https://doi.org/10.5194/acp-2020-416
Preprint. Discussion started: 9 June 2020

Atmospheric Chemistry and Physics Discussions

A Link between the Ice Nucleation Activity of Sea Spray Aerosol and the Biogeochemistry of Seawater.

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Abstract. Emissions of ice nucleating particles from sea spray can impact climate and precipitation by changing cloud formation, precipitation, and albedo. However, the relationship between seawater biogeochemistry and the ice nucleation activity of sea spray aerosols remains unclarified. Here, we demonstrate a link between the biological productivity in seawater and the ice nucleation activity of sea spray aerosol under conditions relevant to cirrus and mixed-phase cloud formation. We show for the first time that aerosol generated from both subsurface and microlayer seawater from the highly productive Eastern Tropical North Pacific Ocean are effective ice nucleating particles in the deposition and immersion freezing modes. Jet droplets aerosolized from the subsurface waters of highly productive regions may therefore be an unrealized source of effective INPs. In contrast, the subsurface water from the less productive Florida Straits produced less effective immersion mode INPs and ineffective depositional mode INPs. These results indicate that the regional biogeochemistry of seawater can strongly affect the ice nucleation activity of sea spray aerosol.

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1 Introduction

Atmospheric ice nucleation strongly affects the Earth's climate (Pruppacher and Klett, 1980). Cloud albedo and lifetime are altered by ice nucleation processes, impacting the global radiative budget. For instance, ice nucleation changes the size and concentration of cloud particles (Kanji et al., 2017; Pruppacher and Klett, 1980). Clouds comprised of more and smaller ice crystals have comparatively higher albedo than those with larger and fewer ice crystals (Twomey, 1977). The net radiative effect of ice nucleation in clouds depends on several factors, such as convection velocities and the resulting ice crystal concentration (Zhao et al., 2019). Ice formation in mixed-phase clouds leads to ice particles with greater settling velocities than liquid cloud droplets (Pruppacher and Klett, 1980). Known as the Wegener-Bergeron-Findeisen process, this effect decreases cloud lifetime and is hydrologically important. Ice nucleation in mixed phase clouds induces over 70% of precipitation globally (Lau and Wu, 2003). In these ways, ice nucleation exerts an important impact on the Earth's climate.

Ice nucleation occurs through two main processes. Homogeneous freezing occurs when ice forms spontaneously from any aqueous aerosol. This process requires temperatures below –36 °C and relative humidities of at least ~140% with respect to ice (Koop et al., 2000). In the presence of ice nucleating particles (INPs), ice can also form at a lower relative humidity and warmer temperatures through heterogeneous ice nucleation mechanisms (Whale, 2018). Several pathways of heterogeneous ice formation exist. At ice supersaturation but below liquid water saturation, ice can deposit directly onto the solid surface of INPs in a process called deposition nucleation. At these conditions, nucleation can also occur through pore condensation freezing. Crevices and pores on the particle surface can promote liquid water condensation that subsequently freezes (David et al., 2019). Ice nucleation can also occur when the soluble components of an internally mixed particle deliquesce below water saturation, exposing insoluble INPs to liquid water (Khvorostyanov et al., 2004; Kong et al., 2018).

Other modes of heterogeneous ice nucleation occur above liquid water saturation. Contact freezing occurs when an INP collides with a supercooled liquid water droplet (Moreno et al., 2013). Immersion freezing first requires an INP to activate as a cloud condensation nucleus, exposing the particulate surface to liquid water before freezing (Murray et al., 2012). Soluble materials are generally ineffective INPs above liquid water saturation (Hoose and Möhler, 2012). However, organic macromolecules have been demonstrated to promote heterogeneous ice nucleation in solution (Pummer et al., 2015). Such substances are known as ice nucleating macromolecules (INMs) (Vali et al., 2015).

Despite their climatic importance, the sources and characteristics of atmospherically relevant INPs remain uncertain. Laboratory and field studies have identified a wide diversity of effective INPs. These include both primary sources, such as mineral dusts, black carbon, fly ash, biological particles, and salts (Atkinson et al., 2013; DeMott et al., 1999, 2003; Diehl et al., 2001; Field et al., 2006; Hoose et al., 2008; McCluskey et al., 2014; O'Sullivan et al., 2015; Steinke et al., 2016), and secondary aerosol sources (Berkemeier et al., 2014; Ignatius et al., 2016; Murray et al., 2010; Wagner et al., 2012; Wilson et al., 2012).

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Research into marine sources of INPs is sparser than studies on terrestrial sources (Brooks and Thornton, 2018; Hoose and Möhler, 2012; Kanji et al., 2017). Early studies quantified the ability of sea spray aerosol (SSA) in the marine boundary layer to activate as immersion freezing INPs. Bigg (1990) observed regional differences in ambient INP concentration over the Southern Ocean, but was unable to discern whether the variability resulted from terrestrial influence or from differences in local biological productivity. Rosinski et al. (1986, 1987) performed measurements in the Eastern Tropical Pacific Ocean, finding that local variability in ambient INP concentration corresponded to intensity of upwelling. These studies thereby identified a tentative causality between marine productivity and INP emission rates, but the link between productivity and INP activity remains understudied.

