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Fate of Rising CO_2 Droplets in Seawater

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The sequestration of fossil fuel CO_2 in the deep ocean has been discussed by a number of workers, and direct ocean experiments have been carried out to investigate the fate of rising CO_2 droplets in seawater. However, no applicable theoretical models have been developed to calculate the dissolution rate of rising CO_2 droplets with or without hydrate shells. Such models are important for the evaluation of the fate of CO_2 injected into oceans. Here, I adapt a convective dissolution model to investigate the dynamics and kinetics of a single rising CO_2 droplet (or noninteracting CO_2 droplets) in seawater. The model has no free parameters; all of the required parameters are independently available from literature. The input parameters include: the initial depth, the initial size of the droplet, the temperature as a function of depth, density of CO_2 liquid, the solubility of CO_2 liquid or hydrate, the diffusivity of CO_2, and viscosity of seawater. The effect of convection in enhancing mass transfer is treated using relations among dimensionless numbers. The calculated dissolution rate for CO_2 droplets with a hydrate shell agrees with data in the literature. The theory can be used to explore the fate of CO_2 injected into oceans under various temperature and pressure conditions.

Introduction

The disposal of fossil fuel CO_2 in the deep ocean has been considered as a possible means to mitigate the growth of greenhouse gas in the atmosphere (*1*−*5*). Much work has been carried out on injection schemes (*2*−*5*). To evaluate the consequences (including safety and environmental effects, e.g., ref *6*) of CO_2 injection, it is critical to understand the fate of injected CO_2 at different levels of ocean water. Recently, Brewer et al. (*7*, *8*) carried out particularly useful direct experiments on the ocean disposal of fossil CO_2. They monitored the dissolution of two rising CO_2 droplets (both having an initial radius of 4.55 mm) with hydrate shells by in situ ocean experiments. However, a theoretical understanding of the dissolution data is still lacking. Such an understanding is important to evaluate the dissolution rate and fate of rising or falling CO_2 droplets in seawater under various temperature (*T*) and pressure (*P*) conditions.

Models on crystal or bubble dissolution (*9*−*11*) cited by Brewer et al. (*8*) either are for dissolution under different hydrodynamic conditions or are empirical with a free fitting parameter. The dissolution model of Broecker and Peng (*9*) and the hydrodynamic model of Opdyke et al. (*12*) with confirmation by direct measurement of alabaster dissolution by Santschi et al. (*10*) are for dissolution of minerals on the seafloor in the presence of a current and do not apply to the hydrodynamics of dissolution of rising CO_2 droplets in water. The bubble dissolution model of Leifer et al. (*11*) has an empirical parameter. Because of difficulties in calculating the dissolution rate of droplets from first principles, workers modeled experimental data on the rising velocity (*8*, *13*), but did not model dissolution rates. One apparent exception was the work of Brewer et al. (*8*). In their work, after presenting experimental data on the rising velocity and dissolution rate of rising liquid CO_2 droplets with a thin hydrate shell, they mentioned the standard model for dissolution rates in the oceans (*9*, *10*). They estimated the boundary layer thickness next to a rising droplet at 0.12 m/s to be 300 μm, based on a reported boundary layer thickness of 500 μm over a horizontal bed for a velocity of 0.08 m/s (*10*). The method of estimation is incorrect because the hydrodynamic condition for a rising droplet differs from that for a horizontal bed with overlying flow. It will be shown later that the value of boundary layer thickness is also incorrect. Brewer et al. (*8*) nonetheless did not use the estimated boundary layer thickness to model the dissolution rate of the rising CO_2 liquid droplets. Instead, they first fit the data of droplet diameter versus time to obtain the dissolution rate (their Figure 5), and then calculated the droplet size decrease "based upon the measured dissolution rate" (their Figure 6). That is, their modeling of droplet size versus time is circular and does not constitute a model for dissolution rate of liquid CO_2 droplets.

In a series of developments (*14*−*17*) mostly by the high-temperature geochemical community, a convective dissolution model has been developed (*17*) to calculate the dissolution rate of a freely rising or falling crystal in magma or water without any free parameters. The model was confirmed by experimental data (*17*). Herzog et al. (*2*) also developed a convective dissolution model for liquid droplets of CO_2. Although the model of Herzog et al. (*2*) and that of Zhang and Xu (*17*) are similar in terms of general approaches, Herzog et al. employed four sets of velocity/mass transfer relations to produce four sets of results, none of which is confirmed experimentally.

