



Plume Sample Modification at Icy Moons: Implications for Biosignatures

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Water from the plumes of icy moons is a potential sampling target that may preserve the aqueous chemistry of the interior oceans, as well as organics and other biosignatures or prebiotic chemical precursors. Water within the plumes will be modified both as it is transported far above the moon's surface, and as samples are taken of the plume water. Plume water is found to freeze rapidly by evaporation and sublimation, increasing the concentration of solutes by a factor of 20%. Organics within samples of the plume water are also potentially subject to significant alteration as they are collected, particularly oxidation resulting from reaction with oxidants entrained on ejection in the plume or formed via breakdown of H₂O on the surface as the drops are exposed in space. Mitigation of this oxidation will be critical to successful sample collection.

Keywords: plume, oxidation, astrobiology, biosignature detection, Europa - satellite (moon) of the planet Jupiter

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INTRODUCTION

The discovery of a water plume at Europa (Roth et al., 2014) and at Enceladus (Hansen et al., 2006) both provide an opportunity for the first direct sampling of liquid water from the outer Solar System (with potential for sample return). Liquid water is believed to be highly important for the development of life on other worlds, and hence such a discovery—and the accompanying analyses—could identify how habitable these moons might be (e.g., McKay et al., 2014; Barge and White, 2017).

The Enceladus plume has been characterized as having an alkaline pH (Glein et al., 2015), with low redox conditions, consistent with both carbonate and ammonia present within the plume water (a redox potential of about -0.5 V, see Postberg et al., 2011). The source of the water has been postulated to be in direct contact with rock based on its salinity (Glein and Shock, 2010), and on the presence of H₂, likely from serpentinization (Waite et al., 2017).

The surface of Enceladus is generally characterized as being pure water ice (Souček et al., 2016), with trace amounts of reduced compounds such as ammonia and tholins (Hendrix et al., 2010). Plume particles reach sizes of a few μm in radius (Ingersoll and Ewald, 2011) and are ejected at speeds of hundreds of m/s to km/s (Dong et al., 2011; Spencer and Nimmo, 2013).

The discovery of the Europa plume is comparatively recent, and postdates active Jovian space missions, hence little is known about the European plume water composition. The Europa plume appears to be transient lasting only days to months, and may be driven by tides (Roth et al., 2014; Rhoden et al., 2015; Sparks et al., 2016). The source region of the plume is likely subsurface, and may be the ocean, or beneath the icy crust from melt pockets, or some intermediate region with mixing between the two. If the source is the ocean, then the plume may provide a glimpse as to the global habitability of Europa, by constraining the oceanic conditions (pH, redox conditions, solutes and salt content), as well as organic content.

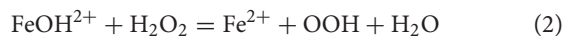
The crust of Europa consists primarily of water ice, as well as oxidants such as hydrogen peroxide (H_2O_2), molecular oxygen (O_2), and dark material consisting of some yet-unidentified hydrated salts (Carlson et al., 1999; McCord et al., 1999). These salts may consist of sulfate minerals (Orlando et al., 2005) or hydrated sulfuric acid (e.g., Maynard-Casely et al., 2014). The surface of Europa is hence very oxidizing with up to a few percent of strong oxidants, and organic compounds at the surface should be unstable, decaying to CO_2 or carbonate salts, though the timescales of such reactions may be long.

In contrast to the surface, less is known about the composition of Europa's subsurface ocean, though a variety of models have sought to determine the minerals and solutes present in the ocean, as well as possible pH and redox conditions (e.g., Kargel et al., 2000). Prior work (Pasek and Greenberg, 2012) predicted an acidic ocean if surficial oxidants react with hydrothermally-released reducing agents such as H_2S on a large scale. Alternatively, the ocean may be alkaline or neutral if transport of oxidants from the surface to the subsurface does not occur, or if the rocky ocean floor can buffer acid generation by dissolving into the ocean (Vance et al., 2016).

Whatever the source region of the plume material (ocean and/or icy crust), the material will be modified during ejection. Depressurization of the material results in evaporation and sublimation of the water, which in turn is coupled to heat loss and freezing. Loss of mass results in a higher net concentration of non-volatile solutes such as salts in the frozen droplet.