More recently, Wang et al. (2015) and DeMott et al. (2015) simulated blooms in a laboratory setting by co-culturing phytoplankton and heterotrophic bacteria. A positive correlation between primary productivity, dissolved organic matter concentration, and INP emission in these experiments suggested changes in seawater chemistry induced by metabolic activity and grazing can impact the ice nucleation activity of SSA. Wilson et al. (2015) observed that the ice nucleation potential of SSA was correlated to the organic content of aerosols generated from North Atlantic seawater samples. Film burst SSA generated from the organically enriched sea surface microlayer decreased the critical ice supersaturation – the supersaturation at which nucleation initiates – by 10 to 28% compared to more inorganic particles generated from subsurface water. Based on the geography and timing of the sample collection, the authors proposed diatom exudates were responsible for the observed deposition and immersion mode nucleation (Knopf et al., 2011). A variety of other phytoplankton, including *Prochlorococcus*, *Synechococcus*, and pico- and nano-eukaryotes, are also effective sources of deposition and immersion mode INPs (Ladino et al., 2016; Wilbourn et al., 2020; Wolf et al., 2019).

SSA encompasses a range of particle chemistries that affect ice nucleation ability. Winds in excess of 4 m s^{-1} induce whitecaps, which entrain bubbles below the ocean surface (O'Dowd and de Leeuw, 2007). These bubbles accumulate hydrophobic or amphiphilic organic matter as they rise towards the surface (Wilson et al., 2015). Bubble bursting at the surface eject smaller and organically-enriched film burst particles (Wang et al. 2017; Wolf et al. 2019). The depression in the ocean's surface left by the burst bubble then rapidly fills with the subsurface seawater, ejecting larger jet droplets (Pruppacher and Klett, 1980). The film burst and jet drop mechanisms can produce aerosols with distinctive chemical characteristics. SSA particles produced from jet drops are composed mainly of inorganic salts but may also contain whole or fragments of cells and soluble organic molecules in subsurface waters (Wilson et al., 2015; Wolf et al., 2019). Film burst particles can contain higher mass fractions of semi-soluble and insoluble organic molecules in the sea surface microlayer (Cochran et al., 2017).

The biogeochemistry of seawater can have a large impact on the composition of SSA. Regions of high primary productivity, such as upwelling environments or springtime phytoplankton blooms, exhibit different planktonic species than regions with low primary productivity (Righetti et al., 2019). Whereas upwelling zones and highly productive regions support larger phytoplankton species like diatoms and dinoflagellates, oligotrophic waters are characterized by different clades such as *Prochlorococcus* and *Synechococcus* (Chisholm et al., 1988; Dutkiewicz et

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al., 2020). Which organisms dominate within the water directly impacts the types of organic molecules and vesicles exuded into the seawater (Azam and Malfatti, 2007; Bertilsson et al., 2005; Biller et al., 2014). Marine regions of high primary productivity are generally enriched in INPs (Wilbourn et al., 2020). INPs from organically-enriched marine waters require lower relative humidities and warmer temperatures to initiate ice nucleation (McCluskey et al., 2017; Wilson et al., 2015).

However, the impact of ocean biogeochemistry on the ice nucleation activity of SSA is tenuous. Measurements of INP concentration and activity from diverse marine regions are relatively rare (Brooks and Thornton, 2018). In this study, we identify a link between primary productivity in marine environments and the INP activity of SSA. Two chosen sample regions – the Florida Straits and the Eastern Tropical North Pacific (ETNP) – are typical of low productivity and highly productive marine ecosystems, respectively. Coastal upwelling along the eastern boundary of the Pacific sustains high levels of primary productivity in the ETNP. We demonstrate that both the subsurface and microlayer seawater can be sources of effective INPs in highly productive marine environments. Our findings show for the first time that aerosols formed from subsurface waters in productive regions can be effective INPs. This indicates that jet droplets in these regions may be an overlooked source of INPs. These results demonstrate that SSA composition and INP activity varies between marine biogeochemical environments, yielding important caveats for climate models parameterizing marine INP impacts on global climate.

2 Experimental Methods

2.1 Sampling Locations

Seawater samples and seawater measurements were taken on two cruises to the Florida Straits and ETNP. Sampling in the Florida Straits took place aboard the SSV *Corwith Cramer* from March 28th through March 31st 2018. Sampling in the ETNP took place aboard the R/V *Falkor* from June 30th through July 10th 2019 (Fig. 1, Table S1). At each location, microlayer and subsurface samples were collected. Additional context for these samples was gained through analysis of marine biogeochemical parameters like nitrate, phosphate, pH, and chlorophyll (Table 1). These variables were measured using standard methods (Braman and Hendrix, 1989; Clayton and Byrne, 1993; Evans et al., 2020; Strickland and Parsons, 1972).

2.2 Seawater Sampling

The sea surface microlayer was sampled using the glass plate technique detailed previously (Harvey and Burzell, 1972; Irish et al., 2017). Briefly, a plexiglass plate was fully submerged under seawater and withdrawn at a rate of approximately 5 cm s^{-1}, allowing microlayer organics to adhere to the plate (Figure 2). Sampling occurred on the windward side of the ship to avoid contamination. Although previous studies have sometimes sampled as far as 500 m away from the ship (Irish et al., 2017; Wilson et al., 2015), rough seas precluded this practice on our cruises. The withdrawn plate was allowed to drain for 5 seconds, and then was scraped dry using a neoprene wiper blade cleaned with isopropanol between samples. The sampled microlayer was collected in acid washed 250 mL Nalgene bottles rinsed with subsurface seawater from the sampling station. Approximately 200 mL was collected for each seawater

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sample, requiring an average of 102 dips per sample. Based on the volume of seawater collected per dip and the surface area of the plate, the thickness of the organically-enriched layer adhering to the plate was on average 26 µm. This falls within the range of previous findings (Irish et al., 2017).