In this contribution, the model of ref *17* is adapted to investigate the fate of rising CO_2 droplets in seawater, to explore the behavior of CO_2 droplets under various temperature and pressure conditions in oceans, and to evaluate the safety of CO_2 injections into oceans. In the stability field of CO_2 hydrate, a hydrate shell forms on CO_2 droplet due to reaction of liquid CO_2 with seawater at the interface. This hydrate shell is expected to be very thin because it dissolves in seawater as it grows in a delicate steady state. With a thin hydrate shell, the dissolution rate during the rise or fall of a CO_2 droplet can be modeled in a fashion similar to the dissolution rate of a falling or rising crystal. The density of the droplet is still the liquid density because the hydrate shell is thin, but the CO_2 solubility is that of CO_2 hydrate, which is lower than that of CO_2 liquid (otherwise hydrate would not form). Hence, the formation of the hydrate shell reduces the dissolution rate. The convective dissolution model calculates both the ascent velocity and the dissolution rate without any empirical fitting parameters. The input parameters include: the initial conditions (such as the initial depth and the initial size of the droplet), and the surrounding conditions (such as the temperature and seawater density), as well as other parameters that are independently measured

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or obtainable, such as the density of the CO_2 droplet, the solubility of CO_2 in water (depending on whether there is a hydrate shell), and CO_2 diffusivity in and viscosity of water (both depending on temperature). The effect of convection in enhancing mass transfer is considered rigorously using relations among dimensionless numbers. The input parameters must be gathered from literature and interpolated or extrapolated to the necessary conditions in oceans based on known principles. With these parameters and conditions, the dissolution rate for a rising or sinking CO_2 droplet can be calculated. The theory is applicable to a single droplet rising or falling in an infinite fluid medium and to noninteracting droplets (i.e., the diffusion profile next to one droplet does not overlap with that next to any neighboring droplet).

Below, the previous model is extended as necessary for the specific case of dissolution of CO_2 droplets with or without a hydrate shell. The theory is then applied to calculate and compare with dissolution rates in the direct ocean experiments of Brewer et al. (*8*). Fate of rising or sinking CO_2 droplets in the context of CO_2 sequestration in oceans is then discussed.

Theory for Convective Dissolution of a Rising Liquid CO_2 Droplet With or Without a Thin Hydrate Shell

The following development follows that of ref *17*. Below, the subscript "w" means either pure water or seawater. The subscript "liq" means CO_2 liquid. For convective dissolution of a liquid CO_2 droplet as it buoyantly rises or falls through seawater, mass transfer is enhanced and typically dominated by forced convection due to buoyant descent or ascent of the droplet. The motion of the droplet induces a flow field, and the flow removes water next to the droplet, resulting in a thin compositional boundary layer next to the dissolving droplet. The boundary layer thickness is thinner on the leading side of the droplet and thicker on the trailing side. Although the thickness of the boundary layer is variable on different sides of the moving droplet, an effective boundary layer thickness (δ_c, where the subscript "c" means compositional) is defined, and the convective dissolution rate may be modeled as:

$$-\mathrm{d}a/\mathrm{d}t = \beta_c D/\delta_c \tag{1}$$

where a is the radius of the droplet, $-\mathrm{d}a/\mathrm{d}t$ is the dissolution rate (note that $\mathrm{d}a/\mathrm{d}t$ is negative as a decreases with time), D is the diffusivity of dissolved CO_2 in water, and β_c is a dimensionless parameter defined as

$$\beta_c = (C_{sat} - C_\infty)/(C_{CO_2(liq)} - C_{sat}) \tag{2}$$

where C_{sat} is the concentration (solubility) of CO_2 at the interface water at saturation, C_∞ is the CO_2 concentration in ambient water (usually zero), and $C_{CO_2(liq)}$ is the CO_2 concentration in the liquid droplet to be dissolved (that is, density of CO_2 in the whole droplet); all concentrations are in mol/L, and β_c is dimensionless. Note that C_{sat} in the above equation depends on whether a thin hydrate shell forms on the CO_2 droplet. Without a hydrate shell, C_{sat} is the saturation CO_2 concentration in seawater in equilibrium with liquid CO_2. If a shell forms, C_{sat} is the saturation CO_2 concentration corresponding to hydrate solubility. However, $C_{CO_2(liq)}$ is not affected by the formation of a thin hydrate shell because the bulk of the droplet is still liquid and the density of the droplet is hence unaffected. Equation 1 applies to both diffusive and convective dissolution (*14*).

D is available from literature, and β_c can be estimated from solubility and CO_2 liquid density (Appendix). Hence, the problem of calculating the dissolution rate according to eq 1 becomes the problem of obtaining the average boundary layer thickness δ_c. For forced convection due to free buoyant