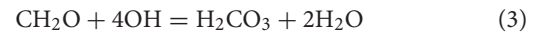
Collection of this plume material by spacecraft may further modify samples, depending on the collecting method used (Leroux et al., 2008). Collecting samples will likely result in heating of the samples, possibly with melting and vaporization of water. This may modify the material, especially if oxidants have been entrained within the collected particles. Oxidants may alter organic compounds by breaking C-H and C-C bonds, ultimately forming CO_2 , especially if during collection the temperature increases rapidly and if the oxidants and certain oxidation-promoting catalysts are abundant.

A major oxidant-producing reaction that would be of concern for sample collection is the Fenton reaction (Walling, 1975). In the Fenton reaction, H_2O_2 reacts to produce free hydroxyl (OH) and peroxy (OOH) radicals via catalytic transition metals (typically iron, but also copper):



Such a reaction follows a complicated set of reaction steps (Cohen, 1985; Kremer, 1999) that can aggressively oxidize organic compounds *in situ*, and if enough stoichiometric H_2O_2 is around, complete oxidation of organics is plausible. Effectively, each reaction of an OH or OOH radical can result in the +1 oxidation of a carbon atom, which range in oxidation state from -4 (methane, CH_4) to +3 (oxalic acid, $\text{C}_2\text{O}_4\text{H}_2$) for organic carbon, and complete oxidation occurs at an oxidation state

of +4 (CO_2 or carbonate). As an example, the oxidation of formaldehyde—the simplest sugar—requires four OH radicals:



Plume activity on Europa likely ejects a mixture of gas and solid/liquid H_2O . Although returning samples of gaseous H_2O would be beneficial from the perspective of understanding the history and sources of water on Europa (e.g., D/H and $^{18}\text{O}/^{16}\text{O}$ ratios), collection of larger water samples would better sample the source chemistry. If the plume source region includes the subsurface ocean, then water droplets ejected from the plume would bear compositions similar to the ocean, detailing the environmental conditions and potential habitability of Europa's ocean. In this paper I constrain the amount of water that would evaporate or sublime from liquid water droplets after ejection in the plume, and the effects this has on concentration of solutes. Additionally, I determine how much oxidation might occur as the sample is collected and heated and the effects this might have on the organic inventory of the water samples.

METHODS

Droplet Freezing

Thermodynamic data for water transitions, including heat capacity (C_p) as a function of temperature, phase change enthalpies (ΔH), and vapor pressures at saturation (P_{Sat}) are retrieved using the thermodynamic equilibrium program HSC Chemistry (version 7.1, Outokompu Research Oy). This code uses the GIBBS energy solver (White et al., 1958) to determine equilibrium concentrations and solve for reaction mass balances, and has been used previously to understand water-rock transitions (Pirim et al., 2014; Herschy et al., 2018), and model Europa ocean chemistry (Pasek and Greenberg, 2012).

The evaporation or sublimation of water drives cooling. Water evaporates so long as the pressure released by vaporizing does not exceed the saturation vapor pressure. The saturation vapor pressure is determined by calculating the mass transfer constant K from the reaction:



Over the range of temperatures (T) of interest (75 K for Enceladus, 135 K for Europa, reaching to 273 K), the vapor pressure (in torr) can be found by:

$$\text{Log}_{10}P_{\text{Sat}} = \frac{-2651.1}{T} + 10.351 \quad (i)$$

Evaporation and sublimation cease to remove mass when condensation and deposition on grains equals the evaporation/sublimation rate, v . This occurs when the vapor pressure is equal to the surface pressure of Europa (10^{-11} - 10^{-12} atm, Leblanc et al., 2002), which corresponds to a temperature of about 135 K. At and below this temperature, water ice droplet sublimation is balanced by condensation.

