Experimental Investigations on the Effects of Dissolved Gases on the Freezing Dynamics of Ocean Worlds

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Abstract The surfaces of icy moons are covered by fractures, other tectonic features, and active or ancient remains of cryovolcanism. These observations suggest active or recent tectonics, but there is still much unknown about the specific conditions surrounding the formation of these features. One important process leading to the fracture of the ice shell is the freezing and consequent pressurization of its ocean, because water expands upon freezing. However, the influence of dissolved non-condensable gases (herein referred to as volatiles) on the aforementioned dynamics remains poorly constrained. In this study, we present a new experimental investigation to explore the effect of dissolved volatiles in the internal pressure evolution of 10 cm diameter water spheres subjected to freezing temperatures between ~−60°C and ~−20°C. Our experiments reveal that spheres with a reduced initial amount of volatiles dissolved undergo an abrupt transition with dramatic increase of (a) the time between consecutive ice shell fractures and (b) the pressure required to break the shell. We show from a simple numerical model that this transition occurs when exsolution (i.e., nucleation and growth of bubbles) occurs and the fluid inside the shell becomes significantly more compressible. Exsolution is, in turn, triggered by the gradual thickening of the ice shell, which increases the concentration of dissolved volatiles and eventually leads to saturation. These results suggest that the content of volatiles of icy satellites plays a significant role in their geologic history and potential for habitability.

Plain Language Summary Icy moons have subsurface oceans which may be freezing. As water freezes, it expands. When a subsurface ocean on an icy moon freezes, this expansion of the ice shell increases the pressure in the ocean and can lead to the formation of water-filled cracks in the icy surface of the moon. To understand how the amount of gas in the ocean water controls when the cracks form, we freeze small spheres of water with different amounts of air under controlled temperature. We find that at some point during the freezing and growth of the ice shell, there is a sharp change in how often cracks occur. This happens because dissolved gases remain in the liquid water during freezing and eventually there is enough gas in the water for bubbles to form. This is important because it tells us how the gas content in the oceans of icy moons might control some of the cracks we observe on the surface of icy moons.

1. Introduction

Icy moons are geologically dynamic and diverse, as well as primary targets for assessing habitability beyond Earth (Castillo-Rogez & Lunine, 2012; Coustenis & Blanc, 2012; Hendrix et al., 2019; McKay et al., 2014). Understanding the connection between the subsurface ocean and the surface is important for characterizing the habitability of ocean worlds, as this allows for ocean material (including perhaps compounds created at a rock-water interface) to become irradiated on the surface. The connection between deeper processes and their surface expression is often challenging, yet it provides important clues about the present or past state of an icy moon.

Icy moons host a myriad of endogenic geologic features formed through a combination of brittle and ductile processes (e.g., Collins et al., 2009; Johnson, 1998; Stephan et al., 2013). Of particular interest here are features associated with fractures, faulting, and cryovolcanism. Although most faulting is associated with extension, strike-slip and convergent faulting is also observed (e.g., Stephan et al., 2013). Faults and fractures may be found on their own or as part of more complicated features such as coronae, tilted blocks, and chaos
terrain (e.g., Beyer et al., 2019; Collins et al., 2009; Stephan et al., 2013). It is also important to note that these can form from global (e.g., tidal, despinning, and true polar wander; Collins et al., 2009; Hemingway et al., 2019; Kimura et al., 2007; Nimmo, 2004) or regional and local stresses (e.g., from convective upwellings in the ice layer or from freezing of small liquid reservoirs; Collins et al., 2009; Hemingway et al., 2019; Howell & Pappalardo, 2018). Cryovolcanism on icy bodies can lead to the formation of particulate deposits (from erupting plumes), lobate extrusions, and smooth terrains (Stephan et al., 2013). Cryovolcanism may be sourced from a global subsurface ocean as on Enceladus (Porco et al., 2014), or from cryomagma chambers within the ice shell, as has been proposed for Charon (Desch & Neveu, 2017), Europa (Lesage et al., 2020), Titan (Martin & Binzel, 2020), and Pluto (Mitri et al., 2008).