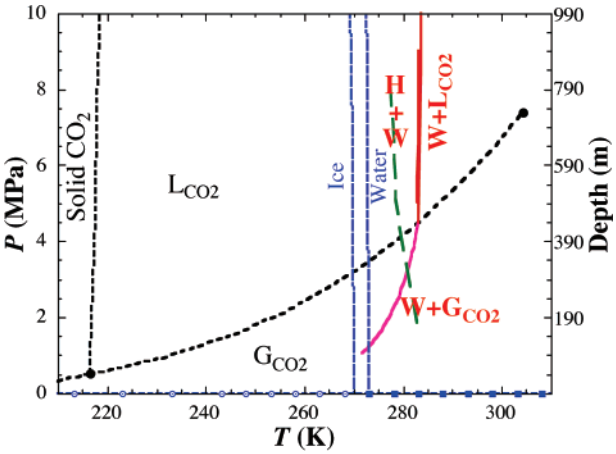

FIGURE 1. Phase diagram of the CO_2 system and the CO_2−H_2O system. The dashed black curves mark phase boundaries for pure CO_2. The phases in the pure CO_2 system are marked in black. The dashed blue curves (and blue squares and dotted circles almost overlapping the horizontal axis) show phase boundaries of CO_2-free "pure" seawater system. The phases in "pure" seawater system are marked in blue. The double blue lines are due to the variability of melting point from pure water to seawater. The solid red-purple curves mark phase boundaries in the CO_2−H_2O system. The phases in the CO_2−H_2O system are marked in red. Between the double blue lines and the solid red-purple curve, there are two phases: hydrate and liquid water (H+W). Between the red solid curve and the dashed black curve, there are two phases, liquid water and liquid CO_2 (W+L_{CO_2}). On the right-hand side of the purple curve, the two phases are liquid water and gas CO_2 (W+G_{CO_2}). The green curve shows a measured temperature-depth profile in the ocean (*8*).

rise or fall of a droplet, δ_c can be estimated from the Sherwood number (Sh), which in turn can be estimated from the compositional Peclet number Pe_c and the Reynold number Re. The dimensionless numbers are defined as:

$$Re = \frac{(2a)u\rho_w}{\mu_w} \tag{3}$$

$$Pe_c = 2au/D \tag{4}$$

$$Sh = 2a/\delta_c \tag{5}$$

where ρ_w and μ_w are the density and viscosity of seawater, and u is the ascent or descent velocity of the droplet. For Re $\leq 10^5$, the three dimensionless parameters are related as follows for a rising or falling sphere (*17*):

$$Sh = 1 + (1 + Pe_c)^{1/3}\left(1 + \frac{0.096Re^{1/3}}{1 + 7Re^{-2}}\right) \tag{6}$$

With the above theoretical development, the procedure for calculating the rising velocity and dissolution rate of a CO_2 droplet is as follows:

(i) Collect all necessary data as a function of T and P, including μ_w, ρ_w, $C_{CO_2(liq)}$, and $\rho_{CO_2(liq)}$ (both are density of CO_2 liquid but expressed in different units, C in mol/L and ρ in kg/m^3), C_{sat} (solubility of CO_2 liquid in seawater, or solubility of CO_2 hydrate in seawater for shelled droplets), and D (diffusivity of dissolved CO_2 in seawater). The Appendix summarizes the various data.

(ii) Specify the initial depth and the variation of density and T with depth. Estimate P. Determine the stable phase of CO_2 under the given T−P condition using the phase diagram of CO_2−H_2O (Figure 1). If CO_2 gas is stable, then the problem is bubble dissolution, which will be discussed in a

future contribution. If CO_2 liquid is stable, then the problem is droplet dissolution, which is addressed in this work, but the effect of wobbling and breakup is ignored. If CO_2 hydrate is stable, then a hydrate shell will form on a released CO_2 liquid droplet, which is also considered in this work. If CO_2 hydrate is released into seawater where CO_2 hydrate is stable, then the problem is crystal dissolution, which has been treated by Zhang and Xu (*17*) and can be treated using the procedures summarized here. The dissolution parameter β_c is calculated from the appropriate density ($C_{CO_2(liq)}$) and solubility (C_{sat}). The Appendix summarizes the calculation of β_c.

(iii) Given the density and radius of the droplet, calculate the ascent or descent velocity u. For $Re < 1$, use Stokes' law: $u = 2ga^2\Delta\rho/(9\mu_w)$, where g is acceleration due to Earth's gravity, and $\Delta\rho$ is the density difference between seawater and liquid CO_2. If $Re > 1$, Stokes' law is not applicable. For $Re \le 3 \times 10^5$, three unknowns (u, Re, and C_D) may be solved iteratively from the following three equations:

$$Re = \frac{(2a)u\rho_w}{\mu_w} \tag{3}$$

$$C_D = \frac{24}{Re}(1 + 0.15Re^{0.687}) + \frac{0.42}{1 + 42\,500Re^{-1.16}} \tag{7}$$