For liquid water at 273 K, evaporative or sublimative cooling results in a phase change to ice, with an enthalpy of fusion (ΔH_{Fus}) of 80 cal/g. The mass of water that must vaporize in order to cause the rest of the drop to freeze is thus the balance between the enthalpy of fusion and the enthalpy of vaporization (677.8 cal/g, see below). To this end, mass from a drop of water will sublimate to drive cooling:

$$\left(\frac{\Delta H_{Vap}}{\Delta H_{Fus}} + 1\right)^{-1} \times m_i = m_l \quad (\text{ii})$$

where m_i is the initial mass of water, and m_l is the mass lost by vaporization. After freezing, the enthalpy (ΔH_{Vap}) of reaction (4) is calculated as 660 cal/g at 75 K to 677.8 cal/g at 273 K, for an average value of 674.7 cal/g over the temperature range of 135 K and greater. This reaction enthalpy can be contrasted to the heat capacity of ice as a function of temperature to determine the amount of mass lost by sublimation that thereby drives cooling to ambient temperatures (135 K at Europa). Using a temperature-dependent heat capacity (C_p) defined as:

$$C_p = 0.001865 T - 0.00348 \quad (\text{iii})$$

the quantity of water (m_l) that evaporates can be determined from:

$$\left(\frac{\Delta H_{Vap}}{C_p \Delta T} + 1\right)^{-1} \times m_i = m_l \quad (\text{iv})$$

The above equations are time-independent. The rate of evaporation or sublimation is calculated from the Hertz-Knudsen-Langmuir equation:

$$v = 0.0437 \alpha_S \sqrt{\frac{M}{T}} \times (P_{Sat} - P_{Surf}) \times 4\pi r^2 \quad (\text{v})$$

where v is the rate of evaporation in g/s, α_S is the temperature-dependent sublimation coefficient of Kossacki and Leliwa-Kopystynski (2014), M is the molecular mass in g/mol, T is the temperature in K, P_{Sat} is the vapor pressure at saturation in torr or mm Hg, P_{Surf} is the pressure above the surface of the drop in torr, and r is the radius of the droplet in question in cm. The 0.0437 corrects for units and includes the Boltzmann constant. Though this evaporation rate equation includes the empirically-derived α_S , which has been shown to vary by three orders of magnitude even for water (Persad and Ward, 2016), the estimations here provide approximations of the sublimation rate of droplets that should be accurate to an order of magnitude.

The loss of water as gas thus drives cooling and determines the temperature (T) of the droplet in Equation (v) by the relationship:

$$\frac{-v \times \Delta H}{C_p \times m_D} = \frac{dT}{dt} \quad (\text{vi})$$

where m_D is the mass of the remaining droplet. Using a finite difference method to calculate temperature changes and its effect on vapor pressure, heat capacity, and evaporation rate, and mass loss with the associated surface area loss, I calculated the effect of evaporation and sublimation on droplets of various starting sizes.

Oxidants and Oxidation

Another change that may occur to water samples that are subjected to the environments of Jupiter and Saturn is the accumulation of radiation damage and formation of an oxidized crust. These oxides may react with organics to alter them or to completely oxidize them to CO_2 upon collection by a spacecraft. This process would be related to the amount of entrained oxides and the exposure timescales of the droplets, followed by their thermal histories (which is a function of droplet size and capture velocity). To this thermal profile I added kinetic calculations associated with the Fenton reaction that produces highly oxidizing OH radicals, to provide an estimate of the fates of organics during collection of water samples at these locations.

The production of peroxide is considered using the H_2O_2 production rate of Carlson et al. (1999). H_2O_2 is estimated to be produced at a rate of 2×10^{11} molecules/ cm^2 s, and is produced primarily by high energy particle bombardment. The number of H_2O_2 molecules formed on a droplet's surface ($N_{\text{H}_2\text{O}_2}$) is thus estimated as:

$$N_{\text{H}_2\text{O}_2} = (2 \times 10^{11}) (\pi r^2) \tau \quad (\text{vii})$$

where τ is the timescale of exposure of these particles, and the particle bombardment is not assumed to come from Europa, hence the surface area of the particle is calculated as its cross-sectional area. In these simple calculations it is assumed that all high energy particles stop at the surface of the water ice droplets, though a more rigorous model could include variation of penetration depth with respect to particle type (Cooper et al., 2001).