One mechanism by which these extensional features and cryovolcanism may occur is stress induced by the pressurization of a freezing ocean (Beyer et al., 2019; Hemingway et al., 2019; Johnston & Montési, 2017; Lesage et al., 2020; Manga & Wang, 2007; Nimmo & Pappalardo, 2016; Roberts & Nimmo, 2008). However, previous experimental treatment of this problem (Manga & Wang, 2007) has not explored the freezing of an ocean in a spherical geometry, the interaction of the ocean pressurization with fracturing the ice shell, or the role of dissolved volatiles on the evolution of the system. Although many studies have considered the effects of ocean chemistry on freezing rate, relatively few have considered how changing ocean chemistry affects the mechanical behavior of a freezing ocean (Crawford & Stevenson, 1988; Gaeman et al., 2012; Journaux et al., 2017; Nimmo & Pappalardo, 2016; Sohl et al., 2010).

The dynamics of a freezing sphere of water are controlled by the interrelations between the formation of the ice shell during the early stages of freezing, the gradual thickening of the shell, pressurization in the sphere interior from the volume change upon freezing water, and fracturing of the shell that contains the water (McCue et al., 2008). More specifically, as the ice shell grows in a spherical geometry, the volume change is accommodated by pressurizing the water. This pressurization causes a tensional stress field throughout the ice shell. Previous experimental work on millimetric water droplets has shown that freezing spherical water droplets with radii greater than 50 μm may explode and shatter their ice shells when the shell is thick enough and the internal pressure is sufficiently large (Wildeman et al., 2017).

Constraining the role of dissolved non-condensable gases (herein referred to as volatiles) in the dynamics of freezing water shells is of special importance to understand the dynamics of icy moons, whose internal liquid oceans contain volatiles (Crawford & Stevenson, 1988; Glein et al., 2015; Sohl et al., 2010; Waite et al., 2006). These volatiles not only affect the ocean chemistry and thereby habitability but also influence the physical properties of the fluid as well as how it behaves under pressure and steady freezing. In this paper, we perform a set of new experiments on 10 cm diameter water spheres subjected to freezing to address the following question: What effects do dissolved volatiles have on the freezing evolution and surface features of an ocean world?

Our paper is organized as follows. First, we present the experimental setup and procedure that we designed to explore the influence of dissolved air on water spheres subjected to freezing. Second, we present our key results, including the pressure evolution inside water spheres with and without volatiles dissolved, as well as the dependence on the freezing temperature. Third, we discuss our results from the perspective of a mechanistic model. Finally, we summarize the main conclusions of this research in the last section of the paper.

2. Experimental Methods
2.1. Experimental Setup

Experiments are performed with non-degassed water and degassed water. The former is deionized MilliQ® (~18 MΩ · cm) pure water. In contrast, the samples of degassed water are prepared as follows. Before each experiment, ~2 L of deionized water is heated until boiling and imposed to reflux for 1 hr with vigorous stirring. The water is cooled in an ice water bath under vacuum (~300 mTorr) for 3.5 hr (Ishida et al., 2000). Finally, with the water still under vacuum, two cycles (15 min each) of ultrasound pulses are applied in the ice water bath surrounding the flask using an ultrasonic liquid processor (SONICS Vibra-Cell) to induce bubble nucleation and remove possible remaining gas (Dell’Ova et al., 1974). This protocol is assumed to reach near perfect removal of dissolved volatiles in water.
The spherical geometry in our ice growth experiments is achieved with a 10 cm diameter acrylic mold. The mold is only 1 mm thick and does not present a significant thermal barrier during early stages of the experiment; this is validated by agreement between measured and analytical freezing rates. The mold, consisting of two halves that are held together with an elastic rubber band and duct tape, is perforated at the top to allow a set of sensors to measure temperature (thermocouple OMEGA’s TJ36-CASS-010G type K) and pressure (Kulite® transducer XCEL-072-1000A) evolution inside the sphere. The degassed water is removed from the vacuum line tubing (supporting information Figure S1), and one of the flask side necks is fitted with a latex tube ending with a needle (length: 10 cm, internal diameter: 2 mm). The flask is then placed on the top of the freezing chamber (Figures 1 and S2), the tubing is purged with the water sample, and the needle is inserted into the mold (with the end touching the mold bottom). The water flux remains low (~100 ml/min) during the filling of the mold, which minimizes the dissolution of ambient air in the water. The same mold filling protocol is applied for the non-degassed water and the degassed water.