$$u = \sqrt{\frac{8ga\Delta\rho}{3\rho_w C_D}} \tag{8}$$

Equation 7 is from ref *18*, and the relative error is +6% to −4% for $Re \le 3 \times 10^5$. Strictly speaking, eq 7 is applicable only to rigid spheres and hence is applicable to a liquid CO_2 droplet with a hydrate shell. Experience shows that it is also applicable to small drops and bubbles (*13*, *19*), which is typically attributed to surfactants at the interfaces. Two notes are in order: (a) If Re is between 1×10^5 and 3×10^5, u may be calculated from the above procedure, but the dissolution rate cannot be calculated because eq 6 is derived using data for $Re \le 10^5$, and its application to $Re > 10^5$ is not guaranteed. (b) Brewer et al. (*8*) substituted $\rho_{CO_2(liq)}$ for $\rho_w C_D$ in eq 8 to calculate the rising velocity, which does not require iteration. It turns out that fortuitously $\rho_{CO_2(liq)}$ and $\rho_w C_D$ are similar under the conditions of investigation by ref *8*, leading to their correct prediction of the rising velocity. However, their equation is inaccurate and should not be generally applied.

(iv) With the above results, Pe_c can be calculated from eq 4, and Sh can then be calculated from eq 6. The value of δ_c is calculated from $\delta_c = (2a)/Sh$ (eq 5). The dissolution rate is calculated from eq 1.

(v) The radius a of the droplet (with or without shell) is solved by integrating da/dt, that is, $a = a_0 - \int(\beta_c D/\delta_c)\,dt$. Depth is solved by integrating u with respect to t, that is, $h = h_0 - \int u\,dt$.

Because of the interdependence of a, u, Re, Pe_c, Sh, and δ_c, the integrations can only be carried out numerically. In this work, the integration is carried out using a spreadsheet program. Estimated relative uncertainty of the calculation is up to 10% due to (a) uncertainties associated with the imperfect expressions for C_D and Sh, and (b) uncertainties in the input parameters, especially in the calculated CO_2 solubility of hydrate (see Appendix).

Comparison with Experimental Data

Although the above kinetic and dynamic model treats both the rising (or falling) velocity and the dissolution rate, the discussion below focuses on the dissolution rate because the rising velocity has been modeled before (*8*, *13*). Brewer et al. (*8*) measured dissolution rate of freely rising CO_2 droplets

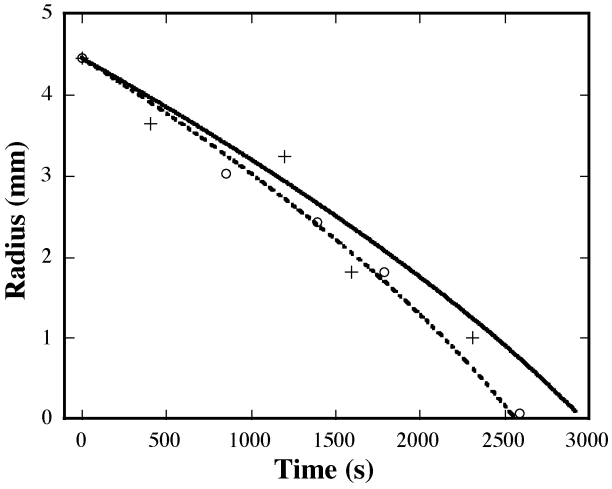

FIGURE 2. Comparison of experimental data of bubble radius versus time and calculations. Circles and pluses are experimental data from ref *8* using the same symbols they used, and the solid and dashed curves are the calculated bubble dissolution as a function of time for the two droplets. The two curves are slightly different due to the difference in initial depth and in temperature. The calculations are in good agreement with experimental data.

with a thin hydrate shell from about 800 m depth to about 400 m depth in the open ocean. At an average temperature of 278.35 K and 600 m (6.13 MPa), they determined a dissolution rate to be 3.0 μmol cm^{-2} s^{-1}, which can be converted to a linear dissolution rate of 1.44 μm/s (3.0×10^{-6} mol cm^{-2} s^{-1} times 48 cm^3/mol = 1.44×10^{-4} cm/s = 1.44 μm/s, where 48 cm^3/mol is the molar volume of liquid CO_2). Using the convective dissolution theory, the linear dissolution rate can be calculated to be 1.45 μm/s using $\beta_c = 0.0504$ for a shelled CO_2 droplet (Appendix), $D = 1160$ μm^2/s at 278.35 K, and a boundary layer thickness $\delta_c = 40.2$ μm calculated from Re, Pe_c, and Sh with an average radius of 3 mm. The calculated dissolution rate of 1.45 μm/s is in excellent agreement with the experimental dissolution rate of 1.44 μm/s. Again, it is emphasized that there is no fitting parameter in calculating the dissolution rate. The inferred boundary layer thickness surrounding the rising liquid CO_2 sphere is 40 μm, much thinner than the incorrect estimate of 300 μm by Brewer et al. (*7*), who applied hydrodynamics of an inappropriate regime. This shows that the correct hydrodynamic regime must be used to estimate the boundary layer thickness.

