1}{B}(U_{\text{liq}}-U_{\text{Clath}})}.
\]

After some algebraic steps, the last relation yields the following form for the solubility in abundance, of carbon dioxide in liquid water in equilibrium with carbon dioxide clathrate grains:

\[
X_{\text{CO}_2}^{\text{CO}_2} = \frac{1}{\left(\frac{n_{\text{H}_2\text{O}}^{\text{liq}} X_{\text{CO}_2}^{\text{CO}_2} 1 - X_{\text{CO}_2}^{\text{Clath}}}{n_{\text{Clath}}^{\text{Clath}} X_{\text{CO}_2}^{\text{Clath}} 1 - X_{\text{CO}_2}^{\text{liq}}} e^{-\frac{1}{B}(U_{\text{liq}}-U_{\text{Clath}})} + 1\right)}.
\]

We now turn to estimate the different variables in the last equation.

The ratio of the number densities of water molecules in the liquid and clathrate phases should be estimated using the equations of state for water at the two phases. For liquid water, we use the equation of state of Wagner & Pruss (2002). We estimate the number density of water molecules in the clathrate hydrate of CO\(_2\) by dividing the number of water molecules in a SI clathrate unit cell, 46, by the unit cell volume:

\[
n_{\text{H}_2\text{O}}^{\text{Clath}} = \frac{46}{V_{\text{cell}}(T, P)}.
\]

Here, the CO\(_2\) SI clathrate hydrate unit cell volume, as a function of temperature and pressure, is modeled as:

\[
V_{\text{cell}}(T, P) = V_{\text{cell}}(T_0, P_0) \left(\frac{B + \bar{B}P}{B + \bar{B}P_0}\right)^{-1/\bar{B}}
\times \exp\left(\int_{T_0}^{T} \chi(T, P_0) dT\right).
\]

Experimentally, clathrate mechanical properties are difficult to derive. This is mainly due to the need to stay in the clathrate hydrate stability field during the experiment, in addition to the difficulty in forming and then experimenting on a pure clathrate hydrate sample (Ning et al. 2012). Therefore, molecular dynamic simulations are an important tool for calculating pure sample characteristics. For the volume thermal expansivity, we adopt the formulation from Hansen et al. (2016), obtained from diffraction experiments. From the molecular dynamics work of Ning et al. (2015), we derive a zero pressure bulk modulus of \(B = 8.5\) GPa for the CO\(_2\) SI clathrate hydrate, and a value of \(\bar{B} = 5.7\) for its pressure derivative. This is in agreement with the general value suggested for the bulk modulus of clathrate hydrates of 9 ± 2 GPa (Manakov et al. 2015). The volume thermal expansivity from Ning et al. (2015) is only about 17% larger than what is reported in Hansen et al. (2016). This may provide an estimation for the level of confidence in the calculation of Ning et al. (2015). The reference temperature, \(T_0\), and pressure, \(P_0\), should be taken to be 271.15 K and 0.12 MPa, respectively. For these reference values, an edge for the cubic SI unit cell of 11.98 Å is adopted (Ning et al. 2015).

In Figure 5, we plot the water number density ratio (liquid over clathrate) as a function of pressure for a 280 K isotherm. Hansen et al. (2016) report an uncertainty in the lattice parameter measurement of about 0.013 Å. This gives an uncertainty in the volume thermal expansivity of about \(3 \times 10^{-7}\) K\(^{-1}\). We find this error to be too small to have an effect on the number density ratio. We also vary the bulk modulus between 7 and 11 GPa. This produces an uncertainty that increases with pressure, reaching a maximum of 4% at 3% uncertainty in the derived solubility at the ocean’s bottom. The low error is due to the low pressure at the bottom of the ocean, relative to the probable bulk modulus of the clathrate.

The abundance of carbon dioxide in the clathrate is estimated by:

\[
X_{\text{Clath}}^{\text{CO}_2} = \frac{2X_{\text{small}}^{\text{CO}_2} + 6X_{\text{large}}^{\text{CO}_2}}{2X_{\text{small}}^{\text{CO}_2} + 6X_{\text{large}}^{\text{CO}_2} + 46},
\]

where we consider that each SI unit crystal is composed of 46 water molecules and eight cages: two small cages that are...
singly occupied by carbon dioxide, at a probability of $y_{\text{small}}^{\text{CO}_2}$; and six large cages, also singly occupied, at a probability of $y_{\text{large}}^{\text{CO}_2}$.

The probability of CO$_2$ entrapment in a cage of type $i$ obeys (van der Waals & Platteeuw 1959):

$$y_i^{\text{CO}_2} = \frac{\hat{f}_{i}^{\text{CO}_2} C_i^{\text{CO}_2}}{1 + \hat{f}_{i}^{\text{CO}_2} C_i^{\text{CO}_2}}. \quad (17)$$

The fugacity $\hat{f}_{i}^{\text{CO}_2}$ is again derived using the Soave–Redlich–Kwong (SRK) equation of state (Soave 1972). It was shown by Yoon et al. (2002, 2004) that this equation of state, in conjunction with the van der Waals and Platteeuw model for clathrates, can accurately predict the dissociation curve of various clathrates, including SI CO$_2$ clathrates. These authors were primarily concerned with low-to-medium pressures, up to approximately 1000 bar. At higher pressures, $\hat{f}_{i}^{\text{CO}_2} C_i^{\text{CO}_2} \gg 1$, and hence the form of Equation (17) would tend to minimize the effect of errors in the fugacity. Because we are below the critical point for CO$_2$ in our clathrate thermodynamic stability regime, we must model the fugacity of CO$_2$ both as vapor and liquid. This is accomplished within the SRK equation of state by taking the smaller (larger) compressibility root of the cubic polynomial to represent liquid (gaseous) carbon dioxide. We set the transition between liquid and gaseous carbon dioxide in the presence of water by adopting the experimentally derived Clausius–Clapeyron equation for CO$_2$ vapour pressure in mixture with water from Wendland et al. (1999). In cases where CO$_2$ is in its phase I solid state, we adopt the guest-host potential of interaction formalism given in McKoy & Sinanoğlu (1963). This formalism accounts for non-covalent forces only modeled by a Kihara potential. Potential parameters are obtained from the second virial coefficients tabulated in Hirschfelder et al. (1966), using empirical combining rules (see Hirschfelder et al. 1966, pp. 222–223). Applying density functional theory, Khan (2003) found that the CO$_2$ molecule also forms two weak hydrogen bonds with the water lattice when it is entrapped in the large cage. Each such weak hydrogen bond contributes an additional 2 kcal mol$^{-1}$ to the depth of the potential well occupied by the CO$_2$ molecule in the large cage. Intermolecular potential energies are often taken as the sum of two terms: a non-covalent and an electrostatic contribution (e.g., Horn et al. 2004; Abascal et al. 2005; Mohammadi-Manesh et al. 2009). Therefore, for the large cage, we again employ the model of McKoy & Sinanoğlu (1963), but add to it the contribution of the weak hydrogen bonding (i.e., the electrostatic contribution).

In Figure 6, we give the occupancy probabilities for a CO$_2$ molecule in the small $(y_{\text{small}}^{\text{CO}_2})$ and large $(y_{\text{large}}^{\text{CO}_2})$ cages of its SI clathrate hydrate versus pressure and for a 280 K isotherm. Our derived probabilities are in accordance with experimental data. One should keep in mind, however, that when forming clathrates in the laboratory, supersaturation (i.e., disequilibrium) is required in order to initiate the clathrate formation process. The measure of disequilibrium may influence the final measured clathrate composition, thus producing some scatter in the published clathrate compositions among the different experiments (see discussion in Circone et al. 2003). Therefore, according to Equation (13), this should also introduce some scatter between the different solubility experiments if their disequilibrium conditions were not similar.

In Figure 7, we show the variation with pressure of the abundance of carbon dioxide in its SI clathrate hydrate, $X_{\text{Clath}}^{\text{CO}_2}$, for four isotherms. In the pressure regime of a few tens of bars, the data from the literature is quite scattered. There is a general
consent that the large cage is fully occupied, albeit the reported data varies widely for the degree of occupancy of the small cage. Diffraction experiments, although carried out on deuterated rather then hydrogenated clathrates, find a degree of occupancy in the range of 60–80% for the small cage (Henning et al. 2000; Udachin et al. 2001), and sometimes as high as 90% (Ikeda et al. 1999). Analyzing the dissociation curve, Anderson (2003) found both the large and small cages to be fully occupied at 44 bar. For a pressure of 180 bar, Circone et al. (2003) reported that their sample of CO2 SI clathrate was fully occupied. In this work, we are mostly interested in the solubility in equilibrium with clathrates for pressures above 100 bar. Therefore, the uncertainty manifested by the scatter in the data for lower pressures should not result in substantial errors in the geophysical model developed below.

We now turn to estimate $U_{\text{liq}}-U_{\text{clath}}$, the difference in the potential wells trapping our Brownian particle in the liquid and clathrate water phases. As mentioned above, our Brownian particle is a combination of the CO2 molecule and its surrounding water molecules. Therefore, the difference in the potential wells is a superposition of both the difference in the CO2 interaction with the surrounding water structure between the liquid and clathrate phases ($\Delta E_{\text{CO2-H2O}}$), and the difference in the structural energy ($\Delta E_{\text{shell}}$) of the water-made shell influenced by the CO2 transition between the two phases:

$$U_{\text{liq}} - U_{\text{clath}} = \Delta E_{\text{CO2-H2O}} + \Delta E_{\text{shell}}, \quad (18)$$

where the indices liq and clath stand for liquid and clathrate water phases, respectively.

When an enclathrated CO2 molecule transfers to the liquid water, its solid hydration shell (i.e., clathrate cage) restructures to form the hydration shell in the liquid. The change in the hydration shell energy is the work invested in this restructuring. The total work, $\Delta W_{\text{shell}}$, is the sum of the work required to change the orientational configuration of the water molecules composing the shell, $\Delta W_{\text{shell}}$, and work done due to a possible volume change in a mechanical contact with a pressure bath:

$$\Delta E_{\text{shell}} = \Delta W_{\text{shell}} = \Delta \tilde{W}_{\text{shell}} - P \Delta V. \quad (19)$$

It was already suggested by Glew (1962) that the hydration shell in liquid water resembles clathrate cages. Bowron et al. (1998) used fine-structure X-ray absorption spectroscopy to probe the structure of a liquid water hydration shell and a clathrate hydrate cage for the case of a Kr solute. They found that the first peak in the radial distribution function occurs at the same distance in both the liquid and solid hydration shells. Based on this result, we will assume there is no volume change when the hydration shell transitions between the two phases, and thus $\Delta V = 0$. However, a change in the water molecules’ orientation is clearly seen, therefore:

$$\Delta E_{\text{shell}} = \Delta \tilde{W}_{\text{shell}}. \quad (20)$$

Thermodynamics tells us that the element of total work on a system in contact with a heat bath is equal to the difference in Helmholtz’s free energy:

$$dW = dU_{\text{int}} - TdS = d(U_{\text{int}} - TS) \equiv dF, \quad (21)$$

where $U_{\text{int}}$ is the internal energy. Let us consider a system in mechanical equilibrium with a pressure bath. The element of work on the system, not including expansion or contraction against the external pressure, obeys:

$$d\tilde{W} = dW - (-PdV) = dF + PdV = d(F + PV) \equiv dG, \quad (22)$$

where $G$ is Gibbs free energy, which, for a system in mechanical equilibrium with a pressure bath, obeys:

$$dG = -SdT. \quad (23)$$

This means that:

$$\Delta E_{\text{shell}} = \Delta \tilde{W}_{\text{shell}} = G_{\text{liq}} - G_{\text{clath}}. \quad (24)$$

To estimate the Gibbs free energy difference of a water molecule between liquid and solid, we draw an analogy to the theory of homogeneous nucleation and ice surface phenomena as described by Fletcher (1962, 1968). In the picture he describes, liquid water is made up of “flickering” molecular clusters, each made up of tens of molecules. In a thermodynamic regime where liquid water is stable, the clusters with minimum free energy are not the ones whose structure resembles that of ice. Therefore, ice-like clusters are rare in this thermodynamic regime. On the melting curve, the free energy of water molecules in ice-like and non-ice-like clusters becomes equal, except that the surface molecules on an ice-like cluster keep their total free energy high. When entering a state of supercooling, the free energy of a water molecule is lower in an ice-like cluster than in a non-ice-like cluster. However, only when fluctuations create an ice-like cluster that is big enough that the overall effect of the surface molecules is sufficiently diminished can such a cluster become stable and initiate a rapid phase transformation. We argue that, in the transformation of a CO2 molecule between clathrate and liquid water, several water molecules will also have to transform between a non-ice-like arrangement in the liquid state and an ice-like cluster in the clathrate solid. For a constant pressure, remembering that the free energy difference should vanish for melting conditions, we may therefore write:

$$\tilde{G}_{\text{liq}} - \tilde{G}_{\text{clath}} = -\int_{T_{\text{ref}}}^{T} (\tilde{S}_{\text{liq}} - \tilde{S}_{\text{solids}})dT \approx -\tilde{S}_{f}(T - T_{\text{melting}}), \quad (25)$$

where the tilde indicates that the variable is per water molecule. Having only an entropic contribution stems from considering the contribution of orientational configuration of the water molecules only, as discussed above, which is entropic in nature. The entropy difference between the two phases is estimated as the entropy of fusion, $\tilde{S}_{f}$. For ice Ih, the entropy of fusion is equal to $3.65 \times 10^{-16}$ erg K$^{-1}$ mole$^{-1}$ (see Lide 2004, for 0°C). In Figure 1, we have plotted the entropy of fusion for ice VI. Clearly, to a good approximation, the entropy of fusion is the same—even though ice Ih at 1 bar and the melt curve of ice VI span four orders of magnitude in pressure. Also from Figure 1, it seems that the entropy of fusion is insensitive to the temperature. Therefore, we will take the entropy of fusion to be a constant equal to the value above. In accordance with our analogy to the theory of homogeneous nucleation, the clathrate grain is basically a super-heated ice and the melting temperature is the ice to clathrate+liquid transition. We estimate the latter by the first quadruple point temperature taken to be 272.12 K (Yoon et al. 2002).
The difference in the potential wells (see Equation (18)) may thus be written as:

$$U_{\text{liq}} - U_{\text{clath}} = \Delta E_{\text{CO}_2-\text{H}_2\text{O}} - \eta S^\gamma (T - T_{\text{melt}}),$$

(26)

where $\eta$ is the number of water molecules included in a single Brownian particle that contains a single carbon dioxide molecule. Considering that, in a fully occupied SI clathrate hydrate, there are 5.75 water molecules per every carbon dioxide molecule, we expect $\eta \geq 5.75$. However, full occupancy is not always achieved in the laboratory, and values as high as seven water molecules per every carbon dioxide molecule have been reported (see Circone et al. 2003, and references therein).

The interaction of the CO$_2$ molecule with its surrounding water structure depends on the volume of the hydration shell, for both liquid and solid. Therefore, the difference in this interaction between the two phases may be written as:

$$\Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P, T) = \Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P_0, T_0) + \left( \frac{\partial \Delta E_{\text{CO}_2-\text{H}_2\text{O}}}{\partial P} \right)_{T_0} (P - P_0)$$

$$+ \left( \frac{\partial \Delta E_{\text{CO}_2-\text{H}_2\text{O}}}{\partial T} \right)_{P_0} (T - T_0).$$

(27)

Using the definitions for the bulk modulus, $B$, and for the volume thermal expansivity, $\chi$, one may obtain (after a few algebraic steps):

$$\Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P, T) = \Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P_0, T_0) - \left( \frac{V}{B} \frac{\partial E_{\text{liq}}}{\partial V} \right)_{T_0} (P - P_0)$$

$$- \left( \frac{V}{B} \frac{\partial E_{\text{clath}}}{\partial V} \right)_{\text{clath}, T_0} (P - P_0).$$

(28)

The volume thermal expansivity multiplied by a temperature difference of 10 K gives a dimensionless number on the order of $10^{-3}$. A pressure difference spanning our water planet ocean (about 1 GPa), divided by a bulk modulus appropriate for clathrates, gives a dimensionless number on the order of 0.1. Thus, corrections to the CO$_2$ interaction with its hydration shell (in either phase) due to thermal expansion are negligible in comparison to high-pressure compressional effects. Therefore, we may write:

$$\Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P, T) = \Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P_0, T_0) - \left( \frac{V}{B} \frac{\partial E_{\text{liq}}}{\partial V} \right)_{\text{liq}} (P - P_0)$$

$$- \left( \frac{V}{B} \frac{\partial E_{\text{clath}}}{\partial V} \right)_{\text{clath}, T_0} (P - P_0).$$

(29)

For $E_{\text{liq}}$, we adopt a value of $-4.97 \times 10^{-13}$ erg. This value was derived by Sato et al. (2000) using the polarizable continuum model describing the interaction of the CO$_2$ molecule with its liquid water surroundings, the latter being described as a dielectric continuum. This value for $E_{\text{liq}}$ includes the electrostatic interaction, as well as the dispersion and repulsion free energies. For the potential of interaction of the CO$_2$ molecule with its water surroundings in the clathrate, $E_{\text{clath}}$, we average the values for the small and large cages, weighted by their relative abundance in the unit cell. For the small cage, we find a potential of interaction of $-4.71 \times 10^{-13}$ erg. For the large cage, we find a value of $-6.17 \times 10^{-13}$ erg, which gives a value of $-5.80 \times 10^{-13}$ erg for $E_{\text{clath}}$. The energies of interaction differ by about 15% between the two phases. Therefore, the difference in the interaction energy is $\Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P_0, T_0) = 8.30 \times 10^{-14}$ erg. This is the same order of magnitude as the contribution from the Gibbs free energy difference derived above.

We now wish to estimate the correction to $E_{\text{clath}}$ due to the high pressure in the deep ocean. The clathrate equation of state (Equation (15)) gives a relative volume decrease of 7.3% over the depth of the ocean. This means the relative clathrate cage radii decrease by about 2.4%. Solving for the solute–solvent interaction, using the model of McKoy & Sinaoğlu (1963), once for the low pressure cage radii and once for the high-pressure values, gives an energy difference of $4.78 \times 10^{-14}$ erg. Therefore, the pressure correction is:

$$\left( \frac{V}{B} \frac{\partial E_{\text{clath}}}{\partial V} \right)_{\text{clath}} (P - P_0) \approx \frac{P [\text{GPa}]}{1.29 \times 10^{-13}} \left( \frac{1}{4.78 \times 10^{-14}} \right) \text{erg}. \quad (30)$$

At the bottom of the ocean, this is approximately $6 \times 10^{-14}$ erg, an order of magnitude less than $E_{\text{clath}}$. However, as is clear from Equation (29), we are interested in the pressure corrections between the two phases. Unfortunately, we do not have an equation of state for the hydration shell in the liquid for our pressure range of interest. However, if the findings of Bowron et al. (1998) may indeed be extended for the case of CO$_2$, there is reason to believe the two corrections ought be very similar, resulting in their difference being a small number. If this assumption is valid, we end up with the approximate form:

$$U_{\text{liq}} - U_{\text{clath}} = \Delta E_{\text{CO}_2-\text{H}_2\text{O}}(P_0, T_0) - \eta S^\gamma (T - T_{\text{melt}}). \quad (31)$$

As we discuss below, we compare the predictions of our model with high pressure solubility inferred from experiments. We find that our model agrees with experiments, within the experimental uncertainty, as long as the pressure correction to $E_{\text{liq}}$ is not more than 70% lower than the correction in Equation (30) or 20% higher than said pressure correction.

It is interesting to note that, because the fugacity multiplied by the Langmuir constant is much larger than unity (Levi et al. 2013), the probability for CO$_2$ entrapment in the clathrate is not a strong function of pressure. For pressures lower than the bulk moduli of water in liquid and clathrate phases, the water number density ratio may also be estimated as independent of pressure. Therefore, the solubility of carbon dioxide in liquid water in equilibrium with its clathrate (Equation (13)) should be a weak function of pressure. This is corroborated by several experimental works (e.g., Aya et al. 1997; Yang et al. 2000; Servio & Angelozzo 2001; Zatsipina & Buffett 2001; Kim et al. 2008).

We tested our theory against several experimental data sets, which are usually reported in isobaric form. We searched for the value of $\eta$ that gives a minimum AAD when compared to the data sets chosen. The 61 bar and 104 bar data sets of Yang et al. (2000) were well-fitted, with $\eta$ of 6.23 and 6.35 and AAD of 2.01% and 0.52%, respectively. These are well within the $\eta$ criterion mentioned above. The data sets for 20, 42, 50, and...
60 bar of Servio & Englezos (2001) were fitted with $\eta$ of 3.17, 4.11, 5.32, and 5.48, with AAD of 1.07%, 2.55%, 3.11%, and 1.76%, respectively. These values for $\eta$ are below the theoretical minimum of 5.75. One possible explanation is that our chosen parameters may be in error. However, if it is due to an issue in the experiment, then it must be pressure-related, because when a larger isobar is tested, the value for the fitted $\eta$ increases, approaching the minimum of 5.75. For the 300 bar data set reported in Aya et al. (1997), we find that a value of $\eta = 6.11$ fits the experimental data with AAD of 2.15%, again complying with the theoretical requirement. Finally, the four salt-free isobars of 101, 121, 151, and 201 bar, reported in Kim et al. (2008), were best fitted with $\eta$ values of: 5.90, 5.60, 5.62, and 5.93 respectively; the AADs for these four fits are: 1.27%, 1.19%, 1.84%, and 2.33%, respectively. We argue that our theory may provide an indirect method for approximating the clathrate composition from solubility data.

In Figure 8, we plot our theoretically predicted isobaric carbon dioxide solubility in equilibrium with its clathrate hydrate versus temperature. In each panel, the theoretical solubility shown is the one that gave the lowest AAD, by adjusting $\eta$ as explained above, in comparison to the specific experimental data set also shown in the same panel.

The above comparison with experimental values for the solubility indicates that our theory is capable of modeling the solubility in equilibrium with clathrates up to pressures of a few hundred bars. As we will discuss below, this is sufficient for modeling the bottom of the wind-driven circulation.