The oxidation of organics by oxidants such as peroxide requires a liquid medium. Although peroxide in ice likely does not oxidize organics due to diffusion limitations and low reactivity at cold temperatures, melting of the droplets via reheating by impact with Europa's surface, or during sample collection, may cause *in situ* organics to oxidize to CO_2 and lose information on their speciation (which is critical to identifying biosignatures). The amount of melting that occurs during collection is calculated from the conversion of kinetic energy to thermal energy via:

$$\frac{1}{2} V^2 = C_p (\Delta T) + \Delta H_{Fus} \quad (\text{viii})$$

with V the velocity in m/s, C_p having its temperature dependence as per (iii), and equal to 1 cal/g above 273 K, and ΔH_{Fus} being the enthalpy of melting/fusion (requiring 80 cal/g), needed only if temperatures reach 273 K. The velocity required to melt the frozen droplets is ~ 660 m/s, and to reach the boiling point is $\sim 1,400$ m/s.

After heating, the water samples should cool via thermal diffusion as they will likely be in direct contact with a cold collection chamber, on timescales of

$$t \propto \frac{r^2}{k_D} \quad (\text{ix})$$

where k_D is the thermal diffusivity of water ($\sim 10^{-3}$ cm^2/s , James, 1968). Using various sizes, peroxide contents, and a temperature

profile that is assumed to decrease linearly over the timescale t from (ix) to reach the ambient temperature (75 or 135 K), the production of oxides from the Fenton reaction is determined by integrating reaction velocities using a kinetic rate law constant k determined as:

$$k = 3 \times 10^{15} e^{\frac{-9500}{T}} \quad (\text{x})$$

where the factor $-9,500$ is the activation energy divided by R of Lin and Lo (1997), and the frequency factor $3 \times 10^{15} \text{ s}^{-1}\text{M}^{-1}$ is calculated from a reaction k equal to 40 at 298 K (Pignatello et al., 2006).

The rate of oxidant [Ox] production is estimated as:

$$d[\text{Ox}]/dt = k[\text{H}_2\text{O}_2][\text{Fe}^{2+}] \quad (\text{xi})$$

where $[\text{H}_2\text{O}_2]$ is defined as the molarity of peroxide from (v), and $[\text{Fe}^{2+}]$ is the ferrous iron molarity in solution (estimated as 10^{-4} M at circumneutral pH, consistent with Fanale et al., 2001). In the Fenton reaction, Fe^{2+} is regenerated from Fe^{3+} [reaction (2)] and hence it is the total molarity of iron that controls the production of OH and OOH, the oxidants capable of altering organic carbon.

The oxidation rate is integrated over the timescale from (ix) to provide the total molarity of OH generated from H_2O_2 . This represents a measure of the oxidizing power of the peroxide as the plume samples cool. This oxidant production is then compared to the effect of the oxidants on organic carbon, assuming the carbon begins with an oxidation state of zero [consistent with sugar or formaldehyde, as per reaction (3)]. The oxidation of organics occurs rapidly at room temperature in the presence of transition metal catalysts driven by the Fenton reaction (see Walling, 1975; Pasek et al., 2008), but is otherwise slow (Debellefontaine et al., 1996). This oxidation process is a function of peak temperature, cooling rate, drop size and exposure timescale [from (vii)], and fraction of catalyst present. Oxidation states other than zero are not unreasonable for other biological molecules and range from ~ -2 for hydrocarbons, to $+2/+3$ for carboxylic acids.

RESULTS

Here I evaluate the effects of the time of exposure of liquid water to low pressure conditions and to oxidizing radiation. Low pressure and temperature conditions result in rapid evaporation and sublimation of water as it freezes and drops to ambient conditions. Drops are estimated to cool rapidly (seconds) and lose $\sim 17\%$ of their mass during this time. Exposure to radiation results in the buildup of oxidants that may degrade organics that were present in the original liquid droplet, especially by reheating during sample collection of these plumes. Oxidant buildup is most relevant if the drops cool slowly and have accumulated significant oxidants during their exposure time.

Water droplets ejected from the plume are frozen rapidly by evaporation of water from their surface. The water droplets lose $\sim 10\%$ of their mass during this process [calculated from Equation (ii)], over a timescale of μs to s, depending on the initial radius of the drop [Figure 1, calculated coupling Equation (ii) with (v)]. The fraction of mass lost is independent of size. The