Subsurface seawater samples were collected at the same time and location as the microlayer samples with a Seabird conductivity-temperature-depth rosette. Seawater was sampled from the shallowest Niskin bottle on each cast and typically between 2 and 5 meters below the surface. Subsurface samples were collected in sterilized 250 mL Nalgene bottles rinsed with seawater from the same Niskin that was sampled. Both subsurface and microlayer waters were stored at -80 ˚C until analysis. Previous analysis suggests that freezing seawater samples has minimal effect on INPs (Schnell and Vali, 1975).

2.3 Seawater Aerosolization

To investigate the chemical and ice nucleating properties of aerosols generated from collected seawater, samples were thawed by immersing sealed bottles in room temperature water and mixed by inverting bottles ten times. 50 mL of sample were added to a glass container attached to a custom Collison-type atomizer. Aerosols were dried by passing through two consecutive diffusion dryers filled with silica desiccant. Relative humidity at the outlet of the diffusion dryers was 15%, which is below the efflorescence relative humidity of sea salt (Cziczo and Abbatt, 2000; Zeng et al., 2013).

The resulting dried sea salt aerosols were diverted into a differential mobility analyzer (DMA, Model 2002; Brechtel Manufacturing Inc., Hayward, CA). Particles were size selected (mobility diameter = 200 nm) with a sheath to sample flow ratio of 8:1. The DMA sheath flow was dried with silica desiccant to a relative humidity of less than 15%. A 500 nm size cutoff impactor was used upstream of the DMA to remove large multiply-charged particles from entering the sampled aerosol stream. The particle diameter was chosen to align with previous experiments' methods (DeMott et al., 2015b; Wilson et al., 2015), yet we acknowledge INP activity varies with SSA diameter (DeMott et al. 2015b; Si et al. 2018).

2.4 Chemical Characterization

We investigated the composition of SSA generated from seawater samples using the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument (Cziczo et al., 2006). PALMS measures mass spectra on a particle-by-particle basis, allowing the composition of aerosols from like sources to be compared. Sampled particles are first collimated in an aerodynamic inlet. The carrier gas is pumped away under vacuum, yet the residence time before ionization is short enough to minimize the loss of volatile organic components from the particulate surface (Cziczo et al., 2006).

Particles are then ionized using a 193 nm ultraviolet excimer laser. Atomic and small molecular ions are then sampled using time of flight mass spectrometry (Murphy, 2007). PALMS measures either positive or negative mass spectra per particle. Although an organic signal is detected in both polarities, sampling in the negative polarity captures more

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organic nitrogen and phosphate markers (Wolf et al., 2019). We sampled approximately 2,000 particles in the negative polarity for each seawater sample. Particle ionization with the UV excimer is not quantitative (Cziczo et al., 2006; Murphy et al., 1998). However, the average relative intensity of organic signal in a sample's mass spectra can qualitatively indicate which seawater samples are organically-enriched (Wolf et al., 2019).

2.5 Ice Nucleation Measurement

The SPectrometer for Ice Nuclei (SPIN; Droplet Measurement Technologies, Boulder, CO) measured the conditions required for the generated SSA to nucleate ice and the fractional INP activation. The theory and operation of SPIN has been described previously (Garimella et al., 2016, 2017). Briefly, SPIN is a continuous flow diffusion chamber style instrument that simulates ice nucleation conditions in clouds. It consists of two flat parallel plates separated by 1.0 cm and coated in approximately 1 mm of ice.

Aerosol particles are drawn into the nucleation chamber and nominally constrained to a flow centerline with particle free sheath air adjacent to the ice-covered walls. The temperature and relative humidity that the aerosols experience is controlled by varying the temperature gradient between the two walls (Garimella et al., 2016; Kulkarni and Kok, 2012). In this study, SPIN operated in two different temperature and ice saturation ratio (S_{ice}) regimes. To observe deposition and homogeneous freezing, SPIN's aerosol lamina varied between –40 to –46 ˚C and $1.0 \leq S_{ice} \leq 1.6$. These conditions are relevant to cirrus cloud formation. To observe immersion freezing, SPIN's aerosol lamina ranged from –20 to –30 ˚C and $1.0\ S_{ice} \leq 1.5$; conditions that can also correspond to liquid water supersaturation and mixed phase cloud formation.

Turbulent mixing near the aerosol inlet causes particles to spread outside of the aerosol lamina. This exposes particles to a wider temperature range and lower S_{ice} than that of the lamina centerline (Garimella et al., 2017). Particles outside of the lamina are therefore less likely to activate as INPs. To account for this artefact, a correction factor is normally applied to measured INP and fractional activation data (DeMott et al., 2015a; Garimella et al., 2017; Wolf et al., 2019). We apply the methods and correction factors detailed in Garimella et al. (2017) and Wolf et al. (2019) to immersion and deposition nucleation data presented in this study.