To further compare with the experimental data of Brewer et al. (*8*), droplet radius as a function of time and depth is calculated along the oceanic hydrotherm reported in Brewer et al. (*8*). Figure 2 compares calculated results along the oceanic hydrotherm with measured droplet size versus time data (*8*), and the agreement is very good. The two curves are slightly different because the initial depths and hence temperatures of the two droplets are slightly different (one droplet began its ascent from 804 m depth and 4.4 °C, and the other began its ascent from 649 m depth and 5.0 °C). The small difference between the theoretical calculation and experimental data can be attributed to uncertainties in the calculation and in the data.

The success of the above calculations shows that the kinetic/hydrodynamic model is accurate enough to have predictive power. It also shows that the solubility models of liquid CO_2 and CO_2 hydrate as a function of temperature and pressure as summarized in the Appendix are accurate enough to calculate the dissolution rate to an accuracy of about 10% relative.

Dependence of Dissolution Rate on the Droplet Size, Temperature, and Pressure

With confirmation of the above theoretical model, the dissolution rate of CO_2 droplet in oceans at any depth and any temperature may be calculated. In addition to comparison with experimental data, theoretical calculations are carried out to examine the systematics of CO_2 droplet dissolution. The results show:

(1) The dissolution rate (or the boundary layer thickness) does not vary significantly with the radius of a CO_2 droplet. For example, for a given T and P (278 K and 670 m depth), when the radius of a CO_2 droplet varies by a factor of 10 from 5 to 0.5 mm, the boundary layer thickness decreases from 44.2 to 31.6 μm, and the dissolution rate increases by only 40% from 1.26 to 1.77 μm/s. Hence, if T and P were kept constant, the dissolution rate may be regarded as roughly constant and the radius of a droplet varies roughly linearly with time.

(2) The dissolution rate depends relatively strongly on temperature. For a droplet with a hydrate shell, increasing temperature increases the dissolution rate significantly because both D and β_c increase. The boundary layer thickness decreases slightly with increasing temperature because viscosity decreases. For a droplet without a hydrate shell, increasing temperature only increases the dissolution rate slightly because D increases but β_c decreases. For example, for a CO_2 droplet with a radius of 2 mm at a depth of 600 m, when the temperature varies from 274 to 280 K, the dissolution rate increases from 0.90 to 1.89 μm/s (more than a factor of 2) if there is a hydrate shell, but from 2.05 to 2.52 μm/s (23% increase) if there is no hydrate shell (i.e., if hydrate shell formation were impeded by kinetics).

(3) The dissolution rate depends weakly on pressure. At 20−30 MPa (depending on temperature), CO_2 liquid density is the same as that of seawater. Shallower than the depth (i.e., at P < 20 MPa or depth < 2000 m), as pressure (or depth) increases under constant temperature, the boundary layer thickness δ_c increases slightly because the density difference between liquid CO_2 and seawater diminishes. If there is a hydrate shell, β_c decreases as pressure increases. If there is no hydrate shell, β_c changes very little as pressure increases. Combining the effect of pressure on the boundary layer thickness and on β_c, the dissolution rate decreases with increasing pressure. For a CO_2 droplet with a radius of 2 mm at 277 K, as the pressure increases from 5 to 15 MPa, the dissolution rate decreases from 1.36 to 0.95 μm/s if there is a hydrate shell, and from 2.36 to 1.79 μm/s if there is no hydrate shell.

(4) The effect of hydrate shell on protecting CO_2 droplets is significant, especially at lower temperatures (further away from the hydrate formation temperature). For example, at 273 K and 600 m depth for a radius of 2 mm, the dissolution rate without hydrate shell (1.98 μm/s) is 2.5 times the rate with hydrate shell (0.79 μm/ s). Both the temperature and the hydrate effects can also be seen from experimental data (*20*).

If CO_2 droplets were injected deep enough so that they would sink, they also would undergo dissolution as they fall, and the rates can be calculated using the same equations except that the depth increases as the droplet falls freely and dissolves. Figure 3 shows the calculated fate of falling shelled CO_2 droplets. A droplet of 5 mm radius may survive a water column of more than 300 m, and that of radius 10 mm may survive a water column of 1600 m. On the seafloor, a CO_2 liquid or hydrate layer would dissolve gradually.

The dissolution rate of a seafloor CO_2 hydrate layer, or a layer of CO_2 liquid coated by a thin hydrate film, may be calculated using eq 10 in ref *17*; the formulation in ref *10* is not used because it only applies to small length scales (such as 1 m or less). For a depth of 3000 m and a temperature of 275 K, β_c for liquid CO_2 with hydrate shell is 0.0332, $D = 1.05 \times 10^{-9}$ m^2/s, $\mu = 0.00179$ Pa s. For $\rho_w = 1026$ kg/m^3, $u = 0.05$ m/s, and a length scale of 1000 m, the dissolution rate is about 0.011 μm/s (or 0.35 m/yr) using eq 10 of ref *17*. A 100-m layer would dissolve in about 300 years. If the whole liquid CO_2 layer reacts to become a hydrate layer before dissolution, the layer thickness would increase, and β_c would increase roughly proportionally (Appendix). Hence, the same mass of CO_2 would take roughly the same time to dissolve.