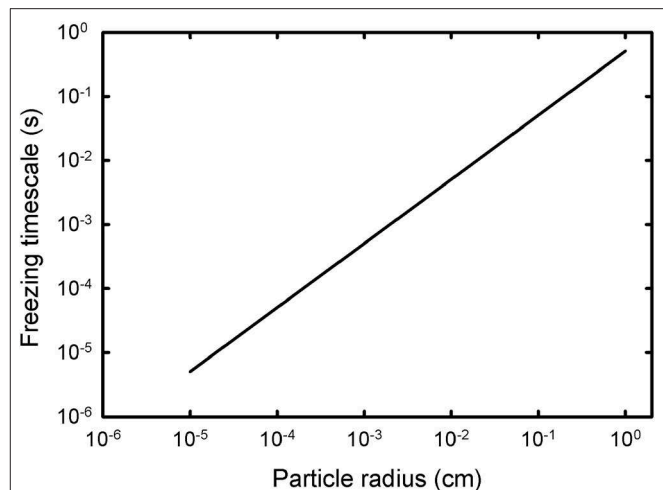


FIGURE 1 | The time required to completely freeze a pure liquid water droplet at 273 K by cooling from evaporation, balancing the mass lost from Equation (ii) with the evaporation rate from Equation (v).

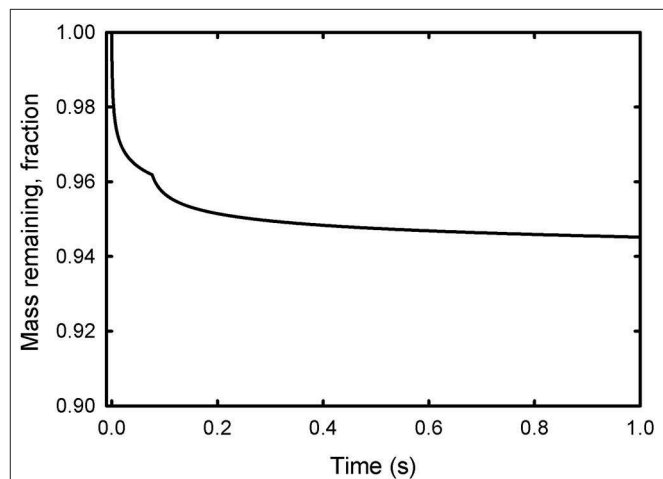


FIGURE 2 | The mass lost as calculated from Equations (v) and (vi) due to sublimation as a function of time for a frozen ice droplet with an initial radius of $10 \mu\text{m}$, relative to its initial mass (set as 1). The change in slope at about 0.1 s is due to a change in the coefficient of sublimation from 0.15 to 1.0 at 215 K (Kossacki and Leliwa-Kopystynski, 2014). The droplet asymptotically reaches 6–7% mass loss in minutes [as per Equation (iv)].

net volume of the drop is changed only slightly, as the loss of 10% of the mass is accompanied by an 8.5% volumetric expansion.

Subsequent sublimation at the surface of the ice droplets also occurs rapidly, and is effectively complete on the order of seconds to minutes [Figure 2, calculated from (vi)]. All droplets eventually reach a 7% mass loss at Europa from sublimation [9% at Enceladus, calculated from (iv)], independent of size, occurring as the ice droplets reach 135 K and ambient pressures (75 K at Enceladus). The net loss of mass due to sublimation and evaporation is thus between 16 and 19%, the sum of the mass lost from Equations (ii) and (iv).

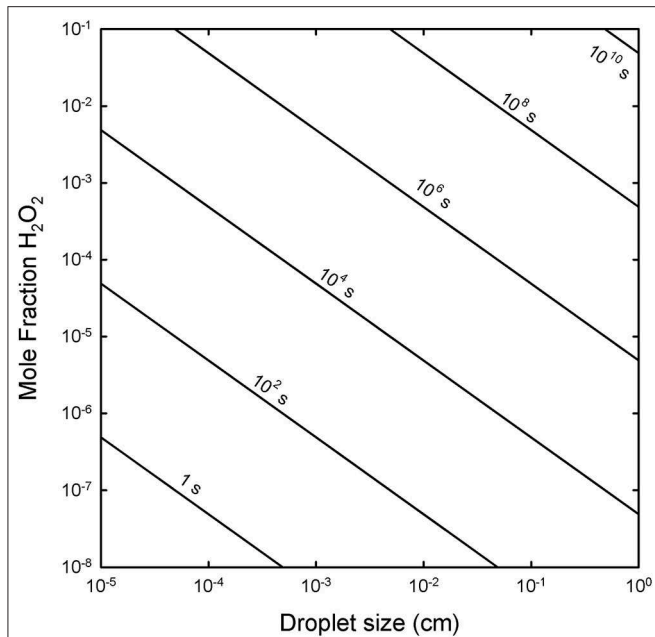


FIGURE 3 | The exposure timescale [in seconds, from Equation (vii)] required to produce a specific mole fraction of H_2O_2 (y-axis) as a function of droplet size (diameter in cm, x-axis). Note that 1 month is about $\sim 10^{6.5}$ s.