The freezing chamber controls ambient temperatures from −15°C to −70°C to a standard deviation in temperature across the chamber of less than a few degrees (Figure 2). Cooling is achieved by vaporizing liquid nitrogen into the chamber; the flux of nitrogen is controlled by a thermostat. The flow of nitrogen inside the chamber is circulated using a 12 cm waterproof 12 V DC fan located below the sphere-holding support (Figure 1). The fan blows directly over a basket containing Drierite®, to absorb any excess moisture in the chamber. The Drierite® is dried at 120°C for at least 12 hr between each experiment. The temperature in the chamber is monitored with four thermocouples placed a few centimeters away from the sphere on the sides, top, and bottom. Temperatures are recorded with a sampling rate of 1 s using a four-channel Type K thermometer SD logger, which has a temperature resolution of 0.1°C and an accuracy of ±0.003 °C (T + 1), where T is the measured temperature in degrees Celsius. Note that this uncertainty is much less than the standard deviation of spatial temperatures measured (Figure 2). The internal surface of the chamber is lined with acoustic foam, and four white LED lights are installed on the top of the chamber.

The miniature pressure transducer (provided courtesy of Kulite®) and 0.25 mm diameter thermocouple inside the sphere are interfaced with LabVIEW through a data acquisition board with 10-bit ADC. The
sensors were insulated using a glass tube filled with Lexel\textsuperscript{®} sealant. The end of the glass tube is covered with a rubber septum pierced by the sensors, allowing only the tips to be in contact with the liquid water inside the sphere. Pressure and temperature data are recorded continuously in LabVIEW at 8 samples/second rate (0.125 s\textsuperscript{−1}), which captures pressure drops associated with each fracture as confirmed in our video and audio data. We perform zero-shifting and detrend the offset from the raw pressure data in the time domain. The pressure data are then filtered with a low-pass third-order Butterworth filter with cut-off frequency of 0.1 Hz, for which we use a sampling frequency defined as the inverse of the mean time difference between two consecutive readings.

A stainless steel washer (11 mm diameter) glued on the glass tube at exactly 5 cm from sensor tips provides stability between ice and glass tube; the perpendicular flat surface of the washer being trapped in ice during freezing prevents the sensors being pushed out of the sphere during the experiment when the pressure builds up. Three Logitech Brio 4k Pro webcams installed on two sides and the top of the chamber record the experiment at 60 fps. OBS Studio open source software is used to record the three webcams simultaneously. To ensure condensation does not occlude the webcam lenses, two aluminum fins under the webcam are heated to 65°C using power resistors controlled by a J-KEM\textsuperscript{®} Scientific thermostat.

2.2. Control Experiments and Mold Removal

During preliminary experiments, we observed that mold removal timing is critical in controlling the spatial distribution of fractures in the ice shell. Especially at low temperatures (−40°C to −60°C), a high concentration of fractures was observed along the mold edges (the weakest part of the mold) when the mold is not removed soon enough. To solve this, the mold is removed as early as possible, when the ice shell thickness can withstand the weight of the water. Therefore, an estimation of freezing rate and ice thickness at working temperatures is necessary. This is accomplished by freezing water at −10°C, −30°C, and −60°C, stopping the experiment after various amounts of time, and measuring the ice shell thickness (Figure 3). Shell thickness (and uncertainty) is calculated as the mean value (and standard deviation) measured with digital calipers (resolution of 0.01 mm and accuracy of 0.03 mm which is an order of magnitude more precise than values we report) in at least eight positions along the fracture edge.