After the nucleation chamber, particles enter an optical particle counter (OPC). The OPC records side scatter intensity and laser light depolarization data on a particle by particle basis for diameters between 0.2 and 15 µm. A machine learning algorithm, detailed in Garimella et al. (2016), is trained using four OPC variables to classify all particles as either unactivated, ice, or liquid droplets. Fractional INP activation is derived by dividing ice crystal concentration assigned by the machine learning output by total particle concentration, as measured by a condensation particle counter (CPC, Model 1700; Brechtel Manufacturing Inc., Hayward, CA) running in parallel to SPIN. Frost shedding from SPIN's iced walls creates a baseline ice crystal concentration. These frost "backgrounds" are measured before and after each experiment. The average value is subtracted from the measured INP concentration. Background

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concentrations are typically below 10 L^{-1} and below the threshold ice concentration used to determine nucleation onset in all experiments presented herein.

3 Results and Discussion

3.1 Seawater Chemistry

Analysis of SSA generated from the two sampled regions suggests that the ocean biogeochemistry impacts the relative composition of subsurface and microlayer waters. We measured the intensity of carbon, organic nitrogen, and phosphorus signals. The integrated carbon signal is defined here as the sum of the areas under the C^- (m/z = 12), C_2^- (m/z = 24), and C_4^- (m/z = 48) mass spectra peaks (Figure 3). The C_3^- (m/z = 36) peak was omitted due to its proximity to two chlorine isotopic peaks (m/z = 35 and 37), the intensity of which vary between spectra. Omitting the C_3^- peak does not affect our analysis, since the ratios of C_n^- peaks are similar across all spectra. Similarly, the integrated nitrogen signal is defined as the sum of CN^- (m/z = 26) and CNO^- (m/z =42) peaks. These peaks may result from the ionization of amine functional groups, such as those found in amino acids. We omit inorganic nitrogen ions, such as NO^- and NO_2^-, as these may result from nitrate salts in SSA and would not increase the INP activity. An organic phosphorus signal, defined as CP^-, was not observed (Figure 3). The phosphorus signal is defined as the sum of PO_2^- (m/z = 63), PO_3^- (m/z = 79), and PO_4^- (m/z = 95). These peaks may indicate the ionization of phospholipids and the phosphate backbones of nucleic acids.

The average integrated carbon, nitrogen, and phosphorus signals (n > 1000 for each data point) are shown in Figure 4. Both the subsurface and microlayer waters of the highly productive ETNP exhibit similar organic carbon signals, indicated by the slope of approximately 1 ± 0.09 (standard error; Figure 4a) when comparing the ratio of organic carbon signals in microlayer and subsurface samples. This suggests that elevated primary productivity in the ETNP sustained organic carbon content in the subsurface waters. This aligns with metrics of higher primary productivity in the ETNP subsurface water, such as higher average chlorophyll concentrations at the deep chlorophyll maximum (Table 1). Conversely, a slope greater than 1 for the Florida Straits samples (slope = 3.85 ± 0.25 (standard error); Figure 4d) indicates a compositional disparity between SSA generated from the subsurface and microlayer waters.

The average organic carbon signal for the ETNP subsurface samples was 1.11 ± 0.62 (1σ variability), whereas the average organic carbon signal for the Florida Straits subsurface samples was 0.41 ± 0.20. Reported uncertainty is a standard deviation of variability across spectra signals. The relatively higher concentration of organics in the ETNP subsurface water is in agreement with the higher rates of primary productivity there than in the Florida Straits. Organic carbon signal can be a better indicator of primary productivity than concentrations of nutrients like nitrate (NO_3^-) and phosphate (PO_4^{3-}) and chlorophyll concentration (Table 1). Low nutrient concentrations can indicate that nutrients are being consumed or that they are low to begin with. Further, the chlorophyll to carbon ratio in seawater can vary (Lefèvre et al., 2003). These results agree with previous measurements of seawater composition. For instance, one study found that microlayer samples were organically enriched in the open ocean but unenriched in coastal upwelling zones similar to the ETNP region sampled here (Zäncker et al., 2017).

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Our PALMS analysis did not demonstrate that organic nitrogen or phosphorus preferentially partitioned into the microlayer in either the ETNP or Florida Straits. Although Zäncker et al. 2017 found that open ocean microlayer samples were enriched in amino acids, both subsurface and microlayer waters in the ETNP and Florida Straits yielded similar organic nitrogen signal intensities (Figures 4b and 4e). This could be caused by PALMS detecting ionization of more soluble organic nitrogen species in addition to amino acids. These include byproducts of microbial protein degradation, which tend to increase the solubility of nitrogenous molecules (Engel et al., 2018). We also did not observe an enrichment in phosphorus in either the ETNP or Florida Straits microlayer samples (Figures 4c and 4f). Although an enrichment of phosphorus in the microlayer due to lipid partitioning at the air-sea interface is expected, we note that lipids are labile and short-lived in seawater (Kattner et al., 1983; Parrish et al., 1992). Organophosphate groups on lipids are rapidly degraded by bacterial processes, thereby increasing their solubility (Ogunro et al., 2015). This leads phosphorous to be more rapidly recycled compared to carbon and nitrogen nutrients.

Our compositional analysis demonstrates that the ocean biogeochemistry impacts the composition of SSA. In the highly productive ETNP, both the subsurface and microlayer samples contained similar and elevated organic contents. The Florida Straits samples indicated a compositional disparity between microlayer and subsurface samples, with SSA generated from subsurface water depleted in organics. This indicates that SSA from productive marine regions may be more effective INPs than SSA from less productive regions.