In Figure 2, we have estimated the solubility of CO$_2$ along the melt curve of ice VI from the experiments of Bollengier et al. (2013). As is shown in Figure 2, in their experiments, Bollengier et al. (2013) reach and may even cross into the CO$_2$ SI clathrate hydrate thermodynamic stability field (left of the vertical red dashed line). Within this narrow domain, our model predicts a solubility that is within the experimental error.

As shown in Figure 2, there is a clear trend in the solubility in the domain of the clathrate stability field. Clearly, there is a particular trend in the solubility characterizing the immediate domain around the vertical red dashed line. This trend is obtained for the case of the non-ideal solution, using Henry’s law for the solubility. In equilibrium, on the phase boundary of the clathrate stability field (on the vertical red dashed line), Henry’s law for the solubility should hold. It is reasonable to infer that kinetic inhibition ought to widen the phase transition boundary. Therefore, in the immediate region around the vertical red dashed line in Figure 2, Henry’s law should hold true and properly represent the solubility in equilibrium with the appropriate clathrate hydrate. Thus, the trend in the solubility in this immediate region is probably real and a consequence of the behavior of the solubility when in equilibrium with clathrates. Although the model presented in this subsection for the solubility in equilibrium with clathrates is derived independently of Henry’s law, we see in Figure 2 that it predicts the same trend in the solubility along the ice VI depressed melt curve. We therefore conclude that our model for the solubility in equilibrium with clathrates also agrees with experiments at pressures prevailing at the bottom of our water planet oceans.

To summarize, in this subsection, we have attempted to model the solubility of CO$_2$ in water while in equilibrium with its clathrate grains. The model of Equation (13) predicts two general behaviors: the first is that the solubility decreases with decreasing temperature, and the second is that the solubility along an isotherm is relatively constant (i.e., it does not increase much) with increasing pressure when in equilibrium with clathrates. Our model predicts these behaviors should hold true in the range from the low-pressure end of the clathrate dissociation curve, up to the pressures prevailing at the bottom of a water planet ocean. We show that these predicted behaviors are verified experimentally at the lower-pressure end of the desired regime, as shown in Figure 8. They are also verified using data inferred from experiments at the higher pressures prevailing at the ocean bottom. Therefore, our model ought to be considered interpolative rather than extrapolative.

For purposes of clarity (and to be used later in the paper), in Figure 9 we plot CO$_2$ solubility profiles versus pressure for two isotherms. The solid and dashed blue curves are for the 275 K isotherm, and the solid and dashed red curves are for the 280 K isotherm. The two dashed curves represent the solubility when in equilibrium with liquid/solid CO$_2$: they are derived by solving Equation (3) for the entire oceanic pressure range, for the two isotherms. They represent a continuation of Henry’s law for the solubility into the clathrate hydrate stability field. The solid curves span the low-pressure solubility outside of the CO$_2$ SI clathrate thermodynamic stability field (solved by Equation (3)) and the solubility in the presence of CO$_2$ SI clathrates when entering their thermodynamic stability field (solved by Equation (13)). The jump seen in the solubility in each of the solid curves is at the clathrate dissociation pressure for the given isotherm. As discussed above, the CO$_2$ solubility in the presence of clathrates remains fairly constant with pressure. It is also clear from the figure that, when outside the clathrate stability field (i.e., the low-pressure end of the solid curve), the solubility increases with decreasing temperature; in the presence of clathrate grains, the solubility increases with increasing temperature. In addition, within the deep ocean, clathrates tend to keep the level of solubility of CO$_2$ much lower than what is predicted by assuming equilibrium with either liquid or solid of CO$_2$ (point $D$ gives a solubility that is higher than at point $B$, by a factor of about 2.2).

We also wish to note the required formation conditions within the ocean of CO$_2$ SI clathrate hydrate grains. Points $A$ through $D$, in Figure 9, all sit along an isobar; therefore, they represent some depth level in our approximated 280 K isothermal ocean. Although the temperature and pressure conditions shared by all these points fall in the thermodynamic stability field of CO$_2$ SI clathrate, that does not mean a clathrate grain placed under such conditions would necessarily be stable. For example, a CO$_2$ clathrate grain placed under conditions represented by point $A$ would see a CO$_2$ subsaturated (with respect to clathrates) liquid water environment and would diffuse its CO$_2$ to the surrounding water and dissociate. In other words, if the CO$_2$ abundance in liquid water is below the saturation value for equilibrium with clathrates (solid red curve for the 280 K isotherm), then clathrate grains will not form from the CO$_2$ dissolved in the ocean. If conditions in the ocean were perturbed to equal that of point $A$, for example, no clathrates would form at the reference depth. For CO$_2$ abundances above point $B$, the depth level examined becomes over-saturated with respect to clathrates, and they begin to form as grains directly from the CO$_2$ dissolved in the ocean. In a case where the ocean was perturbed such that conditions were equal to those represented by point $C$, clathrate grains would readily form. They would sink to the bottom of the ocean, taking along
local CO₂ and decreasing the abundance of CO₂ at the examined depth back toward point B.

Finally, in Figure 10, we plot the solubility of CO₂ in abundance, as a function of temperature in equilibrium with CO₂ SI clathrate grains. The plot is for an oceanic depth matching an isobar of 0.16 GPa. The temperature range spans the minimum and maximum temperatures for which a CO₂ SI clathrate is thermodynamically stable for the given isobar. According to this figure, if a water planet’s ocean was warmer at an earlier stage of its life, then that ocean was able to dissolve more CO₂ before clathrate grain formation ensued. In addition, as the ocean cools and CO₂ solubility with respect to clathrates decreases, any excess in the dissolved CO₂ with respect to the lower solubility would form clathrate grains and sink to the bottom.

With the solubility of freely dissolved CO₂ in water analyzed, we turn to build the phase diagram of the SI CO₂ clathrate hydrate, spanning conditions appropriate for water planets.

### 3. The CO₂ SI Clathrate Phase Diagram

We adopt the theory of van der Waals & Platteeuw (1959), based on the theory of solid solutions, in order to derive the phase diagram for the SI CO₂ clathrate hydrate. On the boundaries of the thermodynamic stability field of a clathrate hydrate with either ice Ih or liquid water, the chemical potential of the clathrate equals that of the other water phase with which it is in contact:

\[ \mu_{\text{H}_2\text{O}}^\text{clathrate} = \mu_{\text{H}_2\text{O}}^\alpha \]

where the \( \alpha \) phase represents either ice Ih or liquid water. For the chemical potential of water ice Ih, we adopt the formalism of Feistel & Wagner (2006). The chemical potential of liquid
temperature, and $\gamma_{\text{H}_2\text{O}}$ is the activity coefficient for water in solution derived using the UNIQUAC method of Abrams & Prausnitz (1975). The latter method is discussed in Section 2.1. The abundance of water in solution, $X_{\text{H}_2\text{O}}$, is the difference from unity of the abundance of CO$_2$ in solution. The latter is calculated using Equation (13), because the water solution is in equilibrium with the clathrate phase on its dissociation curve.

According to the theory of van der Waals & Platteeuw (1959), the chemical potential of a clathrate may be represented as a sum of two terms: the chemical potential of the empty clathrate hydrate (i.e., the $\beta$ phase), and the contribution of the stabilizing guest molecules. Therefore, for a pure clathrate where carbon dioxide is the sole guest species, we may write the following:

$$
\mu_{\text{H}_2\text{O}}^{\text{clathrate}} = \mu_{\text{H}_2\text{O}}^\beta + kT \sum_{i=1}^{2} \nu_i \ln (1 - y_i^{\text{CO}_2}).
$$

(34)

Here, $\nu_i$ is the ratio between the number of $i$ type cages to water molecules per cubic unit crystal. The probability that a CO$_2$ molecule occupies a type $i$ cage, $y_i^{\text{CO}_2}$, is given explicitly in Equation (17). The summation is carried out over the two types of cages formed in the SI clathrate crystal.

The dependency of the empty clathrate hydrate chemical potential on both the pressure and temperature was first given by Holder et al. (1980), in terms of a difference between the empty clathrate hydrate and the other water phase in contact. This method of difference does not account for the extensive experimental knowledge accumulated for liquid water and ice Ih, as compared to that accumulated for clathrates. Therefore, for the $\beta$ phase alone, we write:

$$
\frac{\mu_{\text{H}_2\text{O}}^{\beta}(T, P)}{kT} = \frac{\mu_{\text{H}_2\text{O}}^{\beta}(T_0, P_0)}{kT_0} - \frac{H^{\beta}(T', P_0)}{kT_0^2} dT' + \frac{1}{kT} \int_{P_0}^{p} V^{\beta}(T, P') dP',
$$

(35)

where:

$$
H^{\beta}(T', P_0) = H^{\beta}(T_0, P_0) + \int_{T_0}^{T'} C_p^{\beta}(\tau, P_0) d\tau.
$$

(36)

Here, $H^\beta$ is the enthalpy of the empty hydrate, $V^\beta$ is its volume, $C_p^{\beta}$ its isobaric heat capacity, and $T_0 = 273.15$ K and $P_0 = 0.135$ MPa are our reference temperature and pressure, respectively. The $\beta$ phase is not stable; thus, one cannot characterize it experimentally. In addition, each kind of guest molecule distorts the water clathrate hydrate lattice surrounding it somewhat differently (Klauda & Sandler 2000). Therefore, both the empty clathrate chemical potential and its enthalpy at the reference temperature and pressure are taken to be free parameters. A fit to the experimental dissociation pressure data sets of the CO$_2$ clathrate yields values of $\mu_{\text{H}_2\text{O}}^{\beta}(T_0, P_0) = 5.937 \times 10^{-14}$ erg molec$^{-1}$ and $H^{\beta}(T_0, P_0) = -5.186 \times 10^{-14}$ erg molec$^{-1}$. Estimating the enthalpy of the empty clathrate hydrate as prescribed in Equation (36), we also need to estimate its isobaric heat capacity. A good approximation for the latter is the isobaric heat capacity of ice Ih (Avlonitis 1994). Finally, the CO$_2$ SI clathrate equation of state for the crystal cell volume (see Equation (15)) is used to estimate $V^\beta$. 

---

**Figure 9.** CO$_2$ solubility [mole fraction] profiles vs. pressure for two isotherms: 275 K (solid and dashed blue curves) and 280 K (solid and dashed red curves). The jump in solubility in the solid curves is at the clathrate dissociation pressure for each of the two temperatures. The jump represents the transition into the clathrate thermodynamic stability field where the solubility is fairly constant with pressure. For each isotherm, the dashed curve is the continuation of the solubility, assuming no clathrates are present (see Equation (3)).

**Figure 10.** Solubility of CO$_2$ [mole fraction] in equilibrium with its clathrate grains vs. temperature. The curve is for an isobar of 0.16 GPa, and the temperature range is that spanning the clathrate thermodynamic stability field for this pressure level.

Water in solution with CO$_2$ may be written as a superposition of two terms: one for the pure liquid water, and a correction for it being in a non-ideal solution (Denbigh 1957):

$$
\mu_{\text{H}_2\text{O}}^{\text{liq}} = \mu_{\text{H}_2\text{O}}^{\text{liq, pure}} + kT \ln (\gamma_{\text{H}_2\text{O}} X_{\text{H}_2\text{O}}).
$$

(33)

The chemical potential of pure liquid water is accurately given in Wagner & Pruss (2002), and is adopted here. In the solubility correction term, $k$ is Boltzmann’s constant, $T$ is the temperature, and $\gamma_{\text{H}_2\text{O}}$ is the activity coefficient for water in solution derived using the UNIQUAC method of Abrams & Prausnitz (1975).
Regarding our adopted values for the reference empty clathrate hydrate parameters, there are references in the literature for the empty clathrate hydrate chemical potential (see discussion in Dharmawardhana et al. 1980). Our suggested value is larger than that given in Dharmawardhana et al. (1980) by a factor of 2.75. This is a result of the approach we adopt to modeling clathrates, where instead of optimizing the guest-host potential of interaction parameters, we explicitly account for the weak-hydrogen bonding between CO$_2$ and the water host lattice. As a consequence, the empty clathrate hydrate reference chemical potential and enthalpy need to be optimized. This is based on the idea that every guest specie has its own reference empty clathrate hydrate lattice. The value in Dharmawardhana et al. (1980), which is often adopted, is from measurements for the clathrate hydrate of cyclopropane. This bigger guest molecule only occupies the large cage of the SI clathrate, and thus does not distort the SI small cage, contrary to the case when CO$_2$ is the guest molecule. Thus, for the case of CO$_2$, its empty reference clathrate hydrate should be even less stable than the reference lattice for the case of cyclopropane. This is manifested in our adopted larger value for $\mu_{H_2O}^{\nu}$ ($T_0$, $P_0$).

In Figure 11, we plot the CO$_2$ SI clathrate hydrate phase diagram. The solid red curve is the melting curve of water ice Ih, including the melting point depression due to the effect of CO$_2$ on the liquid water chemical potential. In calculating this melting point depression, care was taken in choosing the appropriate solubility model when crossing into the CO$_2$ SI clathrate hydrate stability field. The dashed light green curve is the melting curve for water ice III, the dashed black curve is the melting curve for water ice V, and the dashed cyan curve is the melting curve for water ice VI (taken from the IAPWS Revised Release on the Pressure Along the Melting and Sublimation Curves of Ordinary Water Substance, 2011 September), all in the pure water system. The solid brown curve is the depressed melt curve of water ice VI when in contact with an aqueous solution saturated in CO$_2$ from the experiments of Bollengier et al. (2013). The solid blue curve is the boundary of the thermodynamic stability regime of the CO$_2$ SI clathrate hydrate. The clathrate hydrate is thermodynamically stable to the left of this curve. At temperatures below the ice I$_h$ melting temperature, the solid blue curve represents a three-phase curve of H-ice I$_h$-CO$_2^{\text{vap}}$. For temperatures higher than the ice I$_h$ melting temperature, the solid blue curve represents three different three phase curves of: H-ice I$_h$-CO$_2^{\text{vap}}$, H-Lw-CO$_2^{\text{vap}}$, and H-Lw-CO$_2^{\text{solid}}$, in succession of increasing pressure. Here, H stands for clathrate hydrate, Lw stands for liquid water solution with CO$_2$, and CO$_2$ is the $\beta$ phase of CO$_2$. At pressures above the melting curve of water ice VI, the blue line denotes the three phase curve H-water ice-CO$_2^{\text{solid}}$. The solid dark green curve is a segment of the pure phase I solid CO$_2$ melting curve (Span & Wagner 1996). The solid light green curve is the vapor pressure curve for CO$_2$ in the presence of water, and the red square is its critical point (see Wendland et al. 1999; Diamond & Akinfeev 2003). The high-pressure arm of the dissociation curve of the CO$_2$ SI clathrate hydrate (solid blue) and the dashed red curve confine the probable stability field of a newly discovered phase called CO$_2$ filled ice (Hirai et al. 2010; Bollengier et al. 2013; Tulk et al. 2014), whose structure was only recently analyzed (see Tulk et al. 2014). The shaded area emphasizes the region where SI CO$_2$ clathrate hydrates can coexist with a solution of liquid water and dissolved CO$_2$.

Still in Figure 11, the solid black curve is where the bulk mass density of our water-rich liquid equals that of fluid carbon-dioxide. In obtaining the latter curve, the mass density of fluid carbon-dioxide was modeled using the formulation in Span & Wagner (1996). We have assumed the solubility of water in the fluid of carbon-dioxide to be negligible (see discussion in Teng et al. 1997). The water-rich liquid was modeled using the equation of state for pure water (Wagner & Pruss 2002), and corrected for the effect of the solubility of CO$_2$ on the density, using the method of Teng et al. (1997). We assume that our water liquid is saturated with CO$_2$. The results of Teng et al. (1997) are in agreement with solution densities from Hebach et al. (2004) and Garcia (2001). We see from Figure 9 that clathrates tend to keep the solubility of CO$_2$ lower than the value found when in equilibrium with the pure fluid of CO$_2$. Therefore, the pure fluid of CO$_2$ is not stable within the stability field of CO$_2$ SI clathrate hydrates. Consequently, the black curve is derived only outside of the clathrate stability field, and the solubility of CO$_2$ there is modeled using Henry’s law (see Equation (3)).

We see from Figure 11 that phases that are potential rich reservoirs of CO$_2$ are in direct contact with the bottom of the ocean. Therefore, it is likely that deep mantle CO$_2$ enters the ocean. How this CO$_2$ can be stored in the deep ocean, and its

![Figure 11](https://example.com/figure11.png)
transport to the atmosphere, are the subjects of the following sections.

4. Deep Reservoirs for CO₂ in Water Planet Oceans

Considering a secondary atmospheric outgassing, most of the CO₂ outgassing occurs at a later stage in the planet’s history. In this case, as solid state convection is initiated, along with outward transport of CO₂, the ocean may be initially subsaturated with respect to CO₂. Making its way into the ocean, the sinks available to CO₂ depend primarily on the thermal profile in the deep to mid ocean. In Figure 12, we show that there are three possible stratification cases (denominated as: α, β, and γ), and we shall deal with each one of them separately in this section. For each of the three cases, we present a quantitative example solution for the reservoirs’ capacity to store carbon using an isothermal profile in the ocean. The real thermal profile will not be isothermal. For example, an ocean thermal profile with a surface temperature beginning in the β domain may largely fall in the type α domain in a case where the temperature decreases with depth in the ocean. Although the isothermal profile is a good first approximation for our analysis of the deposition budget of carbon at the bottom of the ocean, a more exact thermal profile

![Figure 12](image)

**Figure 12.** In this figure, we divide (using vertical thick dashed red lines) the phase diagram of CO₂ SI clathrate hydrate into three domains, each having a different stratification for the sinks of carbon dioxide at the bottom of the ocean. In the α domain, the carbon dioxide sink is solely in the form of a clathrate hydrate layer. In the β domain, a mid-ocean SI CO₂ clathrate hydrate layer forms, while a strata composed of phase I solid CO₂ may accumulate beneath it. In the γ domain, the first layer is composed of phase I solid CO₂, followed by liquid CO₂, ending when the latter becomes less dense than liquid water. The solid red curve is the melting curve of water ice Ih, including the melt depression due to carbon-dioxide. Dashed light green, black, and cyan curves are the melting curves for water ice III, V, and VI, respectively. The solid brown curve is the ice VI depressed melt curve. The solid blue curve is the boundary of the thermodynamic stability regime of the CO₂ SI clathrate hydrate, i.e., the dissociation curve. The hydrate survives to the left of this curve. The solid dark green curve is a segment of the pure phase I solid CO₂ melting curve. The solid light green curve is the vapor curve for CO₂ in the presence of water, and the red square is its critical point. The solid black curve is where the bulk mass density of water rich liquid and fluid carbon-dioxide equals out. The horizontal thin red dashed curve is a possible high-pressure boundary for CO₂ filled-ice stability. The shaded area is as in Figure 11. Solid circles are data points (see Figure 11).

of the ocean ought be derived, when considering a particular water planet, by using its particular energy balances.

4.1. The α Domain

In this case, the bottom of the ocean is composed of either water ice V or VI, if no CO₂ is present. In the presence of CO₂, it is composed of a SI CO₂ clathrate hydrate layer. The clathrate hydrate layer may overlie a CO₂ filled-ice layer in this case, although more experimental data is needed to verify this. However, it is the clathrate layer that will be in direct contact with the overlying ocean, controlling the chemical and physical interaction between mantle and ocean.

![Figure 13](image)

**Figure 13.** CO₂ embedded in the ice mantle is transported outward, along with the ice convection. Upon entering the clathrate thermodynamic stability field, it transforms into CO₂ SI clathrate hydrate. This clathrate layer then becomes the ocean’s bottom surface, consequently making physical contact with the overlying ocean. In the case where the ocean is subsaturated with respect to CO₂, the CO₂ from the clathrates diffuses into the ocean. We refer to this mechanism as the “gentle” outgassing mechanism.

The flux of CO₂ from the ice mantle and into the ocean is dependent on its ability to incorporate into, and be transported with, the mantle water ice convection cell. The flux also depends on the geological behavior of the ice boundary layer composing the ocean’s bottom surface. For example, it is important to know whether this ice boundary layer is rigid, and thus internal CO₂ has to diffuse through it to reach the ocean, or it is breakable, thereby directly exposing the ocean to internal CO₂.

In the case of the α domain, deep ice mantle CO₂ transported outward should transform, along with the water ice surrounding it, into CO₂ SI clathrate hydrate upon entering the latter thermodynamic stability field (see Figure 13). In the case where the ocean is initially subsaturated with respect to CO₂, this clathrate layer at the top of the convection cell (also composing the ocean’s bottom icy surface) would spontaneously revert back to ice V (or VI) and release its CO₂ into the ocean. This mechanism for releasing CO₂ into the ocean may be regarded as “gentle,” meaning it requires no violent geological mechanisms that would break up the ice forming the ocean’s
bottom in order to directly inject CO$_2$ into the ocean. This mechanism can only strive to saturate the ocean with CO$_2$. Once the ocean approaches saturation (CO$_2$ concentration approaches the solubility value in equilibrium with clathrates), the CO$_2$ SI clathrate ice layer composing the ocean bottom begins to stabilize and the “gentle” mechanism shuts off. Consequently, additional mantle CO$_2$ transported outward by the convection cell would not be forced to enter the ocean and would simply continue to cycle internally in the mantle, along with the high-pressure water ice convection cell.

Experiments show that the dissolution of clathrate hydrate in seawater is diffusion-limited. In an interesting experiment, Rehder et al. (2004) placed blocks of CO$_2$ SI clathrate hydrates on the bottom of the ocean, at a depth of 1028 m. With the aid of underwater cameras, they measured the dissolution rates of the clathrate hydrate blocks. The clathrates dissolved due to their placement in an environment subsaturated in CO$_2$ with respect to clathrates. This field experiment clearly shows that the dissolution rate depends on the ability of CO$_2$ to diffuse away from the surface of the clathrate hydrate block and into the bulk ocean. For an ocean that energetically cannot maintain a general circulation, and does not establish convection cells, the extent of the diffusive boundary layer right above its bottom is on the same order of magnitude as the ocean’s depth. Under such circumstances, the “gentle” mechanism would require a timescale of $L_{\text{ocean}}^2/D_{\text{eddy}}$ to bring the ocean close to saturation. Here, $D_{\text{eddy}}$ is the vertical eddy diffusion coefficient for the deep ocean, and $L_{\text{ocean}}$ is the ocean’s depth. We shall return to elaborate on this point in the following sections.