From ice thickness measurements, we interpolated ice thickness at any working temperature from −10°C to −60°C, which is appropriate because for times beyond the initial growth of the ice shell, the Stefan problem...
in a spherical geometry has an approximately linear freezing rate (Figures 3 and S4; Wildeman et al., 2017). We set the target ice thickness for mold removal to 5 mm; smaller values caused the ice shell to rupture during the mold removal process. Time estimation for mold removal ($t_{\text{rem}}$) was obtained using the following empirical equation ($R^2 = 0.9994$):

$$t_{\text{rem}} = 955 |T_{ch}|^{-0.904},$$

(1)

where $t_{\text{rem}}$ is time for mold removal in minutes and $T_{ch}$ is chamber temperature in Celsius. At temperatures lower than $-35^\circ$C, a considerable amount of frost accumulates on the ice surface occluding visual fracture detection. We have found that rubbing a small volume (~5 ml, ~0.2 mm surface layer) of silicon oil (CAS: 63148-62-9) over the ice surface following mold removal dramatically reduces the amount of frost. Control experiments at warmer temperatures indicate no changes in measured behaviors when silicon oil is used.

### 3. Results

In order to study the effect of gas concentration on the freezing of water spheres, we conducted a total of 12 experiments with non-degassed and degassed water in a range of temperature from $-20^\circ$C to $-60^\circ$C (Supporting Information). We note that we call a degassed experiment one where the water has been through the degassing procedure described previously. It therefore implies a lesser amount of volatile present than in the other experiments. All spheres either exploded or released a relatively large amount of water that prohibits further pressurization during a final fracture event (hereafter referred to as failure; Figure 4). In the next subsections, we describe the key results from visual observations, pressure time series, and temperature time series.

#### 3.1. Visual Observations

Video recordings reveal the following first order observations:

1. Fracture formation does not apparently follow any preferred orientation. Fractures randomly cover the whole sphere and do not tend to follow fractures previously formed.
2. Fractures heal at the inner part of the ice shell as the ice shell grows inwards (Figure 4). Water transported from the interior through subsequent fractures can also heal fractures formed previously.
3. Spheres eventually explode after running the experiments for 0.5 to 2 hr, depending on the working temperature.
3.2. Temperature Evolution, Pressure Evolution, and Final Thickness

Readings from the internal thermocouple temperature time series (Figure 2) show that water temperature decreases over time until it stabilizes at just above 0°C and stays stable until the end of the experiment. In contrast, the pressure oscillates with increases associated with shell thickening and sudden decreases concomitant with the opening of new fractures in the shell. As long as the fractures heal, freezing proceeds, and the liquid pressurizes again. Other key observations from the pressure time series of degassed and non-degassed water spheres are detailed in Table 1 (see also Figure 5):

![Figure 4. Ice sphere snapshots from left webcam at different experiment stages: (a) after mold filling (mold on); (b) after mold removal; (c) during further freezing; (d) final fracture (failure). Video clips of fracture events following mold removal and at final fracture can be found in supporting information Movies S1 and S2, respectively.](image)

### Table 1
Summary of Key Observations From the Pressure Time Series Data

<table>
<thead>
<tr>
<th>Key observations from experiments</th>
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<tr>
<td>1. For the same freezing temperature, degassed water spheres require more time to reach failure than non-degassed ones. This corresponds with a thicker ice shell for degassed water spheres since freezing rates are similar for degassed and non-degassed water (Figure S4).</td>
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<td>2. For the same freezing temperature, the peak pressure (pressure right before ice shell fracture) inside the sphere is higher for degassed than non-degassed water spheres. In general, for both degassed and non-degassed water, peak pressure is higher at warmer freezing temperatures.</td>
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<td>3. The time between fractures (i.e., interfracture time) is generally shorter for degassed than non-degassed water spheres. More fractures are formed over an experiment for degassed water.</td>
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<td>4. For both types of water, the lower the freezing temperature, the shorter the interfracture time.</td>
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<tr>
<td>5. In degassed and non-degassed experiments and any freezing temperature, interfracture time lengthens toward the end of the experiments.</td>
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<tr>
<td>6. For degassed water spheres, a dramatic increase in interfracture time and peak pressures is observed before failure.</td>
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Measurements after the failure of the sphere reveal that the final average ice thickness is relatively constant and not correlated with freezing temperature. However, the final thickness differs from degassed to non-degassed water by a factor of ~2 (31.5 ± 2.7 mm and 15.3 ± 2.7 mm, respectively; Figure 6a). As a general trend, the peak pressure increases with increasing freezing temperature and is lower for non-degassed than degassed water. For example, peak pressures of up to ~6 bar and ~2 bar are reached for degassed and non-degassed water, respectively, and chamber temperatures of ~−60°C. Final pressures rise to ~10 bar and ~5 bar for chamber temperatures of ~−20°C (Figure 6b). From the average shell thickness after failure and the final pressure, we can estimate the tensile failure strength of the ice shells by calculating the critical hoop stress at the inner shell surface ($\sigma_{\theta\theta}$; i.e., the hoop stress at failure; Wildeman et al., 2017):