3.2 Deposition Mode Ice Nucleation

To investigate possible links between SSA composition and ice nucleation activity, we quantified the conditions required to initiate ice nucleation in the deposition nucleation regime ($T < -40$ ˚C). The ice supersaturation at ice nucleation onset in the deposition freezing mode – termed critical supersaturation – is a metric of the activity of ice nucleating substances. INPs that activate at lower supersaturations and warmer temperatures are able to initiate cloud formation over a wider range of atmospheric conditions (Kanji et al., 2017; Pruppacher and Klett, 1980). Keeping with previous studies, we characterize ice nucleation onset as when 1% of particles depositionally nucleate ice (Kanji et al., 2017; Wilson et al., 2015).

Aerosols generated from organically-enriched samples generally required a lower S_{ice} to attain 1% fractional activation than organically depleted samples (Figure 5). Aerosols from both the subsurface and microlayer ETNP samples exhibited a similar critical S_{ice}, ranging from about 1.10 to 1.35 (Figure 5a). This finding contrasts with results from the Florida Straits samples, which display divergent INP activity for microlayer and subsurface samples (Figure 5b). Whereas the microlayer samples typically initiated depositional nucleation between $1.13 \leq S_{ice} \leq 1.30$, the subsurface samples often nucleated homogeneously ($S_{ice} > 1.40$). The S_{ice} at onset decreases at a rate of approximately 0.039 and 0.092 per degree cooling for Florida Straits and ETNP microlayer SSA, respectively. These trends are comparable to previous studies on deposition ice nucleation of organic SSA surrogates (Ladino et al., 2016; Schill and Tolbert, 2014; Wolf et al., 2019).

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The range of critical S_{ice} values agrees with results from North Atlantic microlayer samples, as shown in Figure 5b. (Wilson et al. 2015). The critical S_{ice} for microlayer samples at each temperature did not correlate ($R^2 < 0.2$; $p \geq 0.2$) with total carbon, nitrogen, or phosphorus PALMS signal. This suggests individual components of seawater are more important than bulk composition in driving ice nucleation. Likely candidates may be individual proteins or polysaccharides, as these compounds are effective depositional INPs and are enriched in the microlayer (Engel et al., 2018; Russell et al., 2010; Thornton et al., 2016; Wolf et al., 2019; Zäncker et al., 2017).

Whereas the North Atlantic subsurface samples in Wilson et al. 2015 did not nucleate heterogeneously, our subsurface samples from the ETNP nucleated at low ice supersaturations (S_{ice} = 1.1 at T = –46 ˚C). This indicates that SSA from these biogeochemically distinct regions exhibit different ice nucleation activity. Aerosols generated from subsurface waters in less productive regions are ineffective depositional INPs. Such aerosols can originate from jet droplets, which are formed when water beneath the microlayer is ejected as bubbles burst (Quinn et al., 2015; Wu, 2002). Conversely, organically-enriched subsurface water from the highly productive ETNP region demonstrate similar critical S_{ice} values as SSA from microlayer samples (Figure 5a). This indicates that both jet drop particles originating from subsurface water and smaller film burst particles originating from the sea surface microlayer in productive marine environments can be effective depositional INPs. These organically-enriched jet droplets can constitute a large fraction of submicrometer SSA (Wang et al., 2017).

Biological productivity in subsurface water can therefore impact the chemical makeup and INP activity of both jet droplet and film burst SSA (Wang et al., 2015). Our measurements of seawater biogeochemistry indicate that the ETNP had characteristics of higher biological activity than the Florida Straits (Table 1). For instance, average chlorophyll concentrations at sampling stations' deep chlorophyll maxima were 0.35 mg/m^3 higher in the ETNP than in the Florida Straits sampling stations. Satellite-derived regional surface chlorophyll a concentrations were also nearly double in the ETNP stations (0.19 mg m^{-3}) than the Florida Straits stations (0.10 mg m^{-3}) during sampling (Figure S1). This elevated productivity is maintained by higher nutrient concentrations. Nitrate concentrations in subsurface water samples were on average 0.14 µM greater in the ETNP. Nitrogenous nutrients generally limit primary productivity across the tropical and subtropical oceans. However, critical S_{ice} was not directly correlated with metrics of primary productivity or wind speed (Table S2). Even stations with the highest chlorophyll or nutrient concentrations (Table 1) did not correspond to the lowest critical S_{ice} values. This suggests factors other than primary productivity, such as cell lysis and microbial degradation, likely play an important role in determining the INP activity of SSA (McCluskey et al., 2017). Moreover, the standing stock concentration of nutrients does not necessarily reflect productivity as primary producers can dynamically draw down these concentrations. Other governing factors may include the types of plankton supported by the seawater biogeochemistry. While some species, such as diatoms and *Prochlorococcus* have been found to be effective sources of depositional INPs, other plankton species are poor INPs (Junge and Swanson, 2008; Knopf et al., 2011; Wolf et al., 2019).