However, one must bear in mind that this timescale requires that the underlying mantle convection cell be able to transport CO$_2$ with enough efficiency to constantly maintain a clathrate hydrate layer at the bottom of the ocean (top of the convection cell). A full investigation of the ability of the convection cell to transport CO$_2$ outward is in order, but this will depend on the particular characteristics of a given planet.

For the case where more vigorous geological forces are at work, resulting in a flux of internal CO$_2$ into the ocean that is kept higher than what the “gentle” mechanism prescribes, the ocean may try to over-saturate with CO$_2$. The outcome of this over-saturation depends on the bulk mass densities of SI CO$_2$ clathrate grains and the ocean’s water rich liquid. In Figure 14, the ocean’s water-rich liquid is considered saturated with CO$_2$. In the $\alpha$ domain, saturation is the solubility of CO$_2$ when in equilibrium with the clathrate hydrate phase. The mass density correction to the pure liquid water mass density, due to the dissolved CO$_2$, is derived using the work of Teng et al. (1997). We estimate the bulk mass density of a CO$_2$ SI clathrate hydrate grain as:

$$\rho_{\text{clath}} = \frac{46m_w + 2m_{\text{small}} + 6m_{\text{large}}}{V_{\text{cell}}}. \quad (37)$$

Here, $m_w$ and $m_{\text{CO}_2}$ are the masses of a water molecule and a CO$_2$ molecule, respectively. The definitions of the other parameters are the same as in Section 2.2. Also see Section 2.2 for a discussion of the uncertainty in the clathrate hydrate bulk modulus.

Figure 14. Bulk mass densities spanning the depth of the ocean for an isotherm of 275 K. The solid red curve is a water-rich liquid assumed to be saturated with CO$_2$. The chosen isotherm is within the SI CO$_2$ clathrate hydrate stability field. Therefore, the solubility of CO$_2$ is governed by its equilibrium with the clathrate hydrate phase. The solid blue curve is the bulk mass density of SI CO$_2$ clathrate hydrate for a bulk modulus of 8.5 GPa. Upper and lower dashed blue curves are the bulk mass densities of SI CO$_2$ clathrate hydrate for bulk moduli of 7 and 11 GPa, respectively.

From Figure 14, we see that the SI CO$_2$ clathrate grain is more dense than the water-rich liquid across the entire ocean’s depth, for temperatures in the $\alpha$ domain. Consequently, if the ocean tries to over-saturate (reaching CO$_2$ concentrations above the solubility in equilibrium with clathrates, e.g., point C in Figure 9) the excess CO$_2$ outgassed from the ice mantle and into the ocean would form CO$_2$ SI clathrate grains. These grains will sink, due to their high density, and pile up on the ocean’s bottom rather then reach the atmosphere.

As a simple example, we consider a constant CO$_2$ flux from the mantle and into the ocean. Such a flux should eventually saturate the ocean, initiating an inner oceanic “rain” of sinking clathrate grains. With time, these will thicken the clathrate hydrate layer already composing the ocean’s bottom surface. This constant flux may be low, and consequently the SI CO$_2$ clathrate hydrate layer that will pile up on the ocean’s bottom will be quite thin (see right panel in Figure 15). On the other hand, the constant flux may be high enough, and the pile-up of clathrate grains on the bottom surface fast enough, that, again, in a geological timescale most of the ocean solidifies as a single global clathrate layer (see left panel in Figure 15). In the latter scenario, any further outgassing of CO$_2$ will have to end up in the atmosphere.

The constant flux model can be quantified. Let us assume that the ocean became saturated with CO$_2$ (with respect to equilibrium with clathrates) at $t = 0$. The rate at which water molecules from the ocean solidify due to formation of clathrate grains is:

$$5.75F_{\text{CO}_2}4\pi R_p^2, \quad (38)$$

where $R_p$ is the planetary radius and the constant flux of CO$_2$ from the mantle and into the ocean is $F_{\text{CO}_2}$. We also considered that, in a full clathrate crystal, every CO$_2$ molecule requires 5.75 water molecules. Due to the growing hydrate layer, the
The concentration of CO₂ reached the solubility value in equilibrium with clathrates. Any further CO₂ entering the ocean will thus sink as clathrate grains. In the right panel, the flux of CO₂ is low enough that, even after billions of years, little clathrate hydrate was accumulated around active CO₂ sources. In the left panel, the flux was high enough that the entire CO₂ SI clathrate hydrate stability field solidified. In the latter case, what remains of the ocean has a higher salinity than the original deep ocean.

Finally, let us consider the 275 K isotherm in the α domain (see Figure 12), and solve for the particular end scenario where the CO₂ flux from the mantle and into the ocean was high enough that the entire clathrate stability field solidified. We further assume that any additional CO₂ outgassed from within ended up in the atmosphere, due to the exhaustion of the ocean’s ability to sink CO₂ as clathrate. For this isotherm, the CO₂ SI clathrate hydrate thermodynamic stability field spans the pressure range of 1.6 MPa to 0.75 GPa, although the ocean’s bottom is at 0.68 GPa. Assuming a gravitational acceleration of 10³ cm s⁻², the pressure range from the bottom of the ocean out to the point where clathrates cease to be stable corresponds to 57 km. Let us further assume that the planetary radius is 8000 km (Levi et al. 2014). The mass of the ocean within the clathrate stability field would then be approximately \(4.6 \times 10^{23}\) g. From this, we know how many moles of water were in the original subsaturated ocean inside the clathrate stability field. In clathrate formation, every mole of CO₂ requires 5.75 moles of water, so the total mass of CO₂ stored in this maximum clathrate hydrate layer is \(2.0 \times 10^{25}\) g. This comes at the expense of the water in the ocean. The total capacity of this proposed CO₂ reservoir for our particular example is 5.75 moles of water, so the total mass of CO₂ stored in this maximum clathrate hydrate layer is 2.0 \(\times 10^{25}\) g. This comes at the expense of the water in the ocean. This is the total capacity of this proposed CO₂ reservoir for our particular example. It is interesting to note that the carbon budgets in rocks and the ocean for the Earth are \(7.4 \times 10^{22}\) g and \(3.8 \times 10^{19}\) g, respectively (Williams & Follows 2011). If the CO₂ atmosphere that forms around the planet has a partial pressure of 1 bar (10 bar), then the remaining liquid layer (what is left of the ocean after the entire clathrate stability field solidified) has a depth of 150 m (60 m). Because clathrates do not occlude salt, the entire salt content of the original ocean now concentrates at the remaining liquid layer. Therefore, because the original ocean, which had a depth of \(\approx 100\) km, shrunk to a liquid reservoir with a depth of \(\approx 100\) m, the latter layer experiences a rise in salt concentration, with respect to the initial ocean, of three orders in magnitude.
4.2. The \( \beta \) Domain

In this domain, the ice layer composing the bottom surface of the ocean is outside the thermodynamic stability field for CO\(_2\) SI clathrate hydrate. Thus, even in the presence of CO\(_2\), the top of the icy mantle convection cell (the ice layer composing the bottom of the ocean) is largely made of water ice VI. Therefore, the “gentle” outgassing mechanism proposed for the \( \alpha \) domain cannot operate here. It is uncertain whether the filled ice of CO\(_2\) is stable at the \( \beta \) domain range of temperatures (Bollengier et al. 2013; Tulk et al. 2014). Its existence at the bottom of the ocean in this domain is therefore speculative. We elaborate further on this issue in the discussion.

In the \( \beta \) domain, there is a region of space right above the bottom of the ocean that is outside the CO\(_2\) SI clathrate thermodynamic stability field. In this region of space, the lowest chemical potential for CO\(_2\) is for a phase I solid of CO\(_2\). Further out of this region, CO\(_2\) SI clathrates become thermodynamically stable. The latter may extend to the point where the lowest chemical potential for CO\(_2\) turns out to be the liquid form of CO\(_2\). To understand the deposition of CO\(_2\) in the deep ocean for the \( \beta \) domain, one must consider the mass densities of the different phases involved.

In Figure 16, we plot the mass density for various phases of interest for the \( \beta \) domain, assuming an isotherm of 290 K. Each curve spans the thermodynamic stability of the given phase for the isotherm chosen. This figure sheds light on what is likely a complex deposition mechanism. Let us imagine an ocean initially subsaturated in CO\(_2\). As solid convection in the ice mantle ensues, CO\(_2\) trapped within ice VI (or perhaps as filled-ice) comes into contact with the ocean. This CO\(_2\) enters the ocean, trying to saturate it. The solubility, when in equilibrium with clathrates, is a lower value than when in equilibrium with fluid CO\(_2\) (see Figure 9). Therefore, after the ocean saturates with CO\(_2\) to the value in equilibrium with clathrates, any further dissolution of CO\(_2\) into the ocean from the interior would result in SI CO\(_2\) clathrate grain formation. Clathrate grain formation would be restricted to the clathrate thermodynamic stability field. In our example isotherm, the clathrate stability field extends 38 km, for an ocean that is 90 km deep. The clathrate stability field is elevated 28 km above the ice VI bottom, and submerges 24 km below the ocean’s surface.

Within the thermodynamic stability field of the SI CO\(_2\) clathrate hydrate, the clathrate grains are more dense than the surrounding water-rich liquid. As a result, if supersaturation with respect to clathrates is forced, CO\(_2\) clathrate grains would form and sink. However, very close to the high-pressure boundary of the clathrate stability field, the water-rich liquid turns more dense than the clathrate grains (see Figure 16). As a result, SI CO\(_2\) clathrate grains will begin to accumulate there, 28 km above the ocean’s bottom. As more and more CO\(_2\) is injected into the ocean from the interior, and as long as the clathrate layer is thin enough to allow CO\(_2\) to diffuse across it, the thicker this elevated clathrate layer becomes. Eventually, if it becomes thick enough, it may isolate the deep ocean from the upper ocean (see illustration in Figure 17). Because a liquid layer separates this proposed mid-ocean solid SI CO\(_2\) clathrate hydrate layer from the ice mantle, it should experience only a mild shear stress, enhancing its stability.

If the mid-ocean SI CO\(_2\) clathrate hydrate layer indeed becomes thick enough to isolate the deep part of the ocean, then that part of the ocean may experience a further increase in the abundance of dissolved CO\(_2\); in such case, its transport
from the mantle and into the ocean continues. This is because the 28 km layer of water-rich liquid above the ocean’s bottom is outside of the clathrate hydrate stability field. Saturation with respect to pure CO$_2$ can now be reached, resulting in the formation of solid CO$_2$ grains. These grains are even more dense than water ice VI. Therefore, they probably become embedded in every crack and void forming in the ocean’s bottom surface. These are likely because the ocean’s bottom is also the top layer of the ice mantle convection cell, and thus experiences high stresses. In a previous paper, we have discussed full ice mantle convection (Levi et al. 2014). If that is the case here as well, then it is likely that at least some part of the ocean’s ice VI bottom is reprocessed into the interior. In that case, the embedded solid CO$_2$ will likely follow.

In the upper part of the ocean, above the mid-ocean clathrate hydrate layer, the solubility of CO$_2$ is governed by its equilibrium with the clathrate hydrate phase. Thus, the solubility of CO$_2$ is kept low enough to prohibit the formation of liquid CO$_2$ droplets (see Figure 9). Because of restrictions on the solubility of CO$_2$ when in equilibrium with clathrates, it is unlikely that liquid CO$_2$ should form anywhere. In the event that liquid CO$_2$ does form, for example, between clathrate grain boundaries, the mass density difference should drive it to flow out of the clathrate layer. Consequently, it would sink into the deep ocean and transform into the phase I solid of CO$_2$.

Finally, if a thick mid-ocean SI CO$_2$ clathrate hydrate layer forms, it would control the solubility of CO$_2$ in the upper ocean. Therefore, it would also control the atmospheric abundance of CO$_2$. Atmospheric observations would therefore mostly probe this layer, rather than constrain deeper planetary fluxes. We also find that the $\beta$ domain resembles the $\alpha$ domain; in both cases, clathrates of CO$_2$ may dictate the abundance of CO$_2$ available to the atmosphere.

In conclusion, we wish to quantify the mass of CO$_2$ that can be stored in a full mid-ocean clathrate hydrate layer. We use the 290 K isotherm as an example (see Figure 12). We also assume a gravitational acceleration of $10^4$ cm s$^{-2}$ and a planetary radius of 8000 km for our water planet (Levi et al. 2014). For 290 K, the CO$_2$ SI clathrate hydrate thermodynamic stability field lies between the pressures of 0.55 GPa and 104 MPa, corresponding to a layer width of 38 km. The total mass of this clathrate layer is approximately $3.58 \times 10^{25}$ g, of which $1.07 \times 10^{25}$ g is CO$_2$.

4.3. The $\gamma$ Domain

In this domain, the thermal profile in the deep-mid ocean is outside the CO$_2$ SI clathrate hydrate thermodynamic stability field (see Figure 12). Ocean saturation levels with CO$_2$ are now determined via equilibrium with non-clathrate phases. Following saturation, any additional CO$_2$ convected outward from the mantle and into the ocean may pile up on the bottom surface of the ocean as solid and even liquid CO$_2$.

Estimating the CO$_2$ storage capacity in the deep ocean is much more complicated in this domain. In the $\alpha$ and $\beta$ domains, CO$_2$ is stored in the form of clathrate hydrate. This phase is more dense than the liquid ocean, but less dense than ice VI, and is therefore gravitationally stable. Liquid and solid CO$_2$ are more dense than ice VI (see Figure 16). Therefore, in the $\gamma$ domain, gravity will put an upper bound on the storage capacity of the deep ocean. Hypothetically, disregarding this gravitational limit would make the maximum amount of CO$_2$ that can be stored in the ocean in the solid and liquid phases approximately $8 \times 10^{25}$ g, assuming $10^3$ cm s$^{-2}$ for the acceleration of gravity and 8000 km for the planetary radius.

In this section, we have described ways in which CO$_2$ from the ice mantle may become locked deep in the ocean. Are these deep ocean reservoirs stable, or can the ocean mix thus making them available to the atmosphere?

5. Deep Overturning Circulation in the Ocean

In this section, we would like to briefly address the issue of global mixing in water planet oceans. When a fluid in a gravitational field is heated from below, the gravitational energy acts against viscous dissipation to establish convection. When the heating source is at the same level or above the cooling source, convection cannot develop. This is known as Sandström’s theorem (Huang 1999). The ocean is such a system; it is both heated and cooled from its outer surface (Kuhlbrodt et al. 2007). Therefore, the Atlantic Overturning Circulation (AOC), rather than being a heat engine, requires an external input of power to maintain a steady circulation. In the AOC, warm and light surface water flows to the north pole. At the north pole, and other sporadic locations, the surface water cools enough and partially solidifies. Because ice Ih does not incorporate salt, the remaining liquid becomes saltier and thus heavier. At this point, the heavy water sinks to the bottom surface and spreads. In the tropics, the cold and dense abyssal ocean upwells through a warmer and less dense liquid environment. This last arm of the AOC costs energy that is supplied by lunar and solar tidal forcing and winds. The power supplied by either tides or winds, which actually converts to upwelling, is estimated to have an order of magnitude equivalent to approximately 1 TW. This is similar to the power required to maintain a steady-state AOC (Wunsch & Ferrari 2004; Kuhlbrodt et al. 2007).

The pathways for the transfer of energy in Earth’s oceanic circulation are still very much debated. However, it is clear that continental slopes and bottom-surface topography play a major role in internal wave dissipation into turbulent mixing. Indeed, vertical motions are enhanced above rough topography (Kuhlbrodt et al. 2007). Water planets do not have continental slopes. In Earth’s oceans, topographic features can be as high as the depth of the ocean (e.g., Maunakea). This is less likely on water planets, due to the large depth scale of the ocean. Thus, the efficiency with which waves dissipate into turbulent mixing is probably lower in water planets’ oceans than in the Atlantic. As a consequence of the subdued topography, tidal forcing becomes less effective as a source of energy for maintaining a circulation.

The rate of direct input of mechanical energy from winds is proportional to wind speed and surface area. The surface area is not vastly different between our studied water planets and the Earth. Wind speeds are more difficult to assess, although the lack of continents in water planets may indicate lower wind speeds (we will return to this below when we discuss the wind-driven circulation). As a consequence of the above, the power available to establish circulation in water planets’ oceans is probably about 1 TW, as in the case of Earth. But how much power is actually needed to circulate a deep water planet ocean?

In the AOC, surface water sinks to replace abyssal water, and abyssal water is upwelled to replace surface water. One can think of circulation as a process where the outer oceanic water shell is continuously being exchanged with the deepest oceanic
water shell. To derive the power required to maintain such a steady circulation, we follow the arguments of Wunsch & Ferrari (2004). Let us consider a parcel of fluid of volume $dV$ and a potential density of $\sigma_p$. When the parcel is displaced vertically in a gravitational field through a medium of potential density $\sigma(z)$, one invests a power of:

$$d\dot{U}_g = (\sigma_p - \sigma(z))g \cdot w \, dV,$$

where $g$ is the acceleration of gravity and $w$ is the parcel’s vertical velocity. For a constant vertical velocity, the global energy rate is:

$$\dot{U}_g = 4\pi R_p^2 g \cdot w \int_{z_b}^{0} (\sigma_p - \sigma(z))dz,$$

where $R_p$ is the planetary radius, $z = 0$ is the ocean’s upper surface, and $z_b$ is the ocean’s bottom surface. Let us first estimate the vertical velocity of the circulation.

We consider a tangential outer surface current velocity of $v_c$. The latter describes the current regime in the upper boundary layer of the ocean of depth $d_c$. Due to the role Ekman transport plays in the general circulation, we adopt for $v_c$ and $d_c$ the corresponding Ekman layer values. From conservation of mass, we then have:

$$\frac{w}{v_c} \approx \frac{d_c}{R_p}, \quad (43)$$

The appropriate Ekman layer depth is (Kundu et al. 2012):

$$d_c = \frac{2\nu_v}{f}, \quad (44)$$

where $\nu_v$ is the vertical eddy viscosity and $f \equiv 2\Omega \sin \lambda$ is the Coriolis parameter. The Ekman velocity is (Kundu et al. 2012):

$$v_c \approx \frac{2}{\nu_v} \frac{\tau}{\rho_v \rho_w} \quad \text{(45)}$$

Here, $\rho_v$ is the bulk density of ocean water and $\tau$ is the shear stress the wind exerts on the surface water (Stewart 2008):

$$\tau = \rho_{air} C_D U_{10}^2 \quad \text{(46)}$$

The drag coefficient $C_D$, appropriate for moderate to strong winds, is estimated to equal $2.6 \times 10^{-3}$ (see discussion in Sverdrup et al. 1957, p. 490). $U_{10}$ is the wind speed at 10 m above see level, and $\rho_{air}$ is the bulk density of the atmosphere. We therefore approximate the vertical velocity of ocean circulation as:

$$w \approx \frac{C_D \rho_{air} U_{10}^2}{\sin \lambda \rho_w \Omega R_p} \quad \text{(47)}$$

Let us test the last approximation with respect to circulation in Earth’s oceans. For the bulk density of air, we adopt $\rho_{air} = 1.25 \times 10^{-3}$ g cm$^{-3}$ (Stewart 2008), and $R_p = 6371$ km and $\Omega = 7.27 \times 10^{-5}$ s$^{-1}$ are Earth’s radius and angular velocity respectively. We also adopt near-surface wind speeds of 5–10 m s$^{-1}$ (Stewart 2008). For mid-latitudes, this gives a vertical velocity between $10^{-5}$ and $10^{-4}$ cm s$^{-1}$. Indeed, vertical velocities for Earth’s oceans are inferred to fall within this range of values, when far from sharp topographic features (Wunsch & Ferrari 2004).

Sinking of surface water to the abyss takes place where it costs the least amount of energy. For the reasons described above, this is at the poles for the AOC. In water planets, a substantial ice mantle separates the ocean from the rocky interior. If this lack of interaction results in much lower salt concentrations in the ocean, then sea-ice formation will not help promote subduction of surface water. In addition, in our studied water planets, surface water is lighter than abyssal water because it contains much less dissolved carbon-dioxide. At the tropics, due to the high surface temperatures, surface water expands and enhances stability even further. Therefore, it is energetically more efficient for water to sink at the poles in water planets as well. Let us estimate the external energy needed to maintain the down-welling arm of the circulation at the poles.

For a vertical eddy viscosity of 300 cm$^2$ s$^{-1}$ (Yu & O’Brien 1991), the Ekman layer is 24 m deep. This boundary layer at the ocean’s surface is very well mixed. Therefore, the solubility of CO$_2$ may be assumed uniform throughout this layer. Let us assume a 3 bar atmosphere of CO$_2$ for our water planet. According to Henry’s law (see Section 2.1), this fits a dissolved CO$_2$ abundance of 0.0017 for 25°C. This represents our surface tropical water that can now migrate to the poles. Closer to the poles, the surface temperature decreases. Let us also assume that the exposed surface water is at the verge of freezing at the poles. Therefore, the solubility of CO$_2$ at the surface water further increases to about 0.0036. In the cold abyss (assumed here as 275 K, see $\alpha$ domain in the previous section), and within the stability field of clathrates, the abundance of dissolved CO$_2$ would be about 0.016. Converting the surface and abyssal water compositions to the corresponding solutions’ bulk potential densities (Teng et al. 1997) yields $\sigma_p - \sigma(z) = -0.0062$ g cm$^{-3}$ for a 1 bar reference pressure. Therefore, with the aid of Equation (42), the external power required to maintain a steady global circulation is at least:

$$\dot{U}_g > 349 - 3490 \quad \text{[TW]}, \quad \text{(48)}$$

where the range comes from the range of vertical velocities derived above. This is two-to-three orders of magnitude larger than what is actually available.