$$\sigma_{\theta\theta} = \frac{p_f}{2} \left( 1 + 2 \left( \frac{R_{nf}}{R_s} \right)^3 \right) \left( 1 - \left( \frac{R_{nf}}{R_s} \right)^3 \right)^{-1}$$

where $p_f$ is the pressure in the liquid water at failure, $R_{nf}$ is the radius of the inner shell surface at failure, and $R_s$ is the radius of the sphere. We find that the critical hoop stress varies in the range 4–7 bar and is independent of the type of water (degassed or non-degassed) and freezing temperature (Figure 7). The fracture toughness of ice is not well constrained and is affected by intrinsic ice properties as well as ice thickness and temperature, so it may change slightly during the course of the experiment; but the values of critical hoop stress that we obtain are consistent with previous experimental ice strength measurements (Litwin et al., 2012; Wildeman et al., 2017).

Figure 5. Filtered pressure time series for degassed (left) and non-degassed (right) water at −20°C, −40°C, and −60°C. Filtered and raw pressure time series for all experiments can be found in Figure S5. Black box represents mold removal process. The black line at 1 bar is the atmospheric pressure. Each pressure peak and subsequent rapid drop corresponds to a fracture event. In the degassed case, peaks are much more closely spaced (sometimes only a few seconds apart) than for the non-degassed case, corresponding to a shorter interfracture time for degassed experiments.

Figure 6. Influence of temperature on dynamics of water spheres upon freezing. (a) Average of ice thickness measured after final fracture at temperature range from −20°C to −60°C. (b) Filtered pressure of final fracture at temperature range from −20°C to −60°C.
4. Discussion

4.1. Ice Shell and Pressure Evolution in Experiments

One potential mechanism for the differences in degassed and non-degassed experiments is that the incorporation of gas in the ice shell may make it weaker and thus easier to fracture. However, the hoop stress calculations (Equation 2 and Figure 7) indicate that there is no significant difference in ice shell strength between degassed and non-degassed experiments within the uncertainties of our measurements. Thus, variations in ice shell strength are unlikely to explain the contrast in dynamics (e.g., fracture event frequency) between degassed and non-degassed experiments. Additionally, we observe an abrupt transition with sudden increase of interfracture time and peak pressures over the course of the degassed experiments (Figure 5 and Table 1). The sharp transition displayed by degassed experiments suggests the existence of a threshold rather than a continuous, gradual process. In contrast, the non-degassed experiments display long interfracture time intervals with slow pressure increase, but never display such abrupt transition. Motivated by our experimental observations (Table 1) and that the obvious first-order difference between the two types of experiments is abundance of dissolved volatiles, we propose that the observed transition in the degassed pressure time series is the result of gas exsolution (see conceptual model in Figure 8). Exsolution occurs because gas molecules (primarily N₂ and O₂) are rejected from the ice, thus gradually increasing the concentration of dissolved volatiles in liquid water upon freezing (Bari & Hallet, 1974). This process ultimately leads to exsolution of bubbles and an abrupt change in compressibility of the fluid phase. It is likely that no transition is observed in the non-degassed water because it saturates early in the experiments.