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3.3 Immersion Mode Ice Nucleation

We observed a similar relationship between seawater biogeochemistry and immersion mode ice nucleation. INP active site densities are defined as the equivalent number of sites that promote ice nucleation per unit particle surface area (Vali et al., 2015). Active site density (n_s) is a metric of the effectiveness of different aerosols as INPs (Kanji et al., 2017; Vali et al., 2015). We calculated n_s values for each aerosol sample by dividing the activated immersion mode INP concentration (n_i) by the total aerosol surface area concentration (n_A):

$$n_s = \frac{n_i}{n_A} = \frac{f_i}{n_a} \quad (1)$$

where f_i is the fractional INP activation in the immersion mode and n_a is the surface area of a single particle. In deriving n_a, it is assumed effloresced SSA particles are spherical. Parameterizations of n_s can be size-dependent when aerosol composition varies with size. Atomizing seawater creates SSA with more uniform composition than natural seawater aerosolization processes, as it does not mimic the film burst and jet drop aerosolization processes that create organically enriched and depleted SSA, respectively. Since the majority of 200 nm particles in ambient SSA arise from the film-burst production process (Pruppacher and Klett, 1980; Wang et al. 2017), our sampled particles are likely less organically enriched. Our derived n_s values may therefore be lower estimates for immersion mode INP activity.

SSA generated from both subsurface and microlayer ETNP samples yielded comparable n_s values (Figure 6a). Average n_s values for ETNP microlayer and subsurface samples were indistinguishable within a standard deviation of variability. For instance, the average microlayer n_s at -30 ˚C was $3.3 \pm 1.9 \times 10^5$ cm^{-3}, compared with $2.1 \pm 1.3 \times 10^5$ cm^{-3} for subsurface samples. In contrast, the organically-depleted Florida Straits subsurface samples were less effective immersion mode INPs than the organically-enriched microlayer samples (Figure 6b). Values of n_s for these subsurface samples were typically one to two orders of magnitude lower than the average microlayer n_s value at a given temperature. Possible substances causing immersion mode ice nucleation are organic macromolecules. Such INMs include carbohydrates, liposaccharides, and ice nucleating active proteins (Ogunro et al., 2015; Pummer et al., 2015) as well as their byproducts of microbial degradation (McCluskey et al., 2017).

Our n_s values agree well with previous measurements of similarly sized SSA across various marine regions (Figure 6). Values for 250 nm aerosol from productive coastal waters (Si et al., 2018) are closer to the n_s of the organically-enriched samples from the ETNP and Florida Straits microlayer (Figure 4). Further, organically-depleted samples from the Florida Straits subsurface waters are more in agreement with open ocean measurements (DeMott et al., 2015b). This finding demonstrates the importance of seawater biogeochemistry in determining immersion mode INP activity. Both film burst and jet droplet particles generated from microlayer and subsurface waters in productive regions such as the ETNP are likely to be sources of effective INPs. In less productive regions, film burst particles may be the dominant source of marine INPs.

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3.4 Atmospheric Implications

Our results demonstrate that SSA generated from subsurface waters in highly productive marine environments can be comparably effective INPs as aerosols generated from the microlayer. Figure 7 summarizes the ice nucleation activity of SSA generated from the ETNP and Florida Straits. In the immersion freezing mode, subsurface SSA from the ETNP demonstrate n_s values orders of magnitudes greater than those from the Florida Straits subsurface (Figure 7a). We also show for the first time that subsurface waters can be an effective source of depositional INPs in highly productive marine environments. Critical S_{ice} values to attain 1% fractional activation for subsurface ETNP samples overlapped with S_{ice} thresholds for microlayer samples (Figure 7b). Samples from less productive regions, such as the Florida Straits and the North Atlantic Ocean (Wilson et al. 2015), did not identify subsurface samples as sources of effective depositional INPs (Figure 7b). The subsurface is aerosolized through bubble bursting mechansism, which create jet droplets (Pruppacher and Klett 1980, Wilson et al. 2015, Wang et al. 2017). This implies that jet droplet aerosols generated in coastal upwelling regions or during spring phytoplankton blooms can be a source of INPs.

These results augment previous findings that particle composition determines the ice nucleation activity of SSA (DeMott et al., 2015b; McCluskey et al., 2017; Wilbourn et al., 2020; Wilson et al., 2012; Wolf et al., 2019). We also found that that INP activity is uncorrelated with variables like nutrient concentration, wind speed, and chlorophyll concentration (Table S2). This indicates that factors other than rates of primary productivity are also important determinants of SSA composition and INP activity. These processes likely include plankton diversity and microbial degradation of organic components in seawater (DeMott et al., 2015b; McCluskey et al., 2017; Wang et al., 2015). These considerations are likely to matter most in environments without significant continental aerosols. For instance, modeling studies indicate that SSA constitute a greater fraction of ambient INP in remote regions free from intrusions of mineral and desert dust aerosol (Burrows et al., 2013; Vergara-Temprado et al., 2016). Highly productive marine regions like the ETNP are generally found near coasts, where terrestrial INP sources most often dominate over marine emissions (Burrows et al., 2013; Sarmiento and Gruber, 2006; Vergara-Temprado et al., 2017). An exception is the Southern Ocean, where austral summer marine primary productivity is high, and ambient atmospheric dust concentrations are low (Jickells, 2005). Despite these factors, recent measurements found low concentrations of immersion-mode INP over the Southern Ocean (McCluskey et al., 2018). This demonstrates that even highly productive marine environments are not always effective sources of INPs.