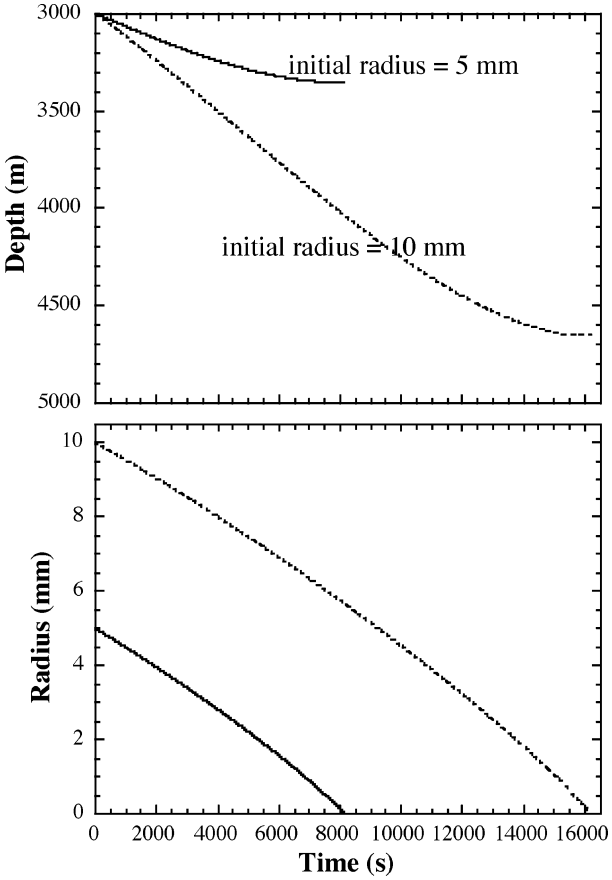

FIGURE 3. Calculated falling and dissolution history for two CO_2 droplets in seawater with a temperature of 275 K, density of 1026 kg/m^3, and salinity of 35‰. Both started at a depth of 3000 m (hence they fall in seawater). The initial radius of one droplet is 5 mm, and that of the other is 10 mm.

Discussion

Avoiding CO_2-driven eruptions (*21*−*23*) from CO_2 injected in oceans is obviously a consideration in any schemes for CO_2 disposal in oceans because it would defeat the purpose of CO_2 sequestration and could be a hazard. Starting from a depth of 800 m and a temperature of 5 °C, model calculations show that a CO_2 droplet of 5.5 mm radius would be able to rise to 400 m depth. Starting from a depth of 600 m, a CO_2 droplet of 4 mm in radius would be able to reach 400 m depth. If CO_2 droplets rise to the depth for CO_2 liquid to gas transition (at about 400 m depth), and hydrate dissociation depth (350 m), then CO_2 bubbles would form. If furthermore the CO_2 quantity is very large and bubbles are highly concentrated, the resulting CO_2 bubble plume could erupt, with dynamics similar to that of lake eruptions (*24*) or the hypothesized, methane driven, ocean eruptions (*25*). Moreover, if a large amount of CO_2 liquid is injected into seawater, depending on the density difference between CO_2 liquid and seawater, the number density of droplets (number of droplets per unit volume of seawater), and the size of the

droplets, there would be a critical condition under which the system becomes unstable and the parcel of seawater containing numerous droplets may rise as a plume. This rapid rise into shallow seawater may lead to rapid CO_2 gas formation, which under the appropriate conditions may also lead to CO_2-driven water eruptions.

To avoid the formation of rising CO_2 droplet plumes, and to avoid CO_2-driven eruptions, injection of CO_2 liquid into the shallow oceans needs to be controlled, using low injection rates and dispersing CO_2 liquid to a large volume of seawater. Safer injection schemes (but not in terms of the acidity of the ocean) include: (i) injection of CO_2 liquid to great enough depths that liquid CO_2 density is greater than ambient seawater (e.g., at depth of >2000 m at 272 K and >3000 m at 281.8 K for seawater density of 1026 kg/m^3) so that CO_2 liquid would sink and gradually dissolve in seawater, or (ii) dissolution of CO_2 gas in seawater to be brought down by thermohaline circulation (*1*).