Exsolution occurs in our experiments with degassed water (section 2.1) because a finite amount of gas remains dissolved in the water after the degassing protocol and perhaps some air is reabsorbed during mold filling, though this is a minor consideration, as we argue below. When degassed water is exposed to atmospheric air, only a layer growing from the interface reaches saturation. This small volume will maintain its saturated concentration from then onward, and the dissolved gas will diffuse into the rest of the water. For oxygen and nitrogen gas, the diffusion coefficient in water at 5°C is $1 \times 10^{-5}$ cm²/s, and saturated gas concentration is 1.5 mM (although the solubility of gases in aqueous solutions increases with decreasing temperature; Ferrell & Himmelblau, 1967). Assuming quiescent water in our experiments, and taking into account that the mold filling procedure and the formation of a continuous ice shell lasts for tens of minutes, we therefore find that N₂ diffuses a few millimeters into the water during the mold filling procedure. However, note that more N₂ is expected to entrain and dissolve back into the water during the mold filling procedure, because the surface of contact with air versus the volume of water is greater during the filling procedure than it is once the mold is filled. This can account for a partial re-gassing of the initially degassed water. However, in an additional experiment to test this re-gassing, we allowed degassed water to be exposed to air and vigorously stirred for 75 min before mold filling and found no discernible difference in behavior.
between the exposed degassed experiment and degassed experiments at the same temperature. This suggests that the volatiles exsolved during freezing of a degassed sphere are those which were not eliminated by our degassing procedure initially or which enter the sphere during fractures.

Because the volume of liquid decreases as water freezes through the course of an experiment and the gas preferentially remains in the liquid as the outer ice shell freezes (Bari & Hallet, 1974), the concentration of gas dissolved in the water increases as the experiment proceeds. Assuming an initial concentration of dissolved gas in the water and a perfect partitioning of the gases to the liquid phase, the evolution of the dissolved gas concentration, \( c(t) \), can be modeled as a function of the change in ice shell thickness:

\[
c(t) = \frac{m_{\text{gas}}}{\frac{4}{3} \pi R(t)^3 \rho_w}
\]

where \( m_{\text{gas}} \) is the mass of dissolved gas in the water after the filling procedure, \( t \) is time, \( R(t) \) is the 

Figure 8. Conceptual model of the freezing process showing the comparative evolution of gas in the system for a degassed and non-degassed experiment. Next to each schematic sphere, we have included a schematic representation of the total gas, liquid water, and ice content in the sphere. Note that at Time 0 and 1 for the degassed experiment, there is a small amount of gas in the total sphere, though it is dissolved. The schematic meter also has a column dedicated to the liquid and gas portion of the sphere only; the lines between the two columns simply show what portion of the left total column is being portrayed in the right column for liquid only. This shows how, as the ice shell grows, the relative concentration of gas increases until an exsolution threshold is passed, which we have labeled as the regime change. Gas that has passed the exsolution threshold is exsolved in the form of bubbles. Note that at Time 2 for the degassed experiment, the concentration of gas in the liquid only portion of the sphere is comparable (compared following red arrow) to the initial concentration of gas in the non-degassed sphere. In the non-degassed case, there is a sufficient initial concentration of gas to form bubbles from the beginning of the experiment.
The percent relative error is plotted in the lower purple bar chart. The calculations presented in the previous paragraphs support the hypothesis that the abrupt transition of volatiles required for exsolution; rather we focus on characterizing the mechanical effects of this behavior on the system of a freezing water sphere and using our model to predict when the regime change will occur.

A comparison between the time calculated from Equations 3–5 with the time of the transition observed in the degassed experiments shows very good agreement (Figure 9). In addition, our predicted time for N2–O2 saturation in the degassed experiments is consistent for all temperatures, which indicates that the finite amount of gas dissolved in the water as the growth of the ice shell occurs is comparable across degassed experiments. This supports that the effective N2 dissolved in the water of the degassed experiments is controlled by the degassing and mold filling protocol, which is identical for all experiments.