These findings emphasize the heterogeneity of SSA composition, ice nucleation activity, and climatic impact. Smaller film burst particles originating from the sea surface microlayer are generally considered to be the most effective SSA INPs (Wilson et al., 2015; Wolf et al., 2019). However, our results demonstrate that larger jet drop particles originating from highly productive subsurface waters may be a source of effective INPs as well. Our results further highlight a potential shortcoming of commonly employed model parametrizations that use surface chlorophyll concentrations as a predictor of aerosol organic mass fraction and INP activity (Burrows et al., 2013; O'Dowd et al., 2008; Vergara-

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Temprado et al., 2016). Despite similar surface chlorophyll-a concentrations (Table 1), SSA generated from the ETNP and Florida Straits yielded different ice nucleation properties. In biologically active marine ecosystems such as the ETNP, primary production in deeper subsurface waters can increase SSA INP concentration and enhance ice nucleation activity.

4 Conclusions

Sea spray is the largest aerosol source on Earth by mass, with total global emissions estimated to be $1 – 3 \times 10^{16}$ g yr–1 (Erickson and Duce, 1988; Vignati et al., 2010). Despite these large emissions, the impact of seawater biogeochemistry on SSA composition and INP activity remains uncertain. To clarify the importance of primary productivity in these factors, we measured the composition and ice nucleation activity of SSA generated from two biogeochemically diverse marine regions. Our seawater samples from the ETNP represent seawater in highly productive marine environments, whereas samples from the Florida Straits are characteristic of less productive environments.

We studied the impact that regional biogeochemistry has on SSA composition and ice nucleation activity. The highly productive ETNP region exhibits similar organic contents in subsurface and microlayer seawater. The Florida Straits microlayer is conversely organically-enriched relative to subsurface water. We then studied the regional differences in SSA ice nucleation activity. SSA generated from both subsurface and microlayer waters in the ETNP were effective depositional and immersion mode INPs. However, we observed that subsurface SSA from the Florida Straits were less effective INPs than microlayer SSA. These results indicate that ocean biogeochemistry plays an important role in the emission of marine INPs. Organically enriched film burst and jet drop aerosol emitted from highly productive marine regions may have a locally greater influence on ice nucleation, precipitation, and radiative budget than emissions from oligotrophic waters.

5 Acknowledgements

The authors declare no competing financial interests. We thank the crew, technicians, and scientists onboard the SSV *Corwith Cramer* and the R/V *Falkor* for their logistical and scientific support during sampling. We also thank the students of the MIT Field Oceanography Course 12.373/12.777 for their assistance sampling onboard the SSV *Corwith Cramer*. Funding was provided in part by an MIT Environmental Solutions Initiative educational grant to ARB. R/V *Falkor* ship-time was awarded by a Schmidt Ocean Institute grant to Karen Casciotti and ARB. The SSV *Corwith Cramer* expedition was funded by the MIT Houghton Fund and by the MIT/WHOI Joint Program.

6 Author Contributions

MJW, DJC, and ARB designed the experiments and methodology. MJW, MG, ED, LAD, CZ, LJF, CS, ER, DNN, and SM collected seawater samples, performed chemical analyses, and measured ice nucleation activity. MJW, DJC, and ARB prepared manuscript with input from all coauthors.

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Table 1 – Seawater Sampling Station Characteristics

Region	Station	Wind Speed (m/s)	$[NO_3^-]$ (µM)	$[PO_4^{3-}]$ (µM)	pH	Surface [Chl.-a] (mg/m^3)	Max Deep [Chl.-a] (mg/m^3)
Florida Straits	**1**	14.0	0.36	0.24	8.06	0.09	1.27
	2	13.6	0.17	0.25	8.05	0.10	N/A
	3	26.3	0.13	0.14	8.06	0.10	1.08
	4	18.5	0.19	0.02	8.03	0.09	1.10
	5	13.1	0.18	0.19	8.06	0.08	1.19
	6	20.3	0.60	0.10	8.05	0.07	1.18
	7	13.7	0.17	0.17	8.02	0.10	1.18
	8	12.3	0.20	0.09	8.01	0.12	1.42
	9	12.5	0.15	0.06	8.04	0.09	1.49
	10	10.1	0.18	0.02	8.07	0.06	1.24
	11	11.0	0.18	0.04	8.03	0.06	0.87
	Average (± 1σ)	**15.0 (± 4.8)**	**0.23 (± 0.1)**	**0.12 (± 0.1)**	**8.04 (± 0.02)**	**0.09 (± 0.02)**	**1.20 (± 0.2)**
ETNP	**1**	17.8	0.00	0.30	8.08	0.08	1.22
	2	22.7	1.02	0.24	8.07	0.08	1.06
	3	17.2	0.00	0.23	8.06	0.06	1.43
	4	15.3	0.00	0.22	8.07	0.06	3.34
	5	12.1	0.49	0.27	8.06	0.10	1.69
	6	11.6	0.32	0.26	8.07	0.09	1.38
	7	7.9	1.34	0.39	8.03	0.09	1.38
	8	11.0	0.00	0.28	8.05	0.07	1.35
	9	10.3	0.00	0.24	8.07	0.06	0.98
	10	11.6	0.00	0.25	8.07	0.06	0.67
	11	11.3	0.89	0.29	8.07	0.06	1.65
	Average (± 1σ)	**13.5 (± 4.3)**	**0.37 (± 0.5)**	**0.27 (± 0.05)**	**8.06 (± 0.01)**	**0.07 (± 0.02)**	**1.55 (± 0.7)**