Acknowledgments

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Appendix: Values of Various Parameters for Liquid CO_2

In this Appendix, estimations of various input parameters are summarized. The molecular mass of CO_2 is 0.04401 kg/mol. Angus et al. (*25*) summarized the properties of pure CO_2. The density of liquid CO_2 depends on T and P and can be found in Angus et al. (*25*). At 800 m depth (P = 8.14 MPa) and 277.55 K, the density of liquid CO_2 is about 938 kg/m^3, the molar volume of CO_2 is 0.0469 L/mol, and the concentration of CO_2 in liquid CO_2 is C_{CO_2} = 21.32 mol/L. The CO_2 pressure for liquid CO_2 formation is based on data in Angus et al. (*25*) and is given as a function of temperature as follows:

$$\ln\left(\frac{P_{sat}}{P_c}\right) = a_0\left(1-\frac{T}{T_c}\right)^{1.935} + a_1\left(\frac{T_c}{T}-1\right) + a_2\left(\frac{T_c}{T}-1\right)^2 + a_3\left(\frac{T_c}{T}-1\right)^3 + a_4\left(\frac{T_c}{T}-1\right)^4 \quad \text{(A1)}$$

where P_{sat} is the two-phase equilibrium pressure between liquid and gas CO_2, T is temperature in K, T_c and P_c are the temperature and pressure at the critical point (T_c = 304.21 K, P_c = 7.3825 MPa), a_0 = 11.377371, a_1 = −6.8849249, a_2 = −9.5924263, a_3 = 13.679755, and a_4 = −8.6056439. The latent heat of liquid CO_2 vaporization is roughly $2560(T_c - T)^{0.4}$ J/mol (*25*). The heat capacity of liquid CO_2 at 280 K is taken to be 105 J/mol/K.

The diffusivity of CO_2 in seawater is assumed to be the same as that in pure water and is expressed as (*26*):

$$D_{CO_2} = \exp(-12.462 - (2258.5/T)) \quad \text{(A2)}$$

where D_{CO_2} is in m^2/s. Seawater is assumed to have a salinity of 35‰ and a density of 1026 kg/m^3 unless otherwise specified.

The solubility of H_2O in liquid CO_2 is vanishingly small (*8*) and ignored. The calculation of the solubility of CO_2 gas, liquid, and hydrate in seawater is the most complicated step in the dissolution model. The solubility of CO_2 gas in seawater (*27*, *28*) is calculated from the model of ref *27*. For solubility of CO_2 liquid in seawater, the following reaction is considered:

$$CO_2\ (liq) = CO_2\ (aq) \quad \text{(A3)}$$

The equilibrium constant for the above reaction is $K = C_{CO_2(aq)}{}^{sat}$, where $C_{CO_2(aq)}{}^{sat}$ is CO_2 solubility in seawater in equilibrium with liquid CO_2. To estimate K at a given T and P, recall that the solubility of liquid CO_2 in seawater at P_{sat} (vapor pressure of the liquid) for that T equals that of CO_2 gas in seawater at T and P_{sat}. At the same T and higher P (in the CO_2 liquid field), ln K would then change with pressure as $-\int \Delta V\, dP/(RT)$, in which $\Delta V = V_{CO_2(aq)} - V_{CO_2(liq)}$, where $V_{CO_2(aq)}$ = 0.0323 L/mol (*27*), and $V_{CO_2(liq)}$ is obtained from ref *25*. At 800 m (8.145 MPa) and 277.55 K, $\Delta V \approx -0.0146$ L/mol, meaning that ln K would increase by 0.15 as P increases from 4 to 30 MPa (about 3000 m depth) at 277.55 K. That is, the effect of pressure on CO_2 liquid solubility is small, and hence the uncertainty in this calculation is assumed to be small. The solubility of CO_2 in seawater is smaller than that in pure water. For example, CO_2 solubility in seawater with a salinity of 35‰ is about 84% of that in pure water (*27*).

TABLE 1. Estimation of β_c for the Dissolution of CO_2 Droplets (No Shell) in Seawater

temp (K)	depth (m)	density of CO_2 liquid (kg/m^3)	solubility C_{sat} (mol/L)	C_{liquid} (mol/L)	β_c
277.55	800	938	1.55	21.32	0.0782
278.35	600	916	1.51	20.82	0.0780
279.5	400	886	1.46	20.14	0.0780
277.55	3000	1041	1.75	23.65	0.0799
275	3000	1049	1.82	23.84	0.0826

As an example, consider the solubility of CO_2 liquid in seawater at 4.4 °C and 800 m depth (P = 8.145 MPa) ignoring hydrate formation. For T = 277.55 K, P_{sat} = 3.908 MPa. At T and P_{sat}, liquid volume is 0.04896 L/mol, gas volume is 0.39172 L/mol, and the solubility of CO_2 in seawater with a salinity of 35‰ is 1.50 mol/L. To estimate the solubility of CO_2 at P = 8.145 MPa = 80.4 atm, first find liquid CO_2 volume at 8.145 MPa to be 0.04691 L/mol. Using the average liquid volume of (0.04896 + 0.04691)/2 = 0.0479 L/mol, ΔV for reaction A3 is −0.0156 L/mol. From 3.908 to 8.145 MPa, $-\int \Delta V\, dP/(RT) \approx 0.0287$. Hence, the solubility of liquid CO_2 in seawater at 800 m depth and salinity of 35‰ is 1.55 mol/L.