The calculations presented in the previous paragraphs support the hypothesis that the abrupt transition observed in our experiments with degassed water is controlled by the exsolution of bubbles and thus by the change of compressibility of the fluid phase. The consequences of volatile exsolution on the pressure time series can be inferred from mass conservation, assuming a purely elastic response of the ice shell (viscous relaxation is limited over the time scale of the pressure increase in our experiments) and taking into account that the pressure in the water increases because of the volume change associated with the inward freezing of the ice shell

$$\frac{dp(t)}{dt} = \beta * \left( \frac{3}{R(t)} \frac{dR(t)}{dt} \right) \left( \rho_i - \rho_w \right)$$

where \(p(t)\) is the time dependent pressure in the fluid, \(\frac{1}{\beta}\) is the bulk compressibility of the fluid, \(R(t)\) is the time-dependent radius of the inner surface of the shell, and \(\rho_w\) is the density of water. In turn, the evolution of the radius \(R(t)\) can be solved numerically by integrating the energy equation

$$\frac{\partial T}{\partial t} = \frac{\kappa}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) - \frac{L}{c_w} \frac{\partial f}{\partial t}$$

implicitly with a finite difference scheme based on the enthalpy method (Voller et al., 1987). \(T\) is the temperature, \(\kappa\) is the thermal diffusivity, \(r\) is a radial coordinate, \(L\) is the latent heat of solidification, \(c_w\) is the specific heat of water, and \(f\) is the melt fraction, which is given by

$$f = \begin{cases} 1 & \text{if } h > (c_w T_m + L) \\ \frac{h - c_w T_m}{L} & \text{if } (c_w T_m + L) \geq h > c_w T_m 0 \\ \text{else}, \end{cases}$$

where \(h\) is the specific enthalpy and \(T_m\) is the freezing temperature. Given that the freezing rate for degassed and non-degassed water is the same, we treat material constants as independent of the concentration of volatiles in the water.

Solving for Equations 3–5, we can provide estimates for the time it takes to freeze the mass of ice required to increase the dissolved gas concentration in the water to the dissolved concentration in the experiments with non-degassed water. This time represents the duration required for degassed water experiments to reach conditions similar to non-degassed experiments with respect to the dissolved volatile content in the water. For a non-degassed sphere, the initial dissolved volatile content is estimated at 16 ml in a 10 cm diameter water sphere at 5°C (calculation provided in supporting information Text S1). However, it should be noted that these calculations are approximate and it is not the goal of this work to determine the specific concentration of volatiles required for exsolution; rather we focus on characterizing the mechanical effects of this behavior on the system of a freezing water sphere and using our model to predict when the regime change will occur.
Enceladus may be actively freezing (not in steady state) and this may be re-occurring (Hemingway & Mittal, 2019; Nimmo et al., 2018; Roberts & Nimmo, 2008). Additionally, as on Earth, it is possible that the rate of ice shell fracture events changes over time throughout a moon's evolution and this may be re-occurring (Hand et al., 2007; Hendrix et al., 2019). Even if a planet can produce the chemical and thermal conditions necessary for life, it may not be habitable unless those key ingredients and conditions interact in the same place for some amount of time. Connections between the ocean and surface may allow for this colocation to occur. Moreover, our results suggest that the rate of ice shell fracture events changes over time throughout an icy moon's evolution and this may be reflected in the geologic record.