As in Earth’s oceans, lifting cold and dense deep water through the warmer shallow water generates gravitational potential energy. The rate of potential energy generation, using Equation (42), can crudely be described as (Wunsch & Ferrari 2004):

$$\dot{U}_g \sim 4\pi R_p^2 g \rho \frac{\partial \sigma}{\partial T} \Delta T \text{L}_{\text{ocean}}. \quad \text{(49)}$$

Let us consider a temperature variation of $\Delta T = 10$ K over the depth of the ocean, $L_{\text{ocean}}$. Raising the temperature from 275 K to 285 K decreases the density of pure water by $4.2 \times 10^{-4}$ g cm$^{-3}$ (Wagner et al. 1994), for a 1 bar reference. Adopting Earth’s parameters and a shallow 4 km ocean gives about 0.9 TW for the lower value derived for the vertical velocity. This agrees with the available external input of power, as discussed above. For oceans that are at least an order of magnitude deeper, circulating water against the temperature gradient could prove too energetically expensive.

In conclusion, driving a global oceanic circulation and ocean homogenization in water planets, with the same efficiency as it
operates on Earth, requires much more external power. Simply scaling up Earth’s oceanic circulation and global vertical mixing is inappropriate for describing water planets’ oceans. Due to the exploratory nature of this paper, we do not dismiss vertical mixing entirely, but rather explore the effects of various deep-ocean vertical eddy diffusion coefficients. However, in light of the energy constraints just described, it is reasonable to estimate that the vertical diffusion coefficient values are lower than the inferred values for Earth’s deep oceans.

6. CO₂ Fluxes Between the Atmosphere and Upper Ocean

Coupled ocean-atmosphere models for our studied water planets have not yet been developed. The principal difficulty is that every physical phenomenon we wish to consider based on analogy to the Earth needs to be re-evaluated. For example, basic issues like global ocean circulation may differ substantially between water planets and Earth’s analogs. Recently, coupled ocean-atmosphere models were tested for a planet with a rather shallow ocean (Earth-like) and no land mass (Smith et al. 2006; Marshall et al. 2007). This planetary case is intermediate between Earth and our studied water planets, with their very deep oceans. In both works, global circulation is assumed, which is energetically reasonable for a shallow ocean; however, they still ended up with different results. Smith et al. (2006) argued that, in the absence of land, the meridional temperature gradient is very subdued, i.e., polar temperatures are high. On the contrary, Marshall et al. (2007) argued that the poleward heat transport in Smith et al. (2006) was greatly exaggerated; they further reported that sea-ice formed, and was very stable throughout the entire time duration of their numerical run—which was thousands of years. They found the ice caps to extend as far south as 60° latitude, and have temperatures as low as 250 K. Both groups find marked wind patterns of easterlies and westerlies as on Earth’s surface. A weaker meridional temperature gradient would weaken the winds. However, the lack of land mass is argued to reduce viscosity, which would tend to cancel the former effect (Marshall et al. 2007). It is interesting to note that Marshall et al. (2007) found no polar easterlies in their model runs.

In light of these models, it seems reasonable to assume that excess solar heating at the tropics would tend to form circulation cells in the atmosphere of water planets as well. Resulting surface wind patterns of easterlies and westerlies also seem to be robust. These surface wind patterns are of paramount importance because they force surface water to either converge or diverge. The convergences and divergences drive vertical motions known as Ekman pumping in the upper ocean (Gill 1982). The relation between the surface wind stress (τ) and vertical flow in the ocean is:

\[
\nu_e = \frac{1}{2\Omega \rho_o} \nabla \times \left( \frac{\tau(\lambda)}{\sin(\lambda)} \right) = -\frac{\hat{\rho}}{2\Omega \rho_o R_p \cos(\lambda)} \frac{d}{d\lambda} \left[ \sigma(\lambda) \cot(\lambda) \right],
\]

where \( \Omega = 7.27 \times 10^{-5} \text{ s}^{-1} \) is the planetary rotation period, \( \rho_o = 1 \text{ g cm}^{-3} \) is the ocean surface bulk density, \( R_p \) is the planet radius, and \( \lambda \) is the latitude. We adopt the surface wind stress variation with latitude from Marshall et al. (2007) for a planet with no continents, and convert it to vertical Ekman velocities in the upper ocean. The results are shown in Figure 18.

Figure 18. Vertical Ekman velocities vs. latitude for an Earth-sized planet without continents.

In the subtropics, centered around latitude \( \lambda_{sb} \approx 28^\circ \), lies the peak in Ekman transport convergence (see Figure 18). The resulting downwelling from the bottom of the local mixed layer has a velocity of \( \nu_e = 1.4 \times 10^{-4} \text{ cm s}^{-1} \). The cross-section of our flow tube of interest is \( \Sigma_e \) in its vertical flow segment. The subtropic surface temperature of the ocean is \( T_{so} \), which we assume to be 20°C. Due to Ekman pumping, this will be the temperature in the downwelling water column. This causes a deepening of the local thermocline. Due to the sensitivity of the

6.1. Wind-driven Circulation

Circulation in the ocean is often divided between global and wind-driven. In this subsection, we will only consider the latter. The setting in Figure 19 is of particular importance to secondary outgassing in water planets, following the evaporation of a primordial hydrogen- and helium-dominated atmosphere.

In the subtropics, centered around latitude \( \lambda_{sb} \approx 28^\circ \), lies the peak in Ekman transport convergence (see Figure 18). The resulting downwelling from the bottom of the local mixed layer has a velocity of \( \nu_e = 1.4 \times 10^{-4} \text{ cm s}^{-1} \). The cross-section of our flow tube of interest is \( \Sigma_e \) in its vertical flow segment. The subtropic surface temperature of the ocean is \( T_{so} \), which we assume to be 20°C. Due to Ekman pumping, this will be the temperature in the downwelling water column. This causes a deepening of the local thermocline. Due to the sensitivity of the
dissociation pressure of clathrates to the temperature, the clathrate thermodynamic stability field will also locally deepen. Let us first estimate the influx of CO$_2$ molecules in the downwelling arm of the circulation at the expense of the atmosphere. Consider an atmosphere with some partial pressure of carbon-dioxide, $P_{\text{atm}}^{\text{CO}_2}$. The number density of carbon-dioxide dissolved at saturation at the ocean surface is proportional to the atmospheric partial pressure of CO$_2$. The coefficient of proportionality is directly related to Henry’s solubility constant; it is dependent on the oceanic surface temperature, but independent of the atmospheric partial pressure of carbon-dioxide. One may therefore write, for the subtropics:

$$n_{\text{sat}}^{\text{sub}}(P = P_{\text{atm}}^{\text{CO}_2}) = \tilde{\beta}(T_{\text{sub}})P_{\text{atm}}^{\text{CO}_2},$$  \hspace{1cm} (51)

where $\tilde{\beta}$, as a function of temperature, is here derived from Equation (3) because the ocean surface is assumed to be outside the clathrate thermodynamic stability field.

A few tens of meters below the ocean surface is the well-mixed layer where composition gradients are small, and the above number density may be assumed constant. Below the mixed layer, which approximately coincides with Ekman’s layer, the vertical flow will carry this CO$_2$ inward at a velocity of $w_e$ yielding a carbon-dioxide influx of:

$$\tilde{\beta}(T_{\text{sub}})P_{\text{atm}}^{\text{CO}_2} w_e.$$  \hspace{1cm} (52)

However, not all of the above flux comes at the expense of the atmosphere. Some of the CO$_2$ in the downwelling arm originates from CO$_2$ that dissolved at the tropics from upwelled water parcels, and was then transported to the subtropics. The number density of this can also be derived by use of Equation (51), except that the surface temperature at the subtropics must be replaced by the surface temperature at the tropics, $T_{\text{trop}}$. The influx of CO$_2$ at the subtropics at the expense of the atmospheric budget is therefore:

$$J_{\text{CO}_2}^{\text{in}} = (\tilde{\beta}(T_{\text{sub}}) - \tilde{\beta}(T_{\text{trop}}))P_{\text{atm}}^{\text{CO}_2} w_e.$$  \hspace{1cm} (53)

Outside of the clathrate hydrate stability field the solubility increases with the increasing pressure. Thus, along the downwelling arm the CO$_2$ remains dissolved in the descending water parcels.

Large-scale flow below the Ekman layer is dominated by the Coriolis force and horizontal pressure gradients. This is known as geostrophic flow. Sverdrup examined the role of geostrophic flow in the wind-driven circulation, and showed there is a return geostrophic mass transport from the subtropics to the tropics. In an ideal Sverdrupian flow, there exists a depth, $L_s$, where horizontal pressure gradients vanish, as does the geostrophic and any vertical flow. This depth of no motion is approximately 1 km below the ocean surface (see chapter 11 in Stewart 2008). The depth of no motion is of particular interest to us because it distinguishes the wind-driven circulated upper ocean from the unmixed deep and cold abyss. Across this boundary, CO$_2$ can be diffusionally exchanged between the two parts of the ocean. Because this exchange is our primary interest here, we focus on the geostrophic flow at the vicinity of this boundary, and give the geostrophic part of the flow tube a cross-section, $\delta_h$, that encompasses the bulk of any such diffusional exchange:

$$\delta_h \approx \sqrt{D_{\text{eddy}} t}.$$  \hspace{1cm} (54)

Here, $D_{\text{eddy}}$ is the eddy diffusion coefficient for the deep ocean. We will discuss its value below. We estimate the time $t$ in the last equation as the maximum amount of time a fluid parcel confined to our flow tube stays in diffusional contact with the deep unmixed ocean. In other words,

$$t \approx \frac{L_g}{u_g} = \frac{R_p \Delta \lambda}{u_g},$$  \hspace{1cm} (55)

where $u_g = 0.1$ m s$^{-1}$ is the geostrophic velocity (see chapter 10 in Stewart 2008 and chapter 5 in Olbers et al. 2012), $R_p = 8000$ km is the planetary radius (Levi et al. 2014), and $\Delta \lambda = 30^\circ$ is the latitude difference between the subtropics and the tropics. The length of the horizontal geostrophic arm of the flow tube is $L_g = 4200$ km. Therefore, the timescale of a fluid parcel cycling through our flow tube is:

$$T_{\text{cy}} = 2 \frac{L_s}{w_e} + \frac{L_g}{u_g} = 47$$  \hspace{1cm} (56)

Considering that changes to the bulk density due to diffusion of CO$_2$ are much smaller than the difference between the vertical and horizontal flow velocities, mass conservation relates the cross-sections of the flow tube in the vertical and horizontal arms:

$$w_e \delta_v \approx u_g \delta_h.$$  \hspace{1cm} (57)
From Equations (54) and (55), we then have:

$$\delta_h \sim \sqrt{\frac{D_{\text{edd}}}{u_g} \frac{R_p \Delta \lambda}{w^2}}. \quad (58)$$

When inserted into Equation (57), this yields:

$$\delta_v \sim \sqrt{\frac{D_{\text{edd}}}{u_g} \frac{R_p \Delta \lambda}{w^2}}. \quad (59)$$

Fluid parcels in the downwelling arm of the flow tube reaching close to the boundary of no motion at $L_{\text{edd}}$ have a CO$_2$ number density given by Equation (51). There, the parcels begin to flow horizontally with geostrophic speed and exchange CO$_2$ with the unmixed deep ocean. When the parcels begin to upwell, their dissolved CO$_2$ number density is $n_\text{out}^{\text{CO}_2}$, which obeys:

$$n_\text{out}^{\text{CO}_2} = n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}}) + \frac{1}{\delta_h} \int_t^{t + \delta t} F_{\text{ Sv}} dt', \quad (60)$$

where $F_{\text{ Sv}}$ is the flux of CO$_2$ between the parcel and the deep ocean. $t$ and $t + \delta t$ are the times a specific fluid parcel enters and leaves the geostrophic arm of the flow tube, respectively. Solving for $F_{\text{ Sv}}$, we first need to solve for the transport of CO$_2$ across the deep unmixed ocean.

In a saturated ocean, the nature of the reservoir of CO$_2$ at the ocean’s bottom controls the deep ocean’s dissolved CO$_2$ number density, $n^{\text{deep}}_\text{CO}_2$. We have quantified the various reservoirs in Section 4 of this paper. Here, we estimate the transport of CO$_2$ across the deep ocean as a problem of eddy diffusion between two CO$_2$ number densities:

$$\frac{\partial n^{\text{CO}_2}}{\partial t} = D_{\text{edd}} \frac{\partial^2 n^{\text{CO}_2}}{\partial z^2}$$

$$n^{\text{CO}_2}(z, t = 0) = n_{\text{initial}}$$

$$n^{\text{CO}_2}(z = L_{\text{ocean}}, t) = n^{\text{deep}}_\text{CO}_2$$

$$n^{\text{CO}_2}(z = 0, t) = n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}}). \quad (61)$$

Here, $z = 0$ is the boundary between the wind-driven circulation and the unmixed deep ocean, and $L_{\text{ocean}}$ is the depth of the ocean. The solution for this system using separation of variables is (Crank 1956):

$$n^{\text{CO}_2}(z, t) = n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}}) + \frac{n^{\text{deep}}_\text{CO}_2 - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}})}{L_{\text{ocean}}} z$$

$$+ \sum_{n=1}^{\infty} C_n \exp \left\{ -\frac{n^2 \pi^2}{L_{\text{ocean}}^2} D_{\text{edd}} t \right\} \sin \left( \frac{n \pi z}{L_{\text{ocean}}} \right) \quad (62)$$

where

$$C_n = \begin{cases} 
\frac{2(n^{\text{deep}}_\text{CO}_2 - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}}))}{n \pi} & \text{n even} \\
\frac{2(n_{\text{initial}} - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}}) - n^{\text{deep}}_\text{CO}_2)}{n \pi} & \text{n odd,} 
\end{cases}$$

$$\quad (63)$$

Sinusoidal series do not converge fast enough for small $t$, unlike expansions in terms of error functions (Carslaw & Jaeger 1959), and can introduce fictitious fluxes. The solution, in terms of complementary error functions, is (see Appendix A.3 for derivation):

$$n^{\text{CO}_2}(z, t) = (n^{\text{deep}}_\text{CO}_2 - n_{\text{initial}}) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{(2r + 1)L_{\text{ocean}} - z}{2 \sqrt{D_{\text{edd}} t}} \right)$$

$$+ (n_{\text{initial}} - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}})) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{2rL_{\text{ocean}} - z}{2 \sqrt{D_{\text{edd}} t}} \right)$$

$$+ (n^{\text{deep}}_\text{CO}_2 - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}}) - n_{\text{initial}}) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{(2r + 1)L_{\text{ocean}} + z}{2 \sqrt{D_{\text{edd}} t}} \right)$$

$$+ n_{\text{initial}}. \quad (64)$$

The vertical flux at the bottom of the wind-driven circulation is:

$$F_{\text{ Sv}} = D_{\text{edd}} \frac{\partial n^{\text{CO}_2}}{\partial z} \bigg|_{z=0}, \quad (65)$$

which, for the sinusoidal expansion solution, gives:

$$F_{\text{ Sv}} = D_{\text{edd}} \left[ \frac{\pi}{L_{\text{ocean}}} \sum_{r=1}^{\infty} C_n \exp \left\{ -\frac{n^2 \pi^2}{L_{\text{ocean}}^2} D_{\text{edd}} t \right\} \sin \left( \frac{n \pi z}{L_{\text{ocean}}} \right) \right] L_{\text{ocean}} \quad (66)$$

In terms of error functions, the solution is:

$$F_{\text{ Sv}} = (n_{\text{initial}} - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}})) \sqrt{\frac{D_{\text{edd}}}{\pi t}}$$

$$+ (n^{\text{deep}}_\text{CO}_2 - n_{\text{initial}}) \sum_{r=0}^{\infty} \frac{D_{\text{edd}}}{\pi t} \exp \left\{ -\frac{(2r + 1)^2 \pi^2 t}{8 D_{\text{edd}} t} \right\}$$

$$+ (n_{\text{initial}} - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}})) \sum_{r=0}^{\infty} \frac{D_{\text{edd}}}{\pi t} \exp \left\{ -\frac{(2r)^2 \pi^2 t}{8 D_{\text{edd}} t} \right\}. \quad (67)$$

The integration in Equation (60), using the sinusoidal expansion, equals:

$$\frac{1}{\delta_h} \int_t^{t + \delta t} F_{\text{ Sv}} dt' = D_{\text{edd}} \frac{n^{\text{deep}}_\text{CO}_2 - n^{\text{sat, sbt}}_\text{CO}_2 (P = P_{\text{atm}})}{L_{\text{ocean}}}$$

$$- \frac{\pi}{L_{\text{ocean}}} \sum_{n=1}^{\infty} C_n \lambda_n \exp \left\{ -\frac{\lambda_n t}{\delta_h} \right\} \left[ \lambda_n (e^{-\lambda_n t} - 1) \right]. \quad (68)$$
Here, the Astrophysical Journal, compensate for our
which it begins to upwell to the mixed layer. In order to
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geostrophic arm of the
and is more appropriate for describing the initial segment of the

\[ \lambda_h \equiv \frac{n^2 \pi^2}{L_{\text{ocean}}} D_{\text{eddy}}. \]  

(69)

For the error function expansion, it is:

\[
\frac{1}{\delta_h} \int_{t}^{t+\delta t} F_s dt' = \frac{n_{\text{deep}}^\text{CO}_2 - n_{\text{initial}}}{\delta_h} \sum_{r=0}^{\infty} \frac{(2r + 1)L_{\text{ocean}}}{\sum_{r=0}^{\infty} \sqrt{\pi}}
\]

\[
\times \left[ \Gamma_{-\frac{1}{2}} - \gamma_{-\frac{1}{2}} \left( \frac{(2r + 1)^2 L_{\text{ocean}}^2}{4 D_{\text{eddy}} (t + \delta t)} \right) \right]
\]

\[
- \Gamma_{-\frac{1}{2}} \left( \frac{(2r + 1)^2 L_{\text{ocean}}^2}{4 D_{\text{eddy}} t} \right)
\]

\[
- 2 n_{\text{sat, sbt}}^\text{CO}_2 (P = p_{\text{atm}}^\text{CO}_2) - n_{\text{initial}} \sum_{r=1}^{\infty} \frac{rL_{\text{ocean}}}{\sqrt{\pi}}
\]

\[
\times \left[ \Gamma_{-\frac{1}{2}} - \gamma_{-\frac{1}{2}} \left( \frac{r^2 L_{\text{ocean}}^2}{D_{\text{eddy}} (t + \delta t)} \right) \right]
\]

\[
- \Gamma_{-\frac{1}{2}} \left( \frac{r^2 L_{\text{ocean}}^2}{D_{\text{eddy}} t} \right)
\]

\[
- 2 n_{\text{sat, sbt}}^\text{CO}_2 (P = p_{\text{atm}}^\text{CO}_2) - n_{\text{initial}} \frac{D_{\text{eddy}}}{\pi} \sqrt{t + \delta t - \sqrt{t}}.
\]

(70)

Here, \( \Gamma_{-\frac{1}{2}} \) is the gamma function of \(- \frac{1}{2}\), and \( \gamma_{-\frac{1}{2}} \) and \( \Gamma_{-\frac{1}{2}} \) are the equivalent incomplete lower and upper gamma functions, respectively.

The \( \tau = 0 \) boundary in the set of Equation (61) is not exact, and it is more appropriate for describing the initial segment of the geostrophic arm of the flow tube. At more advanced segments, the fluid parcels equilibrate with the upper layer of the deep unmixed ocean, and the flux between the two ought to diminish substantially. Thus, our \( F_s \) represents a maximal flux, and should not be integrated over the entire length of time that a parcel lingers in the geostrophic arm. A fluid parcel is in contact with the deep ocean for a time period of \( L_g / \mu_g \) after which it begins to upwell to the mixed layer. In order to compensate for our flux being a maximal value, we integrate it over half of the latter time, \( \delta t = L_g / 2 \mu_g \).