Knowing CO_2 liquid density ($C_{CO_2(liq)}$) and the solubility of liquid CO_2 (C_{sat}), the dissolution parameter β_c, defined in eq 2 as $\beta_c = (C_{sat} - C_\infty)/(C_{CO_2(liq)} - C_{sat})$ where $C_\infty = 0$, can be estimated. Some results are shown in Table 1. The value of β_c does not change much with depth. For rough calculation, β_c can be taken as a constant.

In the region of hydrate stability, liquid CO_2 reacts with seawater to form hydrate. A thin hydrate shell would coat the CO_2 droplet. Because CO_2 hydrate is more stable than CO_2 liquid, the dissolution rate of a shelled droplet is smaller. To account for this effect, C_{sat} in eq 2 should be CO_2 solubility in seawater for hydrate, but $C_{CO_2(liq)}$ does not change because the bulk of the droplet is liquid CO_2 and hence $C_{CO_2(liq\ with\ hydrate\ shell)}$ is that of liquid CO_2. At a given T, to estimate the CO_2 solubility of CO_2 hydrate, first find the pressure at which CO_2 liquid (or gas) and water are in equilibrium with CO_2 hydrate (Figure 1). At this pressure, the solubility of hydrate is the same as that of CO_2 liquid (or gas). At higher pressures, hydrate solubility depends on volume differences between hydrate and dissolved CO_2+water. Because hydrate density is about 1100 kg/m^3 (*20*), increasing pressure would increase the stability of hydrate and decrease its solubility. For the reaction:

$$CO_2(H_2O)n\ (hydrate) = nH_2O\ (liq) + CO_2\ (aq) \quad \text{(A4)}$$

where n = 7, molar volume is 0.155 L/mol for hydrate and 0.018 L/mol for H_2O, and 0.0323 L/mol for CO_2(aq). Hence, ΔV for the above reaction is roughly 0.0038 L, so small that hydrate solubility does not decrease much with pressure.

TABLE 2. Estimation of β_c for the Dissolution of CO_2 Droplet with a Hydrate Shell in Seawater

temp (K)	depth (m)	density of CO_2 liquid (kg/m^3)	solubility C_{sat} (mol/L)	C_{liquid} (mol/L)	β_c
277.55	800	938	0.944	21.32	0.0463
278.35	600	916	1.000	20.82	0.0504
279.5	400	886	1.084	20.14	0.0569
277.55	3000	1041	0.910	23.65	0.0400
275	3000	1049	0.765	23.84	0.0331

TABLE 3. Estimation of β_c for the Dissolution of CO_2 Hydrate in Seawater

temp (K)	depth (m)	density of CO_2 hydrate (kg/m^3)	solubility C_{sat} (mol/L)	$C_{CO_2,hydrate}$ (mol/L)	β_c
277.55	800	1100	0.944	6.47	0.171

For example, at 277.55 K, CO_2 gas and water react to form hydrate at 2.083 MPa. Hence, hydrate solubility at 2.083 MPa is the solubility of CO_2 gas, which is 0.954 mol/L. As pressure increases from 2.083 to 8.145 MPa, the solubility decreases by only 1%, to 0.944 mol/L. Hence, the effective β_c for a CO_2 liquid drop with a thin hydrate shell is 0.0462 (Table 2). That is, at 4.4 °C, the dissolution rate of liquid CO_2 droplet is 1.69 times that of a shelled CO_2 droplet.

Now the dissolution of a liquid CO_2 layer with a hydrate shell may be compared to that of a solid CO_2 hydrate layer. For the same amount of CO_2, the volume of CO_2 hydrate is roughly 3.3 times that of CO_2 liquid (because CO_2 hydrate is mostly made of H_2O). For dissolution of solid CO_2 hydrate, the dissolution parameter $\beta_c = (C_{sat} - C_\infty)/(C_{CO_2(liq)} - C_{sat})$ would be different from that of the shelled CO_2 droplet because now $C_{CO_2(liq)}$ must be replaced by $C_{CO_2(hydrate)}$. For a density of 1100 kg/m^3, $C_{CO_2(hydrate)} = 6.47$ mol/L. At 277.55 K and 800 m depth, $\beta_c = 0.171$ (Table 3), about 3.7 times β_c for CO_2 liquid with hydrate shell. Because the volume difference is 3.3 and the difference in β_c is 3.7, the dissolution of a layer of the same amount of CO_2 would take roughly the same amount of time whether CO_2 is in the form of liquid with only a hydrate shell, or CO_2 liquid is completely converted to CO_2 hydrate. The thicker layer of CO_2 hydrate would take slightly less time to dissolve.

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