One particularly interesting point of comparison may be Saturn's moon Enceladus. The subsurface ocean on Enceladus may be actively freezing (not in steady-state) despite the tidal heating Enceladus experiences during its orbit (Hemingway & Mittal, 2019; Nimmo et al., 2018; Roberts & Nimmo, 2008). Additionally, as on Earth, it is possible that the rate of ice shell fracture events changes over time throughout a moon's evolution and this may be re-occurring.
our ice spheres, there is evidence for fractures which directly connect the ocean and surface (Postberg et al., 2009). The nature of this connection at the bottom of the ice shell is an open question, that is, whether fractures are partially fluid-filled or if there is a gas-capped chamber at the base of the tiger stripe fractures (Ingersoll & Nakajima, 2016; Kite & Rubin, 2016; Nakajima & Ingersoll, 2016; Porco et al., 2014; Postberg et al., 2009, 2018). In our experiments, fractures do not remain open and connected to the interior water for any measurable amount of time; after the ice shell cracks, we observe immediate re-pressurization (Figures S5 and S5). Any applications of our work to Enceladus would also need to take into account the relevant solubility and compressibility for the gases present in the ocean on Enceladus, including species such as carbon dioxide, nitrogen, carbon monoxide, and methane (Waite et al., 2006). There are many other factors which would need to be addressed in applying our results to Enceladus. Enceladus is well known for its complicated south pole terrain, perhaps the result of unequal tidal dissipation from a porous and/or irregular core (Nimmo & Pappalardo, 2016; Porco et al., 2014). In any case, the ice shell on Enceladus varies significantly in thickness from pole to pole, which would serve to concentrate stress and fractures from a freezing ocean (Cadek et al., 2016); such a stress concentration is not modeled in our experiments. More importantly, Enceladus experiences stresses from its orbital dynamics and, potentially, convection within the ice shell (Hemingway & Mittal, 2019; Nimmo et al., 2018; Porco et al., 2014; Roberts & Nimmo, 2008).

In light of the limitations to the comparisons drawn between our results and icy moons, future work should consider the influence of salts and ammonia on the system as well as investigate the effects of including a relatively incompressible core at the center of the ocean. Other factors relevant to icy moons, including non-uniform ice shell thickness and non-spherical geometries (e.g., equatorial bulges), should be investigated. Exploring these parameters will allow us to understand more about the competition between stresses caused by different processes and how they are modulated by different conditions (composition, orbital dynamics, etc.). For example, salt would not only affect the liquid’s mechanical properties as it concentrates in the liquid but would also affect the freezing rate and structure of the ice shell. Other factors to be considered include contributions from other forces (e.g., tidal), viscous deformation, and asphericity. Even so, these experimental results allow us to understand fundamental physical processes associated with freezing a spherical body of water.

Extrapolating results from these experiments to icy moons should be approached conservatively until future work has quantitatively explored scaling and considered the many complexities associated with icy moons. As such, more appropriate comparisons should consider icy moons for which (1) the chemistry is relatively simple (minimal effects from exotic ices, high pressure water ice phases, and complicated ocean chemistries) and (2) other sources (e.g., tidal, despinning, true polar wander, and radiogenic heat) of stress and heating are not important factors in the moon’s evolution. Another potential application of this work is for the freezing of water or brine lenses within ice shells on icy moons. These have been proposed to explain the formation of smooth deposits and/or chaos terrain on Europa and putative cryovolcanic features on Titan, Pluto (e.g., Virgil Fossae, Wright Mons, and Piccard Mons), and Charon (e.g., Kubrick Mons; Desch & Neveu, 2017; Lesage et al., 2020; Martin & Binzel, 2020; Mitri et al., 2008).

5. Conclusion

We have conducted experiments to study the effects of dissolved volatiles on the freezing evolution and surface features of ocean worlds. Controlling the freezing temperature and varying the amount of dissolved air, we find that the presence of dissolved volatiles in the water has significant influences on the tectonic evolution of the body, frequency of fracture events, and, in the case of our experiments, the final thickness of the ice shell before final failure. More specifically, we find that experiments with partially degassed water display a sudden change in fracture event frequency that coincides with the time at which the liquid water is expected to become saturated with gases in response to freezing. This process informs several important observables: Increased initial gas content leads to shorter overall experiment time to the final fracture that leads to the failure of the ice shell, a thinner final ice shell, lower final pressure peaks, and fewer fractures over the full duration of an experiment. These results have implications for the geologic history and habitability of icy moons, specifically that oceans should become more volatile-rich over time and that this will affect the frequency at which the ice shell fractures. Moreover, future work will be undertaken to understand
the cause of the observed critical failure of the ice shell, as well as to codify other physical and chemical factors which exhibit control on the behaviors of freezing ocean worlds.

References


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