For convenience, in the sinusoidal expansion, we define:

\[
\eta_0^c(t) \equiv \frac{D_{\text{eddy}} L_g}{2 \mu_g \delta_h L_{\text{ocean}}} \left[ e^{-\lambda_h t} - n_{\text{deep}}^\text{CO}_2 \left( e^{\lambda_h t} \right) - 1 \right]
\]

\[
\times \left[ \sum_{n=1,3,5,\ldots}^{\infty} e^{-\lambda_h t} \frac{n^2}{\pi} (2n_{\text{initial}} - n_{\text{deep}}^\text{CO}_2) \left( e^{\frac{\lambda_h t}{2 \mu_g}} - 1 \right) \right]
\]

\[
+ \sum_{n=2,4,6,\ldots}^{\infty} e^{-\lambda_h t} \frac{n^2}{\pi} n_{\text{deep}}^\text{CO}_2 \left( e^{\frac{\lambda_h t}{2 \mu_g}} - 1 \right) \right]
\]

(71)

\[
\eta_1^c(t) \equiv -\frac{D_{\text{eddy}} L_g}{2 \mu_g \delta_h L_{\text{ocean}}}
\]

\[
+ \frac{L_{\text{ocean}}}{\delta_h} \sum_{n=1,3,5,\ldots}^{\infty} e^{-\lambda_h t} \frac{2}{\pi} (e^{-\lambda_h t / 2 \mu_g} - 1) e^{-\lambda_h t}.
\]

(72)

Also for convenience, for the error function expansion, we further define:

\[
\eta_0^f(t) \equiv \frac{n_{\text{deep}}^\text{CO}_2 - n_{\text{initial}}}{\delta_h} \sum_{r=0}^{\infty} \frac{(2r + 1)L_{\text{ocean}}}{\sqrt{\pi}}
\]

\[
\times \left[ \Gamma_{-\frac{1}{2}} - \gamma_{-\frac{1}{2}} \left( \frac{(2r + 1)^2 L_{\text{ocean}}^2}{4 D_{\text{eddy}} (t + \delta t)} \right) \right]
\]

\[
- \Gamma_{-\frac{1}{2}} \left( \frac{(2r + 1)^2 L_{\text{ocean}}^2}{4 D_{\text{eddy}} t} \right)
\]

\[
+ 2 n_{\text{initial}} \sum_{r=1}^{\infty} \frac{rL_{\text{ocean}}}{\sqrt{\pi}} \left[ \Gamma_{-\frac{1}{2}} - \gamma_{-\frac{1}{2}} \left( \frac{r^2 L_{\text{ocean}}^2}{D_{\text{eddy}} (t + \delta t)} \right) \right]
\]

\[
- \Gamma_{-\frac{1}{2}} \left( \frac{r^2 L_{\text{ocean}}^2}{D_{\text{eddy}} t} \right)
\]

\[
+ 2 n_{\text{initial}} \frac{D_{\text{eddy}}}{\pi} \left[ \frac{r^2 L_{\text{ocean}}}{2 \mu_g} - \frac{l}{\sqrt{t}} \right]
\]

(73)

and

\[
\eta_1^f(t) \equiv -\frac{2}{\delta_h} \sum_{r=1}^{\infty} \frac{rL_{\text{ocean}}}{\sqrt{\pi}} \left[ \Gamma_{-\frac{1}{2}} - \gamma_{-\frac{1}{2}} \left( \frac{r^2 L_{\text{ocean}}^2}{D_{\text{eddy}} (t + \delta t)} \right) \right]
\]

\[
- \Gamma_{-\frac{1}{2}} \left( \frac{r^2 L_{\text{ocean}}^2}{D_{\text{eddy}} t} \right)
\]

\[
- \frac{2}{\delta_h} \frac{D_{\text{eddy}}}{\pi} \left[ \frac{r^2 L_{\text{ocean}}}{2 \mu_g} - \frac{l}{\sqrt{t}} \right]
\]

(74)

With these definitions, we can rewrite Equation (60) as:

\[
n_{\text{out}}^\text{CO}_2 = n_{\text{sat, sbt}}^\text{CO}_2 (P = p_{\text{atm}}^\text{CO}_2) \left[ 1 + \eta_1^c(t) + \eta_0^f(t) \right].
\]

(75)

While the water parcels were in contact with the abyssal cold ocean (i.e., a heat bath) they also exchanged heat, and the ascending water will have the deep ocean temperature, \( T_{\text{deep}} \).

As water parcels upwell (via Ekman suction), they experience a continuous decrease in hydrostatic pressure. Therefore, there will be a depth above which the fluid parcels will have to start degassing in order to maintain a number density of CO2 equal to the local solubility. This solubility is the value with respect to equilibrium with a fluid of CO2 (see dashed curves in Figure 9). This value for the solubility is higher than the value for the solubility when it is controlled by the presence of CO2 clathrate hydrates (see solid curves in Figure 9). The low heat fluxes in our water planet’s interest (see two Earth-mass planets in Levi et al. 2014) suggest that the deep ocean reservoir of CO2 is, indeed, in the form of clathrates, which would control the value of \( n_{\text{deep}}^\text{CO}_2 \), Thus, although the ascending water parcels are relatively enriched with CO2, their volatile content is stable against degassing. This will change dramatically when the upwelled water reaches
the mixed layer at the tropics. There, it will be rapidly mixed to the ocean surface where the pressure is low, equal to $P_{\text{atm}}^{\text{CO}_2}$, and the temperature is high. The difference between the number density of $\text{CO}_2$ in the upwelled water and what can stay dissolved at the hot tropical surface water must end up in the atmosphere. The outflux of $\text{CO}_2$ associated with this degassing is:

$$j_{\text{out}}^{\text{CO}_2} = \dot{w}_c (n_{\text{CO}_2}^{\text{out}} - \beta(T_{\text{trop}}) P_{\text{atm}}^{\text{CO}_2}).$$  \hspace{1cm} (76)

We now wish to derive the temporal evolution of the atmospheric carbon-dioxide partial pressure. The relation between the surface atmospheric pressure of $\text{CO}_2$ and the number of $\text{CO}_2$ molecules in the atmosphere is:

$$4\pi R^2 p_{\text{atm}}^{\text{CO}_2} = m_{\text{CO}_2} N_{\text{atm}}^{\text{CO}_2} g.$$  \hspace{1cm} (77)

Here, $m_{\text{CO}_2}$ is the molecular mass of carbon dioxide. The influx and outflux of carbon dioxide is related to the variation in the number of atmospheric $\text{CO}_2$ molecules in the following way:

$$dN_{\text{atm}}^{\text{CO}_2} \approx 2\pi R p_{\text{atm}}^{\text{CO}_2} \delta \left( j_{\text{in}}^{\text{CO}_2} - j_{\text{out}}^{\text{CO}_2} \right) N_{\text{wdc}} dt,$$  \hspace{1cm} (78)

where $N_{\text{wdc}}$ is the number of wind-driven circulations operating. Each hemisphere will have two such circulations, one operating between the subtropics and the tropics, and another between the subtropics and the subpolar region. In cases where sea-ice formation extends to low latitudes, this could somewhat hinder the subtropical to subpolar circulations. In addition, the outflux of $\text{CO}_2$ from the higher latitude circulation will also be governed by Equation (76), where the surface temperature at the tropics has to be replaced with the surface temperature at subpolar latitudes. Because the latter is probably lower than at the tropics, the outflux from the higher-latitude circulations will cease, whereas it continues from lower latitudes. Therefore, the low-latitude wind-driven circulation is dominant and we adopt $N_{\text{wdc}} = 2$.

After some algebraic steps, we obtain the relation:

$$\frac{dP_{\text{atm}}^{\text{CO}_2}}{dt} = \frac{\delta \dot{w}_c}{2R} m_{\text{CO}_2} g \left[ \eta_0^{\text{w}} (t) + \eta_1^{\text{w}} (t) \beta(T_{\text{trop}}) P_{\text{atm}}^{\text{CO}_2} \right] - Q_c,$$  \hspace{1cm} (79)

where we have manually added a term, $Q_c$, to account for any possible atmospheric erosion of $\text{CO}_2$.

The steady-state condition is:

$$\lim_{t \to \infty} \frac{dP_{\text{atm}}^{\text{CO}_2}}{dt} = 0,$$  \hspace{1cm} (80)

which gives a steady-state $\text{CO}_2$ partial pressure of:

$$P_{\text{atm, steady}}^{\text{CO}_2} = \frac{\eta_{\text{deep}}^{\text{CO}_2}}{\beta(T_{\text{trop}})} - \frac{4R_p L_{\text{ocean}} Q_c}{N_{\text{wdc}} m_{\text{CO}_2} g D_{\text{eddy}} L_{\beta}(T_{\text{trop}})}.$$  \hspace{1cm} (81)

Clearly, when $Q_c = 0$, a steady state is reached when the number density of dissolved $\text{CO}_2$ downwelling at the subtropics equals the number density of dissolved $\text{CO}_2$, as forced by the abyss.

Before solving Equation (81), we need to estimate the deep unmixed ocean vertical eddy diffusivity, $D_{\text{eddy}}$. The diffusion coefficient of dissolved $\text{CO}_2$ in water is $10^{-5} \text{cm}^2 \text{s}^{-1}$ (Zeebe 2011). This diffusion coefficient is molecular in nature and would not be very efficient at mixing the ocean. However, it is a good approximation for a lower bound value.

In Earth’s ocean, the dominant vertical mixing is caused by eddies. Much like conduction via eddies in Earth’s ocean is much more efficient than molecular conduction (Defant 1961), experiments show that vertical mixing, i.e., vertical eddy diffusivity, is very large where oceanic flow interacts with ocean boundaries (see discussion in chapter 8 in Stewart 2008). The lowest open-ocean value for the vertical eddy diffusivity was found experimentally to be $0.1 \text{cm}^2 \text{s}^{-1}$ (Ledwell et al. 1998). This value was found for a depth that is below the local mixed layer, albeit not as deep as the case we are trying to solve for. In addition, a water planet lacks continents and has a very subdued topography. This lack of boundaries, and the energy constraints of the previous section, mean that the lowest value for $D_{\text{eddy}}$, found for Earth’s ocean is very probably a good estimation for an upper bound value for our desired case study.

In Figure 20, we solve for the steady-state partial atmospheric pressure of carbon-dioxide as a function of the deep unmixed ocean temperature, as well as for two subtropic surface water temperatures. A higher subtropic surface water temperature results in more carbon-dioxide in the atmosphere at steady state. This is because the surface water is hot, and therefore outside the clathrate hydrate stability field. This means that the solubility there decreases with the increasing temperature. However, a steady state requires that the downwelling water at the subtropics have a dissolved concentration of carbon-dioxide equal (for $Q_c = 0$) to that at the abyss. Thus, a higher subtropic surface temperature will require a higher atmospheric pressure to obtain the same solubility as when the surface temperature is lower.

If abyssal ocean temperatures fall within the clathrate hydrate thermodynamic stability field (see domains $\alpha$ and $\beta$ in Section 4), then the SI $\text{CO}_2$ clathrate hydrates control the concentration of $\text{CO}_2$ in the ocean. In this case, as we have shown in Section 2.2, higher temperatures result in more carbon-dioxide being dissolved into the water, in equilibrium with its clathrates. Therefore, the higher the deep ocean temperature is, the higher $n_{\text{deep}}^{\text{CO}_2}$ is, which forces a higher partial atmospheric pressure of carbon-dioxide in steady state.

Consider the ratio $Q_c/D_{\text{eddy}}$, where $Q_c$ is in bar Myr$^{-1}$ and $D_{\text{eddy}}$ is in cm$^2$ s$^{-1}$. The phenomena contained in the term $Q_c$ start affecting the steady state atmospheric pressure when $Q_c/D_{\text{eddy}} > 10$. When $Q_c/D_{\text{eddy}} > 40$, the effect of $Q_c$ on the steady-state partial atmospheric pressure of $\text{CO}_2$ becomes dominant. For $Q_c/D_{\text{eddy}} > 100$, we find that the $\text{CO}_2$ atmosphere is completely eroded.

The values we find for the steady state atmospheric partial pressure of carbon-dioxide are substantially higher than for present day Earth’s atmosphere. However, one should consider that water planets are very rich in volatiles. Luger et al. (2015) showed that a total evaporation of a H/He rich atmosphere yields, at most, a two Earth-mass water planet. Consider such a planet, and assume that half of its mass is ice. Considering cometary composition to be a good approximation for the icy planetesimals that form the icy envelope of water planets, the $\text{CO}_2$ abundance by number in the icy envelope is therefore in the range of 1%-10% (Despois et al. 2005). Thus, a 20 bar atmosphere of $\text{CO}_2$ is only about 0.01%-0.1% of the total ice mantle budget of $\text{CO}_2$. Furthermore, a $Q_c = 0.1$ bar Myr$^{-1}$
means that a system whose age is 10 Gyr will have lost, at this rate, between 1% and 10% of its primordial CO2 budget.

In Figure 21, we plot the temporal evolution of the secondary outgassing of a carbon-dioxide atmosphere. Clearly, the rate-controlling step is the eddy diffusion from the bottom of the deep unmixed ocean up to the wind-driven circulation layer. Therefore, the timescale for reaching a steady-state atmosphere is:

$$t_{\text{steady}} \sim \frac{L_{\text{ocean}}^2}{D_{\text{eddy}}}$$  \hspace{1cm} (82)

For $L_{\text{ocean}} = 80$ km, this gives 20 Myr for $D_{\text{eddy}} = 10^{-1} \text{cm}^2 \text{s}^{-1}$ and 20 Gyr for $D_{\text{eddy}} = 10^{-4} \text{cm}^2 \text{s}^{-1}$. Thus, depending on the vertical eddy diffusivity across the deep ocean, even an old planetary system may have a non-steady-state secondary atmosphere.

A steady-state pressure also implies that the atmosphere-ocean system ought try to restore it, not only during an outgassing period, but also in circumstances where perturbations have increased the partial pressure of CO2 above this value. In Figure 22, we describe the dynamics of this latter scenario for the case where $Q_c = 0$.

In the case that the atmospheric partial pressure of CO2 is higher than its steady state value, for $Q_c = 0$, then the number density of dissolved carbon-dioxide in the surface water at the subtropics is higher than $n_{\text{CO2}}^{\text{deep}}$. This provides the necessary supersaturation required to form clathrate hydrate grains directly from the dissolved carbon-dioxide. Remember that $n_{\text{CO2}}^{\text{deep}}$ is here taken to be the value in saturation with respect to clathrate hydrate formation in the abyss. Nucleation and grain growth will commence when the downwelling fluid parcels enter the part of the flow tube that is within the SI CO2 clathrate hydrate thermodynamic stability field (under the dashed green curve in Figure 22).

In Figure 23, we show that, although the compressibility of liquid water is higher than that of CO2 SI clathrate hydrate, even at the high pressure of the bottom of the water planet ocean, the SI CO2 clathrate hydrate grain is still expected to be more dense than the surrounding water. The exception is a case where we adopt a value of 11 GPa for the bulk modulus of the
CO₂ SI clathrate hydrate (see discussion of the clathrate bulk modulus in Section 2.2). For this somewhat extreme case, sinking clathrate grains turn buoyantly neutral 60 km below the ocean surface, whereas the ocean is 71 km deep. We assume here a gravitational acceleration of $g = 10^3 \text{ cm s}^{-2}$. Therefore, it is very likely that clathrate grains forming in the liquid water from dissolved CO₂ will tend to sink to the bottom of the ocean. This mode of clathrate grain formation has been verified experimentally to yield grains more dense than fresh water or Earth’s sea water (see Warzinski et al. 2000, and references therein).

The sinking velocity of clathrate grains, due to their negative buoyancy, was measured in a field study by Riestenberg et al. (2005). In their experiment, carbon-dioxide was injected into the ocean at a depth of about 1 km (approximately Sverdrup’s depth of no motion), and a formation of CO₂ SI clathrate hydrate on the liquid carbon dioxide particles was reported. The radius of the particles formed following the injection was approximately 0.6 cm. The grains’ descent to the abyss was following a remotely operated vehicle, and a sinking velocity of 5 cm s⁻¹ was derived. This velocity includes turbulent mixing in the ocean and the locality where the experiment was conducted. In their case study, only 40% of the carbon dioxide droplet was converted to clathrate hydrate; the rest remained as liquid CO₂ confined to the droplet core. At the depth where the experiment was conducted, liquid CO₂ is less dense than water. In our case, because the grains form directly from dissolved carbon dioxide, they are expected to be pure clathrate hydrate and therefore more dense than those formed in the experiment of Riestenberg et al. (2005). The experimental velocity is therefore a lower bound for our case of study. With the aid of Stoké’s drag force, we can scale the experimental velocity to other particle sizes:

$$v(a) \approx 5\left(\frac{a}{0.6 \text{[cm]}}\right)^2 \text{[cm s}^{-1}]$$.  \hspace{1cm} (83)

A grain with a radius of $a = 100 \mu\text{m}$ will have a descent velocity of approximately $10^{-3} \text{ cm s}^{-1}$, and take about 100 years to traverse the 100 km depth of the ocean on its way to the bottom. The descent timescale will also be affected by grain coagulation. Nevertheless, we still expect the sinking timescale to remain much shorter than any geological timescale. More importantly, this sinking velocity is at least an order of magnitude larger than any expected vertical motion in the deep unmixed ocean (see Section 5).

In conclusion, the SI CO₂ clathrate hydrate grains that form in the geostrophic arm of our flow tube of interest sink away rather rapidly from the wind-driven circulation. These grains take with them any excess of dissolved CO₂ above the value in equilibrium with the clathrate hydrate grains. Therefore, the CO₂ solubility in the water parcels upwelling in the tropics cannot exceed $n_{CO₂}^{\text{out}}$. Replacing $n_{CO₂}^{\text{out}}$ in Equation (76) with $n_{CO₂}^{\text{deep}}$, and resolving for the temporal evolution of the partial atmospheric pressure of CO₂, we obtain:

$$P_{CO₂}^{\text{atm}}(t) = \left(P_{CO₂}^{\text{atm}}(t = 0) - \frac{n_{CO₂}^{\text{deep}}}{\beta(T_{shb})}\right)e^{-t/\tau} + \frac{n_{CO₂}^{\text{deep}}}{\beta(T_{shb})},$$  \hspace{1cm} (84)
where \( P_{\text{atm}}(t = 0) \) is an initial carbon-dioxide atmospheric pressure, and the timescale for restoring steady state is:

\[
\tau = \frac{2R_p}{u_g \mathcal{R}(T_{\text{std}}) m_{\text{CO}_2} g N_{\text{wdc}}} \approx \left( \frac{16}{9} \right) \text{[kyr]}.
\] (85)

Here, \( u_g \mathcal{R} \) is the geostrophic flux of water supersaturated in CO\(_2\) entering the clathrate thermodynamic stability field that stretches a distance \( \mathcal{R} \) above Sverdrup’s depth of no motion. Even a relatively small value for \( \mathcal{R} \), such as 1 m, gives a timescale of 10\(^4\) years. In other words, steady-state pressure is restored rapidly following perturbations that try to increase it.

6.2. Sea-ice Formation

Marshall et al. (2007) predict subfreezing surface temperatures as low as 250 K at the poles. Under such subfreezing conditions, solidification of surface water in the form of ice Ih is favored even in the presence of gaseous CO\(_2\) (Nguyen et al. 2015; see supplement as well, for water consumption rates). Therefore, the formation of SI CO\(_2\) clathrate hydrate directly from an aqueous CO\(_2\) solution, the mode described in Englezos et al. (1987), is less probable. It is more likely that ice Ih of subfreezing structure initially forms at the ocean’s surface, which would then transform to CO\(_2\) clathrate hydrate when exposed to an atmosphere supersaturated in CO\(_2\). This transformation between the phases is facilitated by a disordered layer of water molecules that is required in order to match both phases’ crystal structures, and provides the necessary low free energy surface for the heterogeneous nucleation to proceed (Nguyen et al. 2015). It is very important to note that an atmosphere supersaturated in CO\(_2\) refers here to an atmosphere in which the partial pressure of CO\(_2\) is higher than the appropriate dissociation pressure of the clathrate. The higher the supersaturation, the greater is the driving force that transforms the ice Ih grains to CO\(_2\) clathrate hydrates.

Moudrakovski et al. (2001) experimented on clathrate hydrates of Xe and found that there is a time interval of tens to hundreds of seconds, following the exposure to Xe, before the first clathrate hydrate crystals form. They refer to this as the induction time for clathrate hydrates. Later experiments on clathrate hydrates of CH\(_4\) and CO\(_2\) disputed the existence of such a time interval (Staykova et al. 2003; Genov et al. 2004). A phenomenological theory describing the rate of transformation of ice Ih grains into clathrate hydrate was presented in Staykova et al. (2003). The theory considers an initial rapid transformation on the ice grain boundaries, followed by a slower transformation controlled by enclathration reaction rates and permeation rates of water and carbon-dioxide molecules through a forming clathrate hydrate layer surrounding the ice grain. This theory was further developed to include transformation of ice into clathrate hydrate inside grain cracks (Genov et al. 2004). Genov et al. (2004) performed experiments on the rate of transformation of ice Ih to CO\(_2\) clathrate hydrate that were then used to estimate the various coefficients of their kinetic theory. The experiments were conducted in the temperature range of 193–272 K, which fully covers our temperature range of interest. We adopt the theories of Staykova et al. (2003) and Genov et al. (2004) in order to derive the mole fraction of ice Ih converted to CO\(_2\) clathrate hydrate, \( \alpha(t) \). This parameter is a complicated function of the pressure of CO\(_2\), temperature and the ice morphology.

Understanding sea-ice formation on Earth is important to modeling climate trends. Therefore, it has rightfully received the attention of climatologists aspiring to incorporate it into atmospheric and oceanic models. When modeling sea-ice formation on Earth, one usually has to consider, for example, brine pockets and a layer of accumulated snow (Maykut & Untersteiner 1971; Semtner 1976). The most up-to-date models can also account for algae accumulations (Honke et al. 2015). Expeditious to the poles provide many of the required parameter values for modeling sea ice (e.g., Lewis et al. 2011; Ackley et al. 2015). If polar sea ice forms on water planets, then its modeling is complicated not only by the lack of field and observational data, but also by the different chemical environment. First, we do not expect brine to exist in any significant quantity in sea ice on water planets. Second, high concentrations of clathrate-forming molecules in the atmosphere would render clathrate hydrates an important phase, one that must be considered when modeling the thermodynamics of sea-ice. In this subsection, we consider sea-ice to be a composite of ice Ih and clathrate of CO\(_2\).

A layer of ice Ih forming under subfreezing atmospheric conditions is initially quite thin. This means that it can support a high conductive heat flux that would cause the freezing of underlying layers. The evolution of sea-ice is therefore governed mostly by conduction of heat (e.g., Maykut & Untersteiner 1971):

\[
\rho_{\text{comp}} C_{\text{comp}} \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left( k_{\text{comp}} \frac{\partial T}{\partial z} \right) + Q. \] (86)

Here, \( \rho_{\text{comp}}, C_{\text{comp}}, \) and \( k_{\text{comp}} \) are the mass density, heat capacity, and thermal conductivity of the composite, respectively. \( Q \) represents a heat source due to the continuous phase change between ice Ih and clathrate.

The solution to the above heat transport equation is greatly complicated by the formation of clathrates. As shown in Figure 23 (the lower-pressure part is of relevance here), the mass density of SI CO\(_2\) clathrate hydrates is higher than that of ice Ih or liquid water. Because the clathrate will form mostly at the interface with the atmosphere, a sea-ice block would be heavier at its top. This is in contradiction to sea ice forming on Earth, and is an unstable configuration. This means the initial and surface conditions become complex functions of time that depend on the stability against flipping. However, this dynamical instability leads us to suggest a simplification; i.e., that sea ice on water planets tends to form rather uniformly. This is because the instability would tend to rotate the block of ice and expose the lower bottom of the less dense ice Ih to the atmosphere. This fresh ice Ih will also begin to transform into clathrate. Therefore, compositional gradients tend to diminish, and the mass density for the sea-ice composite (derived in Appendix A.2) can approximate the entire block of ice:

\[
\rho_{\text{comp}} = (1 - \phi_0 \rho_{\text{pore}}) [\rho_{\text{Ih}} + \alpha (\rho_{\text{pore}} - \rho_{\text{Ih}}) + \zeta \alpha (\rho_{\text{clath}} - \rho_{\text{pore}})] + \phi_0 \rho_{\text{pore}}. \] (87)

Here, \( \phi_0 \) is the initial porosity of the formed sea-ice, \( \zeta \approx 1.133 \) is the expansion factor when a mole of ice Ih converts to SI CO\(_2\) clathrate hydrate, \( \rho_{\text{Ih}} \) and \( \rho_{\text{clath}} \) are the homogeneous ice Ih and clathrate hydrate bulk mass densities, and \( \rho_{\text{pore}} \) is the mass density of the pore filling material. Let us
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consider a few of the interesting features of such a sea-ice composite.