The production of oxidants such as H_2O_2 on ice droplets is strongly related to both the time of exposure and the drop size. The mole fraction of H_2O_2 is shown as **Figure 3**, with the amount of H_2O_2 dependent on different exposure timescales (from vii) and on differing droplet sizes as shown, and the molarity equivalent is this mole fraction multiplied by 55.56 (the moles per L of water). Concentrations of peroxide on the order of ~ 1 molar are feasible for smaller droplets after only a few weeks.

The Fenton reaction is highly effective as an oxidant producer over relatively short timescales ($< 1,000$ s). The production of oxidants by such a reaction is most critical for large droplets that cool slowly and that reach high temperatures during collection. For large droplets, complete breakdown of all H_2O_2 is expected [due to a slow cooling rate, from (ix)], whereas smaller droplets that cool much faster would have much less OH production (**Figure 4**). This effectively means that any H_2O_2 generated by bombardment in the Europa environment will break down into highly reactive OH for the largest droplets, whereas smaller droplets will have less OH generation as they cool faster and H_2O_2 has less time to react.

This generation of OH would correspond to a degradation of organics, as per reaction (3). Organics are altered when an OH reacts with a C-H bond to form a C radical (that can then react internally or with other C radicals to polymerize toward tar), and the final product of such a reaction is CO_2 . This occurs most readily for larger droplets that are slow to cool with a large H_2O_2 to organic C ratio, but may be pertinent to all droplets if the quantity of H_2O_2 present is high (for instance, via entrained crustal material). This effect is quantified by tying Equations (x) and (xi) with reaction (3) in **Figure 5**.

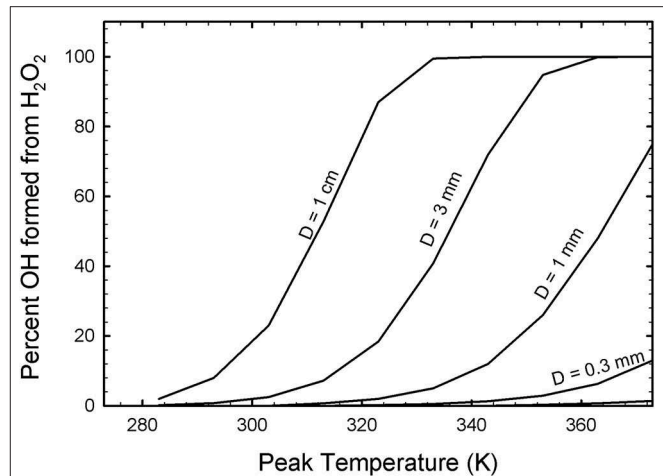


FIGURE 4 | The percentage of H_2O_2 estimated to break down into OH and OOH radicals via the Fenton reaction as a function of droplet size (diameter as given) and peak temperature, as determined from Equations (x) and (xi). When the droplets are large and collected at high velocity, they heat substantially and cool slowly. As a result, the temperature-dependent Fenton reaction is capable of breaking down significant quantities of H_2O_2 into OH and OOH.