The mole fraction converted to clathrate hydrate, \( \alpha \), naturally falls between 0 and 1. However, the requirement that the porosity at any given moment must be positive combined with Equation (124) from Appendix A.2, yields:

\[
\alpha < \frac{\phi_{\text{pore}}^0}{(\zeta - 1)(1 - \phi_{\text{pore}}^0)} \equiv \alpha_{\text{max}}. \tag{88}
\]

This criterion shuts off any further transformation of the ice Ih grains into clathrate hydrate when the expansion due to the transformation fills up the pore space. Beyond this value for \( \alpha \), any further transformation is controlled, not by the permeability of gas into the ice block, but rather by the macroscopic scale diffusion times of atmospheric \( \text{CO}_2 \) through the solid matrix, which should slow down the transformation process considerably. Complying with the above criterion means remaining below the solid blue curve in Figure 24. From the figure, we see that this pore space restriction is effectively lifted when \( \phi_{\text{pore}}^0 > 0.117 \).

For the sea-ice to be able to sink into the ocean, its mass density should be larger than that of the surface ocean water (i.e., \( \rho_w < \rho_{\text{comp}} \)). This results in a lower bound value for \( \alpha \) of:

\[
\alpha > \frac{\rho_w - \rho_{\text{th}} + \phi_{\text{pore}}^0(\rho_{\text{th}} - \rho_{\text{pore}})}{(1 - \phi_{\text{pore}}^0)(\rho_{\text{pore}}(1 - \zeta) - \rho_{\text{th}} + \zeta\rho_{\text{clath}})} \equiv \alpha_{\text{min}}. \tag{89}
\]

For the scenario where only atmospheric gas (of negligible mass density) fills the pores, sinking of the sea-ice requires remaining above the solid red curve in Figure 24. However, the differential buoyancy between the ocean’s liquid water and the SI \( \text{CO}_2 \) clathrate hydrate can drive a Darcy-type flow of the aqueous “magma” into the sea-ice composite. When entering the pores, the liquid would solidify into ice Ih. The velocity associated with this flow may be estimated as (see Section 4.5 in Schubert et al. 2001):

\[
V_{\text{Darcy}} = \frac{1}{32} \delta^2 \frac{g}{\mu_w} (\rho_{\text{clath}} - \rho_w), \tag{90}
\]

where \( \delta \) is the diameter of a pore tube that we assume to be within the range of 10–100 \( \mu \text{m} \), from the size of ice grains that do not have the time to ripen. The dynamic viscosity of ocean water near freezing is \( \mu_w = 1.792 \text{ centipoise} \) (Cho et al. 1999). Thus, crossing a 1 m length scale (depth of sea ice on the Earth) takes between 1 and 110 hr. Some filling of residual pore space with ice Ih is therefore reasonable. We note that, although \( \text{CO}_2 \) trapped in pores partially converts to SI \( \text{CO}_2 \) clathrate hydrate, the higher dissociation pressure of \( \text{N}_2 \) clathrate hydrate would tend to keep \( \text{N}_2 \) in gaseous form. The later filling of the pores with liquid water and its solidification would probably expel this \( \text{N}_2 \) back into the atmosphere. Finally, assuming the pore filling material is ice Ih, the sinking of the sea-ice composite will be possible in the parameter space above the solid green curve in Figure 24. Complying with both the lower and upper bounds for \( \alpha \) requires an initial porosity of at least 0.043.

Let us assume that the sea-ice formation is restricted to between the pole and latitude \( \lambda_{\text{ap}} \), and that the surface atmospheric temperature in this region is \( T_{\text{sp}} \). Therefore, the volume of the sea-ice sheet is:

\[
2\pi R_p^2 (1 - \sin \lambda_{\text{ap}}) h_{\text{ice}}, \tag{91}
\]

where \( h_{\text{ice}} \) is the sea-ice sheet thickness. The sea-ice interacts with the atmosphere, and its SI \( \text{CO}_2 \) clathrate hydrate mole fraction increases. When this fraction reaches the value \( \alpha_{\text{min}} \) (see Equation (89)), the floating sea-ice becomes gravitationally unstable. Therefore, the volume of the SI \( \text{CO}_2 \) clathrate hydrate in the sea-ice composite just prior to it sinking is:

\[
2\pi R_p^2 (1 - \sin \lambda_{\text{ap}}) h_{\text{ice}} \zeta \alpha_{\text{min}} (1 - \phi_{\text{pore}}^0), \tag{92}
\]

where we have used Equation (123) from Appendix A.2. Hence, the total number of \( \text{CO}_2 \) molecules trapped in clathrate cages within the ice sheet is:

\[
2\pi R_p^2 (1 - \sin \lambda_{\text{ap}}) h_{\text{ice}} \zeta \alpha_{\text{min}} (1 - \phi_{\text{pore}}^0) \frac{46}{V_{\text{cell}}} \frac{1}{5.75}, \tag{93}
\]

where we have assumed full occupancy of the clathrate cages. In the case where the time needed to reach \( \alpha_{\text{min}} \) is \( \Delta \tau \), the number of \( \text{CO}_2 \) molecules removed from the atmosphere per unit time is:

\[
\frac{dN_{\text{ice-sink}}}{dt} = \frac{2\pi R_p^2 (1 - \sin \lambda_{\text{ap}}) h_{\text{ice}} \zeta \alpha_{\text{min}} (1 - \phi_{\text{pore}}^0)}{\Delta \tau} \times \frac{46}{V_{\text{cell}}} \frac{1}{5.75}. \tag{94}
\]

Following the sinking of the sea ice, a new sea-ice layer forms and the process repeats.
Consider, for example, the important process of a secondary atmospheric outgassing. If the initial partial atmospheric pressure of carbon-dioxide is below the dissociation pressure value for the SI CO₂ clathrate hydrate, for the temperature \( T_{\text{sp}} \), clathrate-enriched sea ice does not form. Therefore, secondary outgassing is first controlled by the wind driven circulation described in the previous subsection. As the partial atmospheric pressure of carbon-dioxide exceeds the dissociation pressure for the subpolar temperature, a clathrate formation driving force begins to operate. As the atmospheric pressure of carbon-dioxide increases to continue, so does the driving force. This results in a decreasing value for the time interval \( \Delta \tau \). As steady state is approached, the latter will reach some asymptotic value, \( \Delta \tau_{\text{asy}} \). This asymptotic value is the time that the sea ice remains afloat in steady state atmospheric conditions.

We still need to estimate the sea-ice thickness, \( h_{\text{ice}} \), at the time of sinking. Sea-ice grows by solidification of water at its base, releasing the latent heat of fusion, \( L_f \). This heat must be conducted outward through the ice before the ice can continue to thicken. The liquid water at the base of the sea-ice layer must be on the verge of freezing, \( T = T_{\text{melt}} \). Confined from below by the melting temperature of ice Ih, and from above by the atmospheric temperature, the conductive heat flux in the sea-ice is:

\[
\kappa_{\text{comp}} \frac{T_{\text{melt}} - T_{sp}}{h_{\text{ice}}},
\]

Hence, its rate of growth is:

\[
\frac{dh_{\text{ice}}}{dt} \sim \kappa_{\text{comp}} \frac{T_{\text{melt}} - T_{sp}}{L_f \rho_{\text{Ih}}} 1,
\]

which yields the result:

\[
h_{\text{ice}} \sim \sqrt{2 \kappa_{\text{comp}} \frac{T_{\text{melt}} - T_{sp}}{L_f \rho_{\text{Ih}}} \Delta \tau}.
\]

Let us test the last scaling on Earth’s sea ice. The thermal conductivity of ice Ih at \( T = 250 \) K is \( 0.024 \times 10^7 \) erg s⁻¹ cm⁻¹ K⁻¹ (Slack 1980), its bulk mass density is 0.917 g cm⁻³, and its latent heat of fusion is \( 334 \times 10^7 \) erg g⁻¹ (Feistel & Wagner 2006). Considering a temperature difference across the ice of 40 K, and two winter months for the time interval, yields an ice thickness of 1.8 m. This agrees well with satellite measurements for the thickness of Arctic sea-ice (Ricker et al. 2014).

However, it is important to note that, as time goes on, the sea ice will not thicken indefinitely. This is important mostly when the partial atmospheric pressure of carbon-dioxide is very close to its clathrate dissociation pressure, a condition for which \( \Delta \tau \to \infty \). Even if the summer months are disregarded, some heat from the abyssal ocean should cap the sea-ice thickness. This heat flux is hard to estimate without a global hydrodynamic solution, and for Earth is usually estimated from sea-ice thickness measurements assuming the system is in equilibrium (see Ackley et al., 2015, and references therein). There is, however, an interesting compensation in the case of sea-ice on water planets. On the one hand, an inefficient global circulation and the thick planetary ice mantle ought to result in low heat fluxes at the sea-ice bottom. This would suggest a thicker ice sheet. On the other hand, the much lower thermal conductivity of clathrates would tend to encourage a thinner ice sheet. We will return to speculate about the sea-ice thickness below.

Lastly, we wish to remark on the thermal conductivity of the sea-ice composite, \( \kappa_{\text{comp}} \). During the conversion of the continuously shrinking ice Ih grains to SI CO₂ clathrate hydrate, the latter expanded at the expense of the pore space (Staykova et al. 2003; Genov et al. 2004). Therefore, as the composite evolves, it may be approximated as a continuous clathrate hydrate solid within which small ice Ih spheres are embedded. The thermal conductivity of such a composite was solved by Maxwell (Bird et al. 2007), and in our case has the following form:

\[
\frac{\kappa_{\text{comp}}}{\kappa_{\text{clath}}} = 1 + \frac{3 \phi_{\text{Ih}}}{\kappa_{\text{Ih}} + 2 \kappa_{\text{clath}}} \left( \frac{\phi_{\text{Ih}}}{\kappa_{\text{Ih}} - \kappa_{\text{clath}}} \right) \phi_{\text{Ih}},
\]

where the volume fraction of the ice Ih spheres was derived in Appendix A2 (see Equation (125)). In the last relation, \( \kappa_{\text{Ih}} \) is the thermal conductivity of ice Ih taken from Slack (1980). The thermal conductivity of SI CH₄ clathrate hydrate, \( \kappa_{\text{clath},m} \), is not known experimentally. Molecular dynamics simulations suggest that it is about 15% smaller than the thermal conductivity of SI CH₄ clathrate hydrate (Jiang & Jordan 2010). The thermal conductivity of CH₄ clathrate hydrate is known experimentally, and here we adopt the values reported in Krivchikov et al. (2006). In a water planet, the formation of polar sea-ice and the wind-driven circulation operate simultaneously. Therefore, the evolution of the atmosphere is governed by the sum of all the fluxes of the mechanisms we have described:

\[
\frac{dN_{\text{CO₂}}}{dt} = 2 \pi R_p \delta_s (j_{\text{out}}^{\text{CO₂}} - j_{\text{in}}^{\text{CO₂}}) N_{\text{wdc}} - S_w dN_{\text{ice-sink}} \frac{dt}{m_{\text{CO₂}}} - Q \frac{4 \pi R_p^2}{m_{\text{CO₂}}}.
\]

where the different parameters were defined above in Equations (78), (79), and (94). We have also inserted a probability function \( S_w \), which acts as a switch, turning the sea-ice atmospheric CO₂ sink mechanism on and off. We will explain its origin and form in more detail below.

We expect the partial atmospheric pressure of CO₂ to reach a steady state after a very long time:

\[
\lim_{t \to \infty} \frac{dN_{\text{CO₂}}}{dt} = 0.
\]

Inserting the relations:

\[
\lim_{t \to \infty} \eta_0 = \frac{\text{Deddy} L_g}{2u_g \delta_b L_{\text{ocean}}}, \quad \lim_{t \to \infty} \eta_1 = -\frac{\text{Deddy} L_g}{2u_g \delta_b L_{\text{ocean}}},
\]

into Equation (99), the steady-state atmospheric pressure of CO₂ is found to obey:

\[
0 = \pi R_p N_{\text{wdc}} \beta(T_{\text{sh}}) \text{Deddy} L_g \frac{N_{\text{deep}}}{L_{\text{ocean}}} \left[ \frac{p_{\text{CO₂}}}{\beta(T_{\text{sh}})} - p_{\text{CO₂}}^{\text{atm}} \right] - S_w \frac{dN_{\text{ice-sink}}}{dt} - Q \frac{4 \pi R_p^2}{m_{\text{CO₂}}}.
\]
We now turn to numerically solve the last equation for various system parameters.

We start by explaining the role of the probability function \( S_w \). In Figure 25, we solve for the steady-state atmospheric partial pressure of CO$_2$ (see Equation (102)) as a function of the initial ice Ih grain radius. That is, the initial ice Ih grain size that forms when the liquid water first comes in contact with the sub-freezing polar atmospheric temperature, \( T_{sp} \). For the corresponding steady-state pressures, we also plot the duration of time for which the sea-ice remains afloat, \( \Delta \tau_{asy} \). We further assume that \( S_w = 1 \). The initial grain size is important in determining the rate of conversion from ice Ih into SI CO$_2$ clathrate hydrate (Staykova et al. 2003; Genov et al. 2004). The smaller the initial ice Ih grain size, the faster the conversion. Thus, the period of time for which the sea-ice slab remains afloat is shorter. This results in a more efficient mechanism for removing CO$_2$ from the atmosphere. Assuming \( T_{sp} = 240 \) K, the dissociation pressure of SI CO$_2$ clathrate hydrate is approximately 3 bar. In the case that no sea ice forms, a steady CO$_2$ atmospheric pressure of 35 bar is established. From the figure, it is clear that the smaller grain sizes we have solved for remove atmospheric CO$_2$ so efficiently that the resulting steady-state atmospheric pressure of CO$_2$ is only slightly above the dissociation pressure of SI CO$_2$ clathrate hydrate, for the subpolar temperature. This fact means that the driving force to form SI CO$_2$ clathrate hydrate can be rather small and still sink atmospheric CO$_2$ efficiently. However, for this to be true, the duration of time that the sea-ice slab needs to remain afloat and in contact with the atmosphere is very long (\( \Delta \tau_{asy} > 1 \) kyr).

Clearly, sea ice is not anchored in place on water planets, as some sea ice is on the Earth. If sea-ice on water planets floats for a long period of time, it may migrate to a warmer climate, where its clathrates could dissociate and release the enclathrated CO$_2$ back to the atmosphere. Therefore, removal of atmospheric CO$_2$ by sinking sea-ice becomes inactive, i.e., \( S_w = 0 \). If this happens, the pressure of CO$_2$ in the atmosphere would build up and increase the driving force to form clathrates. As a result, \( \Delta \tau_{asy} \) would decrease until it becomes small enough that the sea ice becomes buoyantly unstable before drifting out of the subpolar region. This leads to the criterion:

\[
\Delta \tau_{asy} \lesssim \frac{R_p}{v_{div}} \left( \frac{\pi}{2} - \lambda_{sp} \right) \equiv \Delta \tau_{asy}^{\text{limit}}.
\]

Here, \( v_{div} \) is the divergence velocity that is responsible for the drift of ice slabs out of the polar region. Ice slabs roughly follow atmospheric isobars that constantly change, in addition to colliding with each other. Therefore, sea-ice motion has an important stochastic component (Leppäranta 2011). The free drift velocity of sea ice is easier to estimate. It is mostly due to winds, and is at most 2% of the geostrophic wind speed (Thorndike & Colony 1982). For the latter, we adopt 10 m s$^{-1}$ (see Marshall et al. 2007, for derived subpolar wind velocities). However, the free drift velocity is probably somewhat higher than the divergence velocity, and is perhaps more appropriate for describing a mean free path velocity. Hence, for our adopted velocity, the above criterion is somewhat too stringent, forcing the atmospheric pressure of CO$_2$ to higher values.

Whether the last criterion is satisfied or not switches \( S_w \) between 1 and 0, respectively. We model it using a smooth step function:

\[
S_w = \exp \left\{ - \left( \frac{\Delta \tau_{asy}}{\Delta \tau_{asy}^{\text{limit}}} \right)^d \right\}.
\]

Rather than having a sharp latitudinal limit, the surface temperature ought to gradually increase toward lower latitudes. As a consequence, the local dissociation pressure of clathrates increases and a smooth step function is more appropriate.
Below, by varying the power $d$ we test the sensitivity of the steady-state atmospheric pressure to our adopted model for $S_w$. For $\lambda_{sp} = 60^\circ$, we have $\Delta \tau_{asy} \approx 1$ year. This gives a sea-ice thickness, $h_{ice}$, of 2 m at most. We use this criterion to cap the maximal sea-ice thickness for purposes of modeling its role in sinking atmospheric CO₂. With the sea-ice migration taken into account let us now resolve Figure 25.

In Figure 26, we resolve for the steady-state CO₂ partial pressure dependence on the initial ice Ih grain radius. The horizontal green curve is the dissociation pressure for SI CO₂ clathrate hydrate at a temperature of $T_{sp} = 240$ K. Left panel: the corresponding time that sea-ice remains afloat under steady-state atmospheric conditions. In both panels, the dashed red curve corresponds to $D_{eddy} = 10^{-3}$ cm² s⁻¹ and $d = 2$ in the model for $S_w$ from Equation (104). All the blue curves assume $D_{eddy} = 10^{-2}$ cm² s⁻¹. Dashed–dotted, solid, and dashed blue curves assume $d = 1$, $d = 2$, and $d = 3$ in the model for $S_w$ from Equation (104), respectively. Other system parameters adopted are: $T_{sp} = 240$ K, $T_{shb} = 20^\circ$C, $T_{deep} = 4^\circ$C, $\phi_{pore} = 0.1$, $\rho_{pore} = 0$ g cm⁻³, and $\lambda_{sp} = 60^\circ$. We assume $Q_c = 0$ bar Myr⁻¹.

From Figure 26, we see that varying the vertical deep-ocean eddy diffusion by two orders of magnitude affects the steady-state atmospheric pressure of CO₂ less than varying $d$, from the model for $S_w$ between 1 and 3. This implies that our results are somewhat sensitive to the adopted model for $S_w$. However, the transition between an ice-cap controlled atmospheric pressure to one controlled by the saturated deep ocean falls in the grain size regime of a few hundred micrometers. This result is insensitive to how sharp the step function $S_w$ is.

Clearly, the initial ice Ih grain size distribution is of great importance. Unfortunately, the range of a few hundred micrometers does not allow for an easy determination of whether the sea-ice CO₂ removal mechanism is dominant or not. Grains falling in this range are observed when ice forms from supercooled water (Arakawa 1954). Here, we have used experimentally determined conversion rates of ice Ih to clathrate. These rates were obtained by using artificially sieved spherical ice grain samples. However, when supercooled water freezes, disk crystals are formed first. A more flattened shape would make the inner ice Ih grain more accessible to diffusing CO₂. Therefore, after increasing the rates of conversion from ice Ih to clathrate, Shimada & Furukawa (1997), observed that pure supercooled water disk crystals, although a few mm in diameter, are only 100–200 μm thick. However CO₂ was not introduced in their experiments. It is interesting to note that Shimada & Furukawa (1997) found that an ice crystal thickness of 100 μm is attained after about 10³ s (for their type II disc crystal). According to Genov et al. (2004), this timescale is on the same order of magnitude as that required to form a surface clathrate hydrate layer that may coat the ice Ih grain. Therefore, it is very probable that CO₂ clathrates become incorporated into the grain during its period of growth. The addition of clathrates would also decrease the grain’s thermal conductivity, keeping it thinner and making its interior more accessible. However, these
complications are beyond the scope of this work and need to be addressed experimentally.

Additional complications arise from our supercooled environment being highly influenced by waves, winds, and resulting turbulences of various scales. However, it is clear that sea ice of the right morphology is able to decrease the atmospheric pressure of CO$_2$ by an order of magnitude from the wind-driven value. One would expect that the denser pore filler would make the sinking of the sea-ice more effective, and therefore lower the steady state atmospheric CO$_2$ pressure. In the right (left) panel, we assume an initial porosity, $\phi_{\text{initial}}$, of 0.2 (0.1). Over the range of mass density, we test for the pore-filling material. For the lower initial porosity, the steady-state atmospheric pressure changes by 1.3% and 4.4% for the smaller and larger initial grain sizes, respectively. For the higher initial porosity, the steady-state atmospheric pressure changes by 7.3% and 25.5% for the smaller and larger initial grain sizes, respectively, over the mass density range examined. The lower the initial porosity, the less sensitive the CO$_2$ atmospheric pressure becomes to the pore-filler density. The sea-ice becomes negatively buoyant when reaching a conversion fraction of $\alpha_{\text{min}}$ for ice Ih to clathrate hydrate. As the value for the initial sea-ice porosity increases, so does the difference in the value for $\alpha_{\text{min}}$ between a pore-filling density of vacuum and of ice Ih (see Figure 24).