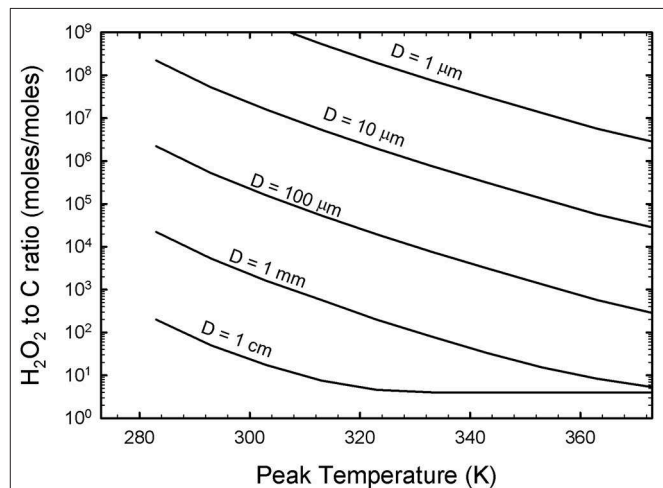


FIGURE 5 | The H_2O_2 to C content on a mole per mole basis of a drop determines how likely it is to alter the organic inventory of a droplet irrevocably. Effectively, the complete oxidation of an organic compound such as formaldehyde requires a 4:1 or greater H_2O_2 to C ratio to potentially result in the complete oxidation of such a molecule. However, concentrations higher than 4:1 may still not alter all of the organics within the droplet, as the peak temperature and droplet size both contribute to the generation of reactive oxidant (OH and OOH) material capable of degrading organics. For this diagram, concentrations of H_2O_2 that greatly exceed the moles of organic carbon are more likely to degrade the organics for large droplets that are heated to high peak temperatures.

DISCUSSION AND IMPLICATIONS

Both the Enceladus and Europa plumes present an opportunity to sample water from these potentially habitable moons. It is necessary to constrain possible chemical alteration that may take

place after leaving the plume source region so as to determine how representative the samples are of their environment, critical to determining biosignatures and habitability. Key results of this study are that water droplets comprising part of plume are frozen rapidly, with loss of about 17% of the water by evaporation and sublimation if the water is originally liquid and at 273 K. The 17% loss of water corresponds to a 20% increase in the concentration of non-volatile solutes such as salts, if the associated water vapor is not collected. Volatiles, such as gases and clathrates (Mousis et al., 2013), will be altered during sublimation, at least as far as their concentration is concerned.

Of far greater concern are oxidants reacting with organic compounds in the droplets on collection. These oxidants may come from particle bombardment of droplet surfaces after ejection, or alternatively, may be entrained from the oxidizing icy crust as the droplets are expelled especially in the case of Europa. If there is little entrainment, then it is possible that oxidation by H₂O₂ should not be much of a concern. Small droplets with the highest expected H₂O₂ are also those that cool the quickest and hence produce little oxidant during capture. Large droplets that can produce more OH from H₂O₂ should generally have less oxidants if their exposure time is short.

However, if oxidants from the crust are entrained in the droplets during ejection, then organic compounds may be altered, especially in large drops. Europa's ice crust may bear up to 1–3% O₂ by mass (Hand et al., 2007) and 0.13% H₂O₂ (Carlson et al., 1999), implying that if a subsurface droplet is contaminated with even 1% of the icy crust material, then the total organic carbon concentration would have to exceed $\sim 10^{-3}$ M to be preserved if all of these oxidants react.

Oxidation of organics will primarily take place when the droplets are liquefied, and if there are transition metals present in the droplets, such as Fe²⁺ or Cu⁺. In the presence of transition metals, H₂O₂ decays to OH radicals, which promote organic breakdown to CO₂. These oxidation reactions occur on timescales of tenths of seconds even at room temperature (Duesterberg and Waite, 2006) and are faster still at elevated temperature. Given that most collection methods will heat samples (Leroux et al., 2008), organic compounds may be

subjected to oxidation unless the samples are quickly cooled, or the transition metals are removed during collection (perhaps by capture in a chelating gel). Either step could be a potential mitigation against this oxidation effect. However, the result of this oxidation would be an alteration or even complete removal of organic speciation as a biosignature.

Given our current state of knowledge of Europa's plume and its composition, this study is preliminary. Further estimates of plume sample compositional modifications should include better estimates on the kinetics of oxidation of organic compounds, for a variety of organics of astrobiologic interest. Furthermore, experimental investigation of organic compound oxidation rates under the worst-case scenario (high H₂O₂ with a large, slow-to-cool drop) could corroborate these model results. Additionally, the plume dynamics will control the sample size distribution, which has several significant effects on evaporation/sublimation, and on oxidation. Little as of yet is known about the source region for the plume, the energetics driving the plume, or interactions of the plume material with the icy crust, especially for Europa. Better constraints on these plume features will help constrain the potential modifications of samples prior to analysis.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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Conflict of Interest: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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