In Figure 27, we plot the steady-state partial atmospheric pressure of CO$_2$ as a function of the subpolar surface temperature. The timescale to reach a steady state is on the order of the eddy-diffusion timescale across the deep unmixed ocean. Therefore, $T_{\text{sp}}$ is an average over many planetary years, rather than a seasonally dependent variable. For our chosen system parameters, we see that the steady-state atmospheric pressure of CO$_2$ is only slightly above the SI CO$_2$ clathrate hydrate dissociation pressure when the subpolar temperature is higher than about 240 K. This small pressure difference means a low driving force to form clathrates. It is the relatively higher temperatures that keep the rate of conversion from ice Ih to SI CO$_2$ clathrate high, and the sea-ice sink mechanism efficient. For the lower subpolar temperatures examined, the low conversion rate between the two water ice phases begins to prevent the ice from reaching buoyant instability before drifting out of the subpolar region. The system responds by increasing the atmospheric pressure of CO$_2$. In other words, it increases the driving force, thus accelerating the phase conversion. This extra driving force is even more necessary when considering larger initial ice Ih grains. Consequently, the steady-state atmospheric pressure has a minimum for these larger grains. We will return to this point in the discussion section below.

To further our understanding of this intricate system, we plot steady-state isobars of atmospheric CO$_2$ in the following figures. These are plotted as a function of the subpolar and subtropic oceanic surface temperatures. In Figures 30 and 31, we vary the initial ice Ih grain radius for a deep ocean temperature of 4°C. In Figure 32, we resolve a warmer deep ocean temperature of 8°C for some grain size cases.

For the smaller initial grain sizes the isobars, are solely dependent on the subpolar temperature throughout the entire temperature spectrum examined. Meaning, the sea-ice mechanism for sinking atmospheric CO$_2$ is the dominant effect. For the 100 and 150 μm cases, the minimum in the atmospheric pressure is clearly seen. The fact that the isobars remain...
The wind-driven circulation tries to equilibrate the atmospheric pressure of CO$_2$ with the dissolved CO$_2$ throughout the deep ocean. This circulation is likely to become the dominant effect for the higher subtropic temperatures, which push the pressure upward, as well as for the lower subpolar temperatures, for which conversion to clathrate hydrate may become kinetically slow. Indeed, this temperature criterion is where the dependency of the isobars on the subtropic temperature, $T_{sbt}$, begins to appear. For the case of the initial grain size of 200 $\mu$m, and for our highest examined $T_{sbt}/T_{sp}$ ratio, the wind-driven circulation becomes the dominant effect.

For the larger initial grain sizes, the isobars become more and more dependent on the subtropic surface temperature, as the wind-driven circulation takes over. However, the isobars remain horizontal for the higher subpolar temperatures. In addition, they keep close to the dissociation pressure of SI CO$_2$ clathrate hydrate, which is approximately 8.2 bar for 265 K. For the case of the hotter deep ocean, the response of the isobars to the different oceanic surface temperatures and grain sizes is similar to the case of the colder deep ocean. When the sea-ice sink mechanism is dominant, the deep ocean temperature hardly affects the observed atmosphere. On the contrary, when the wind-driven circulation becomes dominant, it equilibrates the atmospheric CO$_2$ to a value that is dependent on the deep ocean temperature.

### 7. Discussion

Our model for the SI CO$_2$ clathrate hydrate yields cage occupancies as a function of pressure and temperature. For the pressure range of a few tens of bars, some experiments suggest that the small cage occupancy is lower than predicted by our model (see Figures 6 and 7). Cage occupancies are part of our model for the solubility of CO$_2$ in water while in equilibrium with the clathrate hydrate phase. This possible discrepancy at a
few tens of bars suggests our derived solubility may be exaggerated by approximately 8% for this pressure range. However, our geophysical model relies more on the solubility in equilibrium with the clathrate phase for pressures above hundreds of bars. Hence, we do not expect this uncertainty to introduce a considerable error into the geophysical model.

Recent experiments (Bollengier et al. 2013; Tulk et al. 2014) indicate that, rather than separating to CO$_2$ ice and water ice under high pressure, the SI clathrate hydrate of CO$_2$ transforms into a new phase with a crystallographic structure similar to that of the filled ice of methane. This new phase is probably stable up to 1 GPa. Because little is known of this new phase at the moment, quantifying its influence is impossible and more experimental data is needed. Because this new filled-ice phase becomes unstable at pressures above 1 GPa, it probably does not play a significant role in the transport of CO$_2$ outward from the deep mantle. It may play a role in setting the mechanical properties of the upper boundary layer of the ice-mantle convection cell, and thus the dynamics of the ocean bottom. A filled ice sub-layer may act as extra storage for CO$_2$, in addition to the clathrate layer. That CO$_2$ may become available to the ocean if it tries to unsaturate.

In the $\beta$ domain (see Figure 12), if the ocean’s bottom is composed of CO$_2$-filled ice, then one should inquire what solubility of CO$_2$ is enforced in the overlying ocean due to this new phase. If this solubility is higher than the value we estimate for the equilibrium with the clathrate hydrate phase, then an elevated clathrate layer should still form. This clathrate layer then controls the solubility in the ocean, clearing any supersaturation by forming clathrate grains. Only if the newly discovered filled-ice phase enforces a lower solubility, will supersaturation with respect to clathrates not be achieved and a mid-ocean clathrate layer not form. It is interesting to note that, for the case of CH$_4$, when going from a cage clathrate to filled ice, the ratio of guest to water-host abundance increases (Loveday et al. 2001). This is also true for the filled ice of hydrogen, albeit with more complexity at intermediate pressures due to multiple cage occupancies (see Qian et al. 2014, and references therein). If this trend is also true for CO$_2$, it may suggest that the necessary supersaturation required for clathrate formation within the ocean can be achieved.

A full dynamical investigation of this hypothesized mid-ocean clathrate layer is beyond the scope of this work.

Figure 30. Isobars of atmospheric CO$_2$ as a function of the subpolar, $T_{sp}$ and subtropic, $T_{sbt}$ oceanic surface temperatures. Upper left: initial ice Ih grain radius of 50 $\mu$m. Upper right: initial ice Ih grain radius of 100 $\mu$m. Lower left: initial ice Ih grain radius of 150 $\mu$m. Lower right: initial ice Ih grain radius of 200 $\mu$m. Other system parameters adopted are: $D_{\text{eddy}} = 10^{-2}$ cm$^2$ s$^{-1}$, $T_{\text{deep}} = 4^\circ$C, $\phi_{\text{pore}} = 0.1$, $\rho_{\text{pore}} = 0$ g cm$^{-3}$, and $\lambda_{\text{sp}} = 60^\circ$. Also we assume $Q_c = 0$ bar Myr$^{-1}$ and $d = 2$. 

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However, if such a layer can form and become thick and stable, it may isolate internal processes from the upper ocean. As a consequence, atmospheric observations may predominantly act as probes into the nature of this layer, thus potentially severing connections between the deep mantle and atmospheric observations.

In Section 6.1, we also introduce a possible loss of atmospheric CO$_2$ due to erosion. This is measured in bars lost per Myr, and denominated in the text as $Q_{c}$. Pierrehumbert (2010) has suggested that a high flux of energetic photons in a close orbit around an M-dwarf star could result in some loss of CO$_2$ from the planetary atmosphere. A small planet the size of Mars could be stripped off entirely of its primordial CO$_2$ atmosphere due to the action of solar winds. In the latter case, 8 bar of CO$_2$ could be lost in a 1 Gyr (Pierrehumbert 2010), giving $Q_{c} \approx 0.01$ bar Myr$^{-1}$. The efficiency of erosion of CO$_2$ out of the atmosphere must be compared with the efficiency of the internal reservoirs of CO$_2$ in the deep ocean to replenish what is lost. For $Q_{c}$ in bars Myr$^{-1}$, and a deep ocean vertical eddy diffusion coefficient, $D_{edd,} \text{cm}^2 \text{s}^{-1}$, we find that only when $Q_{c}/D_{edd,} > 40$ does the effect of atmospheric erosion become prominent. For $Q_{c}/D_{edd,} > 100$, the atmosphere can be completely eroded of its CO$_2$ content. A value larger than 100 for $Q_{c} \approx 0.01$ bar Myr$^{-1}$ is only possible if the deep-ocean vertical-eddy diffusion coefficient is close to its minimal possible value. One should also consider that very high values for the ratio $Q_{c}/D_{edd,}$ are probably more likely for a young M-dwarf star while it is still very active. Therefore, for more mature planetary systems, the internal outgassing of CO$_2$ should control the pressure of CO$_2$ in the planet’s atmosphere.

We note that, if cometary composition is a good approximation for the primordial composition of a water planet’s ice mantle, then a 20 bar CO$_2$ atmosphere around a $2M_{\oplus}$ planet with a 50% ice mass fraction represents a very small fraction (about 0.01%–0.1%) of the total ice-mantle budget of CO$_2$. A caveat to this approximation is the possibility that high-pressure chemistry in the deep ice mantle may change the primordial partitioning of carbon between the different carbon-bearing molecules, according to the redox state of the mantle. This issue has not yet been addressed and may change the given percentage margin we estimate here.

Partial filling of the sea-ice composite pore space by water would expel the pore-space gaseous content back into the atmosphere. These are the molecular species that, although in
the pore space, did not experience any impetus to become enclathrated. For example, this includes O\textsubscript{2} and N\textsubscript{2}, which have clathrate dissociation pressures much higher than that for CO\textsubscript{2} (Kuhs et al. 2000). Therefore, removal of atmospheric gas by the sinking of sea ice works selectively on CO\textsubscript{2}.

As we explain in Section 6.2, the partial atmospheric pressure of CO\textsubscript{2} likely has a minimum value as a function of the subpolar surface temperature (see Figure 29 and its related text for more detailed information). The minimum in the atmospheric pressure of CO\textsubscript{2}, and the subpolar surface temperature corresponding to this minimum, depend on the sea-ice grain morphology. This is clearly seen in Figures 30–32 where we have plotted atmospheric isobars of CO\textsubscript{2} as a function of the subtropic and subpolar surface temperatures.

Whether this intricate behavior produces a negative or a positive feedback mechanism requires coupling our model to a radiative-convective atmospheric model. We will address this issue quantitatively in future work. The greenhouse effect increases the surface temperature when more CO\textsubscript{2} enters the atmosphere. However, increased Rayleigh scattering takes over at some threshold, causing cooling of the surface when more CO\textsubscript{2} is added. Therefore, the greenhouse effect has a maximum (Kasting et al. 1993). Various investigations of this phenomenon place the threshold at about 8 bar of CO\textsubscript{2} (Kasting et al. 1993; Kopparapu et al. 2013; Kitzmann et al. 2015). This does not include the effect of clouds, which are difficult to account for in 1D radiative-convective models for the atmosphere (Kopparapu et al. 2013). The threshold also depends on the type of star, and other molecular species in the atmosphere. Nevertheless, it is interesting to note that the threshold may fall somewhat above the minimal value we find for the partial atmospheric pressure of CO\textsubscript{2}, versus the subpolar surface temperature, for initial ice Ih grains smaller than 400 \textmu m (see Figures 30–32). Thus, a water-rich planet experiencing a reduction in stellar irradiation, causing a drop in high-latitude surface temperatures, may respond by increasing the abundance of CO\textsubscript{2} in its atmosphere while the greenhouse effect is still dominant. If the drop in high-latitude surface temperatures is excessive, sufficiently so to cause a shut down of the sea-ice sink mechanism, the abundance of CO\textsubscript{2} in the atmosphere may spiral to values where Rayleigh scattering becomes dominant, causing further cooling of the surface.

In this work, we find there are two end scenarios for the steady-state atmospheric pressure of CO\textsubscript{2}: one controlled by the pore space, did not experience any impetus to become enclathrated. For example, this includes O\textsubscript{2} and N\textsubscript{2}, which have clathrate dissociation pressures much higher than that for CO\textsubscript{2} (Kuhs et al. 2000). Therefore, removal of atmospheric gas by the sinking of sea ice works selectively on CO\textsubscript{2}.

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In this work, we find there are two end scenarios for the steady-state atmospheric pressure of CO\textsubscript{2}: one controlled by the
polar sea ice and the other by the wind-driven circulation and deep-ocean CO$_2$ saturation values. The transition between these two end scenarios happens when the initial sea-ice grain sizes are on the order of hundreds of micrometers (see Figure 26). This grain size is not unreasonable, and is found in natural environments (e.g., Klapp et al. 2007). Therefore, experiments for our studied system are required in order to resolve this issue.

The likely SI CO$_2$ clathrate hydrate bottom of the ocean has a mass density allowing it to sit stably at the deep ocean, and moderate the abundance of CO$_2$ dissolved in the ocean. In other words, it makes sure the ocean stays saturated if it tries to unsaturate. We therefore conclude that a sub-bar CO$_2$ atmosphere around water-rich ocean exoplanets is less likely. Our results suggest the atmosphere has two discrete states: one of a few bars of CO$_2$, probably no less than 2 bar, and a second discrete state where the planet is surrounded by tens of bars of CO$_2$. Which state is materialized depends on what ocean-atmosphere flux mechanism is dominant; polar sea ice in the first case, and wind-driven circulation in the second case.

The pressure–temperature conditions within the ice mantle of a 2$M_E$ planet are probably not high enough to induce the dissociation of CH$_4$. The incorporation of CH$_4$ in filled ice aids its transport across the ice mantle, if solid-state convection is established (Levi et al. 2014). Therefore, it is likely that CH$_4$ locked in the deep ice mantle would reach the bottom of the ocean, in ocean exoplanets, and then the atmosphere. This outgassed CH$_4$ may potentially affect our model. For example, its existence in the atmosphere may affect the composition and dynamics of the sea ice. If the partial atmospheric pressure of CH$_4$ exceeds the dissociation pressure of SI CH$_4$ hydrate for the subpolub surface temperature (e.g., 8.2 bar for 240 K), then CH$_4$ also may become enclathrated within the sea ice. Because the mass density of SI CH$_4$ hydrate (0.912 g cm$^{-3}$, see Davidson 1983) is less than that of liquid water, it will contribute to the buoyancy of the sea ice. Thus, sea-ice migration to warmer climate may become enhanced, resulting in an increased abundance of CO$_2$ in the atmosphere. Such a mechanism may limit the CH$_4$/CO$_2$ ratio in the atmosphere. This sort of analysis may help astronomers pinpoint ocean exoplanets.

Another way in which CH$_4$ may influence our model is by becoming a part of the clathrate layer in the deep ocean. This will affect the abundance of CO$_2$ in this layer; some clathrate hydrate cages will be filled with CO$_2$, and others with CH$_4$. As a consequence, the solubility of CO$_2$ in equilibrium with the clathrate phase may change, influencing the solubility of CO$_2$ in the overlying ocean and its atmospheric abundance. It would also be important to know how the addition of CH$_4$ varies the mass density of the ocean’s bottom clathrate layer—especially whether this decreases its mass density below that of the water-rich liquid. We hope to address this ternary system in the future.

8. Summary

In this paper, we focus on water planets, which we define to be planets whose water mass fraction is large enough to form an external mantle composed of high-pressure water-ice polymorphs, and also lack a substantial H/He atmosphere. We consider such planets in their habitable zone, so their outermost condensed mantle is a vast and deep liquid ocean.

We study the solubility of CO$_2$ within the parameter space of such oceans, both outside (Section 2.1) and inside (Section 2.2) the thermodynamic stability field of the SI CO$_2$ clathrate hydrate phase. We show that, outside the SI CO$_2$ clathrate hydrate thermodynamic stability field, the solubility can be modeled using Henry’s law for the entire $P$–$T$ space of interest for water planet oceans. The upper bound of this parameter space is the melting curve of water ice VI when in saturation with CO$_2$. We find that, in order for Henry’s law to match the inferred solubility from experimental data for the ice VI melt depression, it is necessary to consider the fugacity of solid CO$_2$. Near the bottom of the ocean, CO$_2$ transforms from a fluid into its phase I solid. We find that, in the region of stability of the phase I solid of CO$_2$, the solubility of CO$_2$ in the aqueous solution decreases with increasing pressure. Throughout this work, we use Henry’s law only for interpolating between solubility data points.

We model the solubility of CO$_2$ in water when in equilibrium with its clathrate hydrate phase. Our model uses results from molecular simulations in addition to macroscopic parameters. This approach allows us to overcome the fact that equations of state for the H$_2$O–CO$_2$ system do not cover our entire parameter space of interest. Our model for the solubility, when in equilibrium with the clathrate phase, predicts the solubility to be insensitive to the pressure. It also predicts that, inside the clathrate hydrate stability field, the solubility increases with the increasing temperature. These behaviors are verified experimentally. Our model can accurately describe experimental data for the solubility in the pressure range where such experiments were conducted (up to a few hundred bars).

Our model also predicts solubilities at the bottom of the ocean (pressure of $\approx$10 kbar) that fall within the error of the inferred solubility from experiments on the melt depression of ice VI. Therefore, inside the clathrate hydrate stability field, our solubility model is interpolative rather than extrapolative.

We plot the phase diagram of the SI CO$_2$ clathrate hydrate over the entire pressure–temperature space of interest for water-planet oceans (see Figure 11 in Section 3). We show that phases that are reservoirs for CO$_2$ have direct contact with the bottom of the ocean. These phases aid in the flux of CO$_2$ from the ice mantle and into the ocean. This is because of the nature of how carbon is stored within the solid matrix. In the Earth, carbon can become stably locked in rock. However, in a water planet, CO$_2$ stored in a clathrate hydrate layer will leak CO$_2$ into the ocean if the latter becomes subsaturated.

We investigate the possibility of storing CO$_2$ deep in the ocean (see Section 4). We argue that CO$_2$ outgassed from the interior may accumulate at the bottom of the ocean in three possible sink stratification cases (denoted as: $\alpha$, $\beta$, and $\gamma$ in Figure 12). Which of the three cases occurs depends on the temperature profile, mostly in the deep-to-mid-ocean. If these sinks become exhausted, any further substantial CO$_2$ outgassing from the interior accumulates in the atmosphere.

For temperatures less than 278 K (at the deep ocean), the SI CO$_2$ clathrate hydrate phase is stable at pressures higher than the melting pressure of water ice VI. We call this the $\alpha$ stratification domain (see Figure 12). Therefore, in this domain, as CO$_2$ is transported outward, it will enter the clathrate thermodynamic stability field and transform the water ice V/VI layer into a CO$_2$ SI clathrate hydrate layer. This clathrate layer then becomes the ocean’s bottom surface, consequently making physical contact with the overlying ocean. If the ocean
The rate of clathrate dissolution in a subsaturated aqueous solution can illustrate this mechanism. Field experiments show that the equilibrium with the clathrate phase, any further CO$_2$ outgassing would yield a CO$_2$ outgassing mechanism. If the outgassing fluxes at the ocean exceeding that predicted by the “gentle” mechanism. In that case, after CO$_2$ concentration in the ocean reaches the saturation value in equilibrium with the clathrate phase, any further CO$_2$ outgassing would sediment to the bottom of the ocean as CO$_2$ clathrate grains. If the outgassing flux of CO$_2$ forced into the ocean is low, little clathrate hydrate would pile up on the bottom of the ocean in a geological timescale (illustrated in the right panel in Figure 15). In the case where the outflux is high, then most of the ocean would solidify into a CO$_2$ SI clathrate hydrate layer (illustrated in the left panel in Figure 15) in a geological timescale. In this latter scenario, a thin near-surface water-rich liquid layer will survive solidification where the pressure is too low to stabilize clathrate hydrate. This narrow aqueous layer will be saturated in CO$_2$ and have an enhanced salinity compared to that of the pre-solidified ocean. We find that a constant global mantle CO$_2$ outgassing flux into the ocean, on the order of $10^{11}$ molec CO$_2$ cm$^{-2}$ s$^{-1}$, will transform 10% of the ocean’s initial mass into clathrate hydrate in 1 Gyr. In the α domain, we calculate that, for our choice of planets, a mass on the order of $10^{22}$ g of CO$_2$ can be stored in the clathrate hydrate layer before this sink is exhausted. This is two orders of magnitude more than the carbon stored in rocks on the Earth (see Williams & Follows 2011). In addition, for the extreme scenario where the entire clathrate layer solidifies, the surviving surface liquid layer can be as shallow as 100 m, with an enhancement of its salinity three orders of magnitude enhancement greater than the original ocean.

The region confined between an ocean bottom temperature higher than 278 K and one not exceeding 294 K defines the β domain (see Figure 12). For this domain, the dissociation pressure of the SI CO$_2$ clathrate hydrate will be lower than the melting pressure of water ice VI. In this domain mantle, CO$_2$ (either embedded in ice VI, or as filled ice) comes into contact with the ocean and tries to saturate it, first reaching the value of saturation when in equilibrium with clathrates. If more CO$_2$ is driven into the ocean, clathrate grains will form within this phase’s stability field. For the deep ocean temperatures in the β domain, the clathrate grains become less dense than the surrounding water-rich liquid near the high-pressure boundary of their thermodynamic stability field. An SI CO$_2$ clathrate hydrate layer may thus accumulate, elevated above the ocean’s bottom of high-pressure ice polymorphs. This elevated solid layer made of clathrates should control the solubility of CO$_2$ in the ocean lying above it, and therefore its accessibility to the atmosphere (see illustration in Figure 17). For a 290 K isotherm, and our choice of planetary parameters, we find the maximum mass of CO$_2$ that can be stored in this mid-ocean layer is approximately $10^{22}$ g. For this isotherm, the clathrate layer may extend as far as 38 km, starting at an elevation of 28 km above the ocean’s ice VI bottom and ending 24 km below the ocean’s surface.

In the case where the thermal profile everywhere in the ocean is higher than 294 K, the ocean falls into the γ domain (see Figure 12). In this regime, the SI CO$_2$ clathrate hydrate is stable nowhere. In this case, the ocean may saturate with CO$_2$ to a concentration appropriate in the absence of clathrate hydrates. When saturation is reached, and if outgassing into the ocean continues, the CO$_2$ will first accumulate on the bottom of the ocean as a phase I solid, followed by a liquid CO$_2$ layer when the former is exhausted. The liquid CO$_2$ layer will terminate at the pressure where it becomes less dense than the ocean’s water-rich liquid. For the planets we are considering, these two layers represent a total sink that can contain as much as $10^{26}$ g of CO$_2$ at the deep ocean. However, considering that solid CO$_2$ is more dense than ice VI (see Figure 16) gravity will probably limit the extent of such layers considerably. However, we argue that such high deep-ocean temperatures are less likely because a thick water-ice mantle underlying the ocean translates to low heat fluxes at the ocean’s bottom (see Section 5 in Levi et al. 2014).

An overturning circulation in the ocean creates potential energy, and therefore requires an external energy source to operate. It was shown for the case of Earth that the power supplied by winds and tides is sufficient to support the Atlantic overturning circulation (Wunsch & Ferrari 2004). In Section 5, we estimate the power needed to run an oceanic overturning circulation. In addition to having to lift cold and dense water through warm water, surface water of ocean planets that is relatively poor in dissolved CO$_2$ needs to be sunk through deep water that is more heavily loaded with CO$_2$, and thus more dense. We find that running a general circulation in deep-water planet oceans with vertical velocities similar to those in Earth’s circulation model requires energy two-to-three orders of magnitude higher than what is likely to be available. This means that the deep ocean in water planets is likely either unmixed or inefficiently mixed, and that the deep ocean deposits of CO$_2$ are stable. This also means that the lowest measured vertical eddy diffusion for Earth’s oceans, 0.1 cm$^2$ s$^{-1}$, is likely an upper bound value for the vertical eddy diffusion in water-planet oceans. The lower bound value is the molecular diffusion value of $10^{-5}$ cm$^2$ s$^{-1}$.

Given enough time, the ocean’s composition tries to equilibrate with the appropriate reservoir of CO$_2$ in the ocean’s bottom. The low heat flux at the bottom of these oceans suggests that this deep CO$_2$ reservoir is a layer of SI CO$_2$ clathrate hydrate. Given an ocean depth of 80 km, a vertical eddy diffusion of $10^{-2}$ cm$^2$ s$^{-1}$ yields a timescale of 200 Myr for the ocean’s composition to reach equilibration with the ocean’s bottom CO$_2$ reservoirs. This CO$_2$ then reaches the atmosphere.

We have developed a model for the wind-driven circulation in water planets and its resulting flux of CO$_2$ into the atmosphere. A diagram of this model is given in Figure 19 in Section 6.1. From this model, we deduce the steady-state pressure of CO$_2$ in the atmosphere of a water planet. If no sea
ice forms, and there are no active mechanisms eroding the atmosphere, steady state is attained when the downwelled subtropical surface water has a dissolved CO2 concentration equal to that of the deep ocean. The resulting steady-state atmospheric pressure, for this case, is tens of bars of CO2. The steady-state pressure of atmospheric CO2 increases when the subtropical surface water temperature does, as well as for higher deep-ocean temperatures (see Figure 20).

We find that, if the CO2 atmospheric pressure is perturbed to values higher than the steady-state pressure, then the system tries to restore the steady-state atmosphere. This is because, in this case, the water pushed inward by Ekman pumping in the subtropics becomes oversaturated with CO2. This results in SI CO2 clathrate grain formation when the circulating fluid parcels enter the thermodynamic stability field of this phase. The clathrate grains remove any excess CO2 above the solubility value in equilibrium with the clathrate phase, and sink to the bottom of the ocean within a timescale of less than 100 years. The resulting water upwelled due to Ekman suction at the tropics has a CO2 concentration equal to the value of the deep ocean. This mechanism is illustrated in Figure 22. We find that such perturbations in the CO2 atmospheric pressure can be dampened by the wind-driven circulation in a timescale on the order of 10^4 years.

The wind-driven circulation exposes deep water saturated in CO2 to the atmosphere. The resulting atmospheric pressure of CO2 may become higher than the dissociation pressure of SI CO2 clathrate hydrate at the poles, depending on the temperature at high latitudes. If that is the case, there is a driving force that transforms ice Ih sea ice into a composite containing SI CO2 clathrate hydrate. Because the latter phase is more dense than liquid water the sea-ice composite may sink in the ocean. This removes CO2 from the atmosphere. We quantify this effect, and its influence on the steady-state atmospheric pressure of CO2, in Section 6.2.

The sea ice formed at high latitudes in water planets is likely a composite, composed of ice Ih, SI CO2 clathrate hydrate, and pore space. At the subfreezing conditions found at the poles, ice Ih grains first form on the ocean’s surface, followed by a transformation of these grains into SI CO2 clathrate hydrate. This phase transformation involves an expansion of the solid matrix, at the expense of the pore space. Therefore, enough initial pore space must be present to allow for this expansion. For the sea-ice composite to become more dense than the surrounding water-rich liquid, a minimum initial porosity of 0.043 is required. If the pore space is only filled with gas of negligible mass density, the initial porosity must not be higher than 0.225; otherwise, the sea-ice composite will remain afloat on the ocean’s surface. This upper bound on the initial porosity of the sea-ice is very much alleviated if the pores become partially filled with liquid water or ice Ih (see Figure 24 and related text for more information).

Sea ice rich in CO2 clathrate is not anchored in place, and given time it may migrate to a warmer climate. At lower latitudes, where temperatures are higher, the clathrate dissociation pressure is higher. As a result, the clathrates in the sea-ice slab would dissociate and release their caged CO2 back into the atmosphere. Therefore, sea ice may deposit atmospheric CO2 in the deep ocean if it becomes buoyantly unstable in a timescale less than its drift time out of the subpolar region. This time criterion implies that the transformation of the sea-ice Ih grains into clathrate must be fast enough. The rate of this phase transformation depends on the ice Ih initial grain-size distribution. We find that, if the initial ice Ih grain size is tens of micrometers, the sinking of atmospheric CO2 in sea-ice slabs controls the global CO2 atmosphere. In other words, the atmospheric pressure of CO2 is to a very good approximation the dissociation pressure of SI CO2 clathrate hydrate for the subpolar surface temperature. This atmospheric pressure may be as low as 2 bar of CO2. This is much less than the tens of bars of CO2 that accumulate in the atmosphere when the wind-driven circulation is the only operating mechanism. If the initial ice Ih grain size making up the sea ice is larger than about 1 mm, the phase transformation cannot take place fast enough and the sea-ice slabs are buoyantly stable as they migrate out of the subpolar region. In this scenario, the CO2 abundance in the atmosphere quickly bounces to tens of bars, as dictated by the wind-driven circulation and the deep saturated ocean.

We further find that the atmospheric abundance of CO2, when controlled by the polar sea ice, is insensitive to the extent of the polar sea-ice cap, as long as the ice cap extends at least a few degrees around the pole. Therefore, even a relatively small ice cap may efficiently remove CO2 from the atmosphere. It also means that changes in the surface area of the ice cap hardly establish any feedback mechanism between the ocean and atmosphere.

Because the atmospheric abundance of CO2 is potentially controlled by the subpolar surface temperature, we have investigated how the system reacts to changes in this temperature. We wish to note that the subpolar surface temperature we refer to is an average value over a large timescale, and should not be confused with a seasonally changing value. We find that, for subpolar surface temperatures higher than about 240 K, with an initial ice Ih grain size of 100 μm, the removal of atmospheric CO2 by the sinking sea ice is very efficient. Consequently, the partial atmospheric pressure of CO2 will tend to closely follow the dissociation pressure of SI CO2 clathrate hydrate for the subpolar temperature. This dissociation pressure increases with temperature. Therefore, as the subpolar region becomes hotter, more CO2 may end up in the atmosphere. Increasing the subpolar surface temperature from 240 to 265 K would result in an increase in the atmospheric pressure of CO2 from approximately 3 bar to approximately 8 bar, assuming an initial grain size of 100 μm. If the subpolar surface temperature drops below about 230 K, the phase transition from ice Ih to CO2 clathrate hydrate within the sea ice slows down. The system’s response would be to elevate the partial atmospheric pressure of CO2 in order to increase the driving force responsible for the ice-phase transition. As a result of this behavior, the partial atmospheric pressure of CO2 likely has a minimum value as a function of the subpolar surface temperature (see Figure 29 and its related text for more detailed information). The value of this minimum and its corresponding subpolar temperature depend on the sea-ice morphology (see Figures 30–32). This minimum in the atmospheric abundance of CO2 introduces the possibility of a negative feedback mechanism that may moderate climate change in ocean planets.

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Appendix

A.1. Solid CO$_2$ Fugacity

Modeling the phase diagram of SI CO$_2$ clathrate hydrate at pressures where carbon dioxide solidifies into its phase I requires the fugacity describing this phase. Deriving the fugacity requires an equation of state for the solid of interest. Experimental data for the phase I solid of carbon dioxide are not abundant. A few older compressibility experiments exist, describing the behavior of solid carbon dioxide right above its melt curve in the region of interest for clathrates (e.g., Bridgman 1938; Stevenson 1957). However, the reliability of the data provided by these older experiments has recently been questioned (see discussion in Olinger 1982). For the sake of computational simplicity, we have taken the experimental data of Olinger (1982) and the compressibility data tabulated in Sterner & Pitzer (1994), and modeled the compressibility, $Z$, of solid carbon dioxide of phase I in the temperature range of 250 K < $T$ < 450 K and pressure range of 0.5 GPa < $P$ < 5GPa, using a quadratic polynomial of the form:

$$Z(P, T) = a(T) + b(T)\left(\frac{P - \bar{P}}{\bar{P}}\right) + c(T)\left(\frac{P - \bar{P}}{\bar{P}}\right)^2,$$

where:

$$a(T) = 21.482 - 19.341\left(\frac{T - \bar{T}}{\bar{T}}\right) + 20.079\left(\frac{T - \bar{T}}{\bar{T}}\right)^2$$

$$- 20.654\left(\frac{T - \bar{T}}{\bar{T}}\right)^3, \quad (105)$$

$$b(T) = 18.742 - 18.182\left(\frac{T - \bar{T}}{\bar{T}}\right) + 19.326\left(\frac{T - \bar{T}}{\bar{T}}\right)^2$$

$$- 18.974\left(\frac{T - \bar{T}}{\bar{T}}\right)^3, \quad (106)$$

$$c(T) = -1.8752 + 1.5015\left(\frac{T - \bar{T}}{\bar{T}}\right) - 1.2495\left(\frac{T - \bar{T}}{\bar{T}}\right)^2$$

$$+ 1.2038\left(\frac{T - \bar{T}}{\bar{T}}\right)^3. \quad (107)$$

Here, $\bar{P} = 2.5$ GPa and $\bar{T} = 325$ K are the reference pressure and temperature, respectively.

The volume per CO$_2$ molecule in phase I solid ($V^{\text{solid}}_{\text{CO}_2}$) is derived from the compressibility:

$$V^{\text{solid}}_{\text{CO}_2} = \frac{Z(P, T)kT}{P}, \quad (109)$$

where $k$ is Boltzmann’s constant.

For deriving the fugacity of CO$_2$ solid ($f^{\text{solid}}_{\text{CO}_2}$), we first start with the fugacity coefficient defined as (Smith & Van Ness 1975):

$$\phi^{\text{solid}}_{\text{CO}_2} = \frac{f^{\text{solid}}_{\text{CO}_2}}{P}. \quad (110)$$

The fugacity obeys the following relation (Smith & Van Ness 1975):

$$V^{\text{CO}_2}dP = kTd\ln\phi^{\text{solid}}_{\text{CO}_2}. \quad (111)$$

Differentiating the logarithm of Equation (110) together with Equation (111) gives, after a few algebraic steps:

$$d\ln\phi^{\text{solid}}_{\text{CO}_2} = \left(\frac{V^{\text{solid}}_{\text{CO}_2}}{kT} - 1\right)\frac{dP}{P} = (Z(P, T) - 1)\frac{dP}{P}. \quad (112)$$

To obtain the fugacity coefficient for solid CO$_2$ at pressure $P$ and temperature $T$, we must integrate the last relation. Every $P$–$T$ point may be reached by integrating from the desired temperature $T$ on the CO$_2$ melt curve, where the pressure is $P^{\text{melt}}_{\text{CO}_2}(T)$, up to the desired pressure. The benefit in so doing is that, on the melt curve, the fugacity coefficient for the solid ($\phi^{\text{solid}}_{\text{CO}_2}$) equals that for the liquid ($\phi^{\text{liquid}}_{\text{CO}_2}$). The fugacity coefficient for the liquid, in turn, is reliably calculated using the Soave–Redlich–Kwong (Soave 1972) equation of state. Therefore, one may obtain:

$$\ln\left(\frac{\phi^{\text{solid}}_{\text{CO}_2}(P, T)}{\phi^{\text{liquid}}_{\text{CO}_2}(P^{\text{melt}}_{\text{CO}_2}(T), T)}\right) = \int_{P^{\text{melt}}_{\text{CO}_2}(T)}^{P} (Z(P, T) - 1)\frac{dP}{P}. \quad (113)$$

Inserting the compressibility, as expressed in Equation (105), reduces the last relation to:

$$\frac{\phi^{\text{solid}}_{\text{CO}_2}(P, T)}{\phi^{\text{liquid}}_{\text{CO}_2}(P^{\text{melt}}_{\text{CO}_2}(T), T)} = \left(\frac{P}{P^{\text{melt}}_{\text{CO}_2}(T)}\right)^{a(T) - b(T) + c(T) - 1}$$

$$\times \exp\left\{\frac{b(T) - 2c(T)}{\bar{P}}(P - P^{\text{melt}}_{\text{CO}_2}(T)) + \frac{c(T)}{2\bar{P}^2}(P^2 - P^{\text{melt}}_{\text{CO}_2}^2(T))\right\}. \quad (114)$$

The desired fugacity for solid carbon dioxide is then obtained from the above definition for the fugacity coefficient.

A.2. Sea-ice Composite Density

Here, we derive the mass density of the sea ice forming at the poles of water planets. It is assumed to be made of ice Ih, SI CO$_2$ clathrate hydrate, and pore space. Considering each occupies a volume of: $V_{\text{Ih}}$, $V_{\text{clath}}$, and $V_{\text{pore}}$, respectively, with a total system volume $V$, the mass density of the composite is:

$$\rho^{\text{comp}} = \rho_{\text{Ih}} + \rho_{\text{clath}} + \rho_{\text{pore}} \quad (115)$$

In the last equation, $\rho_{\text{Ih}}$ and $\rho_{\text{clath}}$ are the pure ice Ih and clathrate hydrate bulk mass densities, $\rho_{\text{pore}}$ is the mass density of the pore-filling material, and:

$$\phi_{\text{Ih}} = \frac{V_{\text{Ih}}}{V}, \quad (116)$$

$$\phi_{\text{clath}} = \frac{V_{\text{clath}}}{V},$$

$$\phi_{\text{pore}} = \frac{V_{\text{pore}}}{V}. \quad (117)$$
where $\phi_{\text{pore}}$ is the sea-ice porosity. We wish to relate the composite mass density to the mole fraction of water ice $\text{I} \text{h}$ converted to clathrate hydrate, $\alpha$. Considering that the water molecules first solidify as ice $\text{I} \text{h}$ (see discussion in Section 6.2) we can write:

$$\alpha = \frac{\tilde{n}_{\text{Ih}}}{\tilde{n}_{\text{Ih}} + \tilde{n}_{\text{H}_2\text{O}}}.$$  \hspace{1cm} (117)

where $\tilde{n}_{\text{Ih}}$ and $\tilde{n}_{\text{H}_2\text{O}}$ are the number of moles of water in ice $\text{I} \text{h}$ occupying volume $V_{\text{Ih}}$ and in SI $\text{CO}_2$ clathrate hydrate occupying volume $V_{\text{clath}}$, respectively, which obey:

$$\tilde{n}_{\text{Ih}} = \frac{\rho_{\text{Ih}} V_{\text{Ih}}}{M_w},$$  \hspace{1cm} (118)

$$\tilde{n}_{\text{H}_2\text{O}} = \frac{46 V_{\text{clath}}}{N_A V_{\text{cell}}},$$  \hspace{1cm} (119)

where we consider each SI clathrate hydrate unit cell volume (see Equation (15)) to consist of 46 water molecules, $M_w$ is the molar weight of water, and $N_A$ is Avogadro’s number. After rearranging, we obtain the relation:

$$\frac{1 - \alpha}{\zeta} + 1 = \frac{1}{\phi_{\text{clath}}}(1 - \phi_{\text{pore}}),$$ \hspace{1cm} (120)

where

$$\zeta \equiv \frac{\rho_{\text{Ih}} V_{\text{cell}} N_A}{46 M_w} \approx 1.133.$$ \hspace{1cm} (121)

The latter is the expansion factor when a mole of ice $\text{I} \text{h}$ converts to SI $\text{CO}_2$ clathrate hydrate. The numerical value for $\zeta$ is derived from the tabulated data in Genov et al. (2004).

The field-emission scanning electron images in Staykova et al. (2003) show that the expansion (during conversion to clathrate hydrate) comes largely at the expense of the pore volume. Therefore, if one approximates the total system volume $V$ to be constant, one has:

$$\phi_{\text{pore}} - \phi_{\text{pore}}^0 \approx \frac{1 - \zeta}{\zeta} \phi_{\text{clath}},$$ \hspace{1cm} (122)

where $\phi_{\text{pore}}^0$ is the initial porosity of the formed sea ice before the conversion to clathrate hydrate initiates. Combining Equations (120) and (122) yields:

$$\phi_{\text{clath}} = \zeta \alpha (1 - \phi_{\text{pore}}^0),$$ \hspace{1cm} (123)

$$\phi_{\text{pore}} = \phi_{\text{pore}}^0 + (1 - \zeta) \alpha (1 - \phi_{\text{pore}}^0),$$ \hspace{1cm} (124)

$$\phi_{\text{Ih}} = (1 - \alpha)(1 - \phi_{\text{pore}}^0).$$ \hspace{1cm} (125)

From Equation (124), we see that the initial porosity must be larger than about 0.117 for a complete conversion into clathrate hydrate ($\alpha = 1$) to take place. In Genov et al. (2004), the initial porosity was 0.33, so pore space restrictions were not an issue.

Finally, inserting the last relations into Equation (115) for the composite mass density yields:

$$\rho_{\text{comp}} = (1 - \phi_{\text{pore}}^0) \rho_{\text{Ih}} + \alpha (\rho_{\text{pore}} - \rho_{\text{Ih}})$$

$$+ \zeta \alpha (\rho_{\text{clath}} - \rho_{\text{pore}}) + \phi_{\text{pore}}^0 \rho_{\text{pore}}.$$ \hspace{1cm} (126)

A.3. Error Function Series Solution

Solving for the diffusion equation using separation of variables results in a series solution that converges slowly for timescales less than the system’s squared length scale over the diffusion coefficient. The series solution developed here ought amend this problem. Let us solve for the following system of equations:

$$\frac{\partial^2 \tilde{v}}{\partial x^2} - \frac{1}{\kappa} \frac{\partial \tilde{v}}{\partial t} = 0$$

$$\tilde{v} = v_0 \quad t = 0$$

$$\tilde{v} = v_1 \quad x = 0$$

$$\tilde{v} = v_2 \quad x = l.$$ \hspace{1cm} (127)

Following Carslaw & Jaeger (1959), the Laplace transform for the set of equations is:

$$\frac{d^2 \tilde{v}}{dx^2} - q^2 \tilde{v} = \frac{1}{\kappa v_0}$$

$$\tilde{v}(x = 0) = \frac{v_1}{p}$$

$$\tilde{v}(x = l) = \frac{v_2}{p}.$$ \hspace{1cm} (128)

where bar denotes the Laplace transform and $q^2 \equiv p/\kappa$, and $p$ is the inverse timescale in the Laplace transform. The general solution to Equations (128) is:

$$\tilde{v} = Ae^{qx} + Be^{-qx} + \frac{v_0}{p},$$ \hspace{1cm} (129)

where

$$A = \frac{v_2 - v_0 - (v_1 - v_0)e^{-q}}{p[e^{q} - e^{-q}]},$$ \hspace{1cm} (130)

$$B = \frac{(v_1 - v_0)e^{q} - v_2 + v_0}{p[e^{q} - e^{-q}]}.$$ \hspace{1cm} (131)

This solution is complex enough not to appear in tables for Laplace transforms. Therefore, we will use Taylor’s expansion to develop the denominator in $A$ and $B$:

$$\frac{1}{p[e^{q} - e^{-q}]} = \frac{e^{-q}}{p[1 - e^{-2q}]},$$ \hspace{1cm} (132)

Notice that, for small timescales, $p$ is very large (and hence so is $q$) and the Taylor’s expansion is adequate. Inserting the last expansion into the forms for $A$ and $B$ gives, after some algebraic steps:

$$\tilde{v} = \frac{v_2 - v_0}{p} \sum_{r=0}^{\infty} e^{-q([2r + 1]l - x)} + \frac{v_0 - v_1}{p} \sum_{r=0}^{\infty} e^{-q([2r + 1]l + x)}$$

$$+ \frac{v_0 - v_2}{p} \sum_{r=0}^{\infty} e^{-q([2r + 1]l + x)} + \frac{v_0}{p}.$$ \hspace{1cm} (133)
Now each separate term is simple enough to be transformed back, yielding:

\[
\begin{align*}
    v(x, t) &= (v_2 - v_0) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{(2r + 1)t - x}{2\sqrt{\kappa t}} \right) \\
    &\quad + (v_0 - v_1) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{2(r + 1)t - x}{2\sqrt{\kappa t}} \right) \\
    &\quad + (v_1 - v_0) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{2r + x}{2\sqrt{\kappa t}} \right) \\
    &\quad + (v_0 - v_2) \sum_{r=0}^{\infty} \text{erfc} \left( \frac{(2r + 1)t + x}{2\sqrt{\kappa t}} \right) + v_b,
\end{align*}
\]

where

\[
\text{erfc}(y) = 1 - \text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_{y}^{\infty} e^{-\xi^2} d\xi.
\]  \hspace{1cm} (135)

It is important to pinpoint possible fictitious fluxes due to a slow convergence of a series solution. Our system has a natural timescale of \(t_{sc} = l^2/\kappa\). In Figure 33, we compare the error function series (Equation (134)) and the sine series (Equation (62)) for various times. For \(t \ll t_{sc}\), the sine series fluctuates around the boundaries, which would cause erroneous fluxes if adopted. However, for \(t \gg t_{sc}\), the error function series requires more terms than the sine series to adequately represent the steady-state solution. Therefore, one should switch between the series at \(t \sim t_{sc}\).