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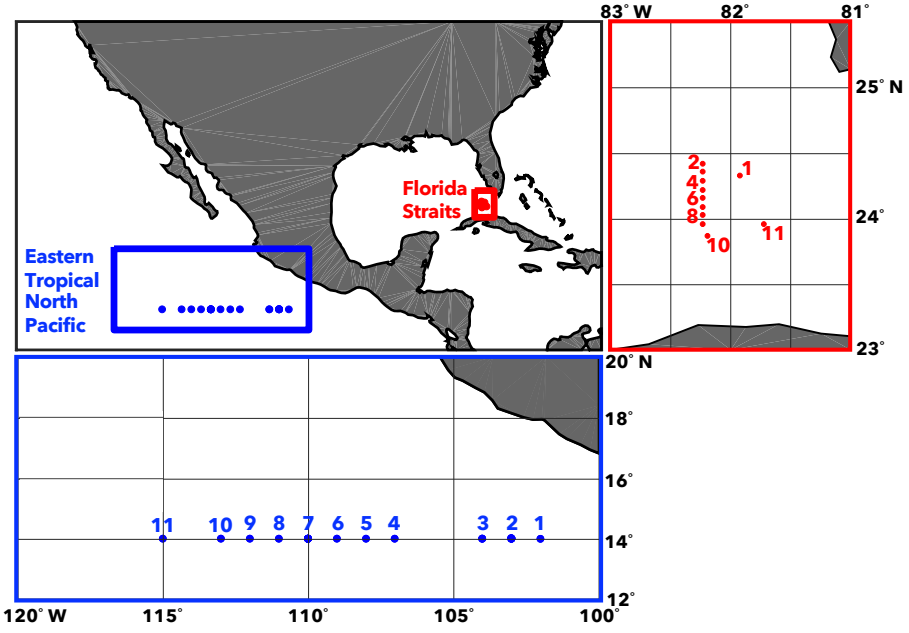

Figure 1 – Sample Locations. Locations of 11 samples in both the Eastern Tropical North Pacific (June – July 2018) and the Florida Straits (March 2017). Microlayer and subsurface samples were collected at each location.

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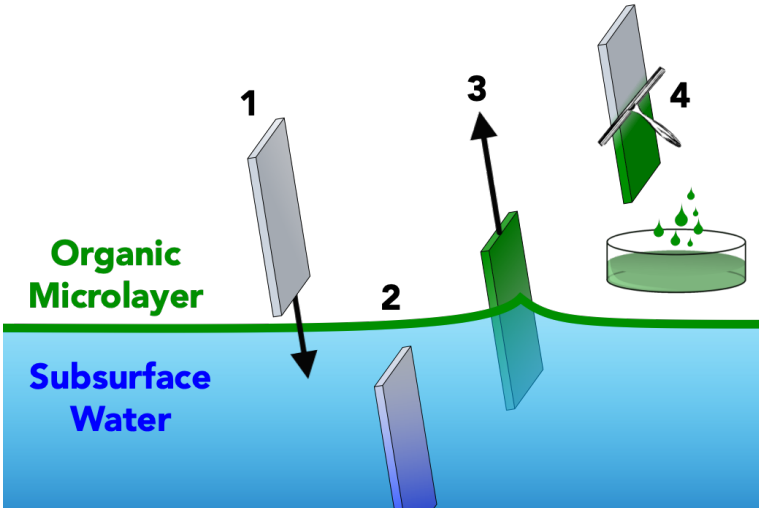

Figure 2 – Sea Surface Microlayer Sampling. The plate is fully submerged below the ocean surface (1 – 2). The plate is then withdrawn at a slow rate (3) to allow the organically-enriched microlayer to adhere. The adhered material is scraped off (4) and the process is repeated until sufficient microlayer is collected.

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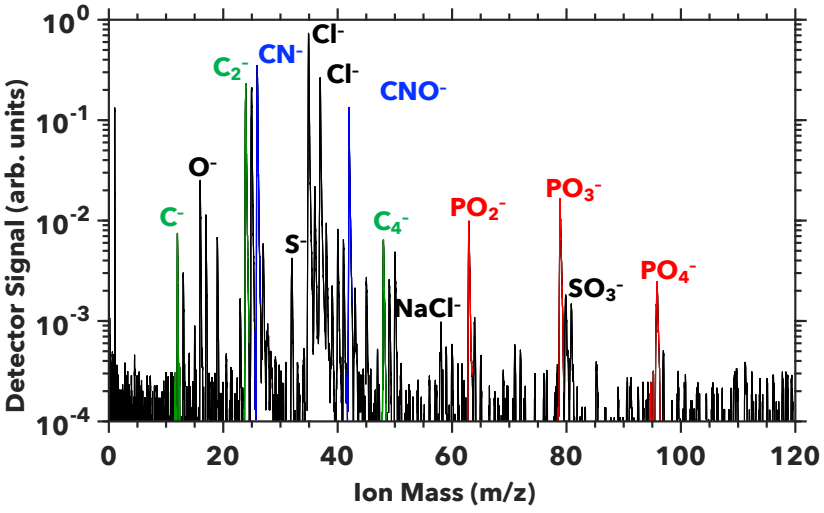

Figure 3 – SSA Mass Spectrum. A representative mass spectrum from PALMS (Pacific Microlayer Sample 2) shows indicators of carbon, organic nitrogen, and phosphorus molecules that may enhance ice nucleation activity of SSA (Wolf et al. 2019). Carbon peaks are labeled in green, organic nitrogen in blue, and phosphorus in red. Inorganic peaks are labeled in black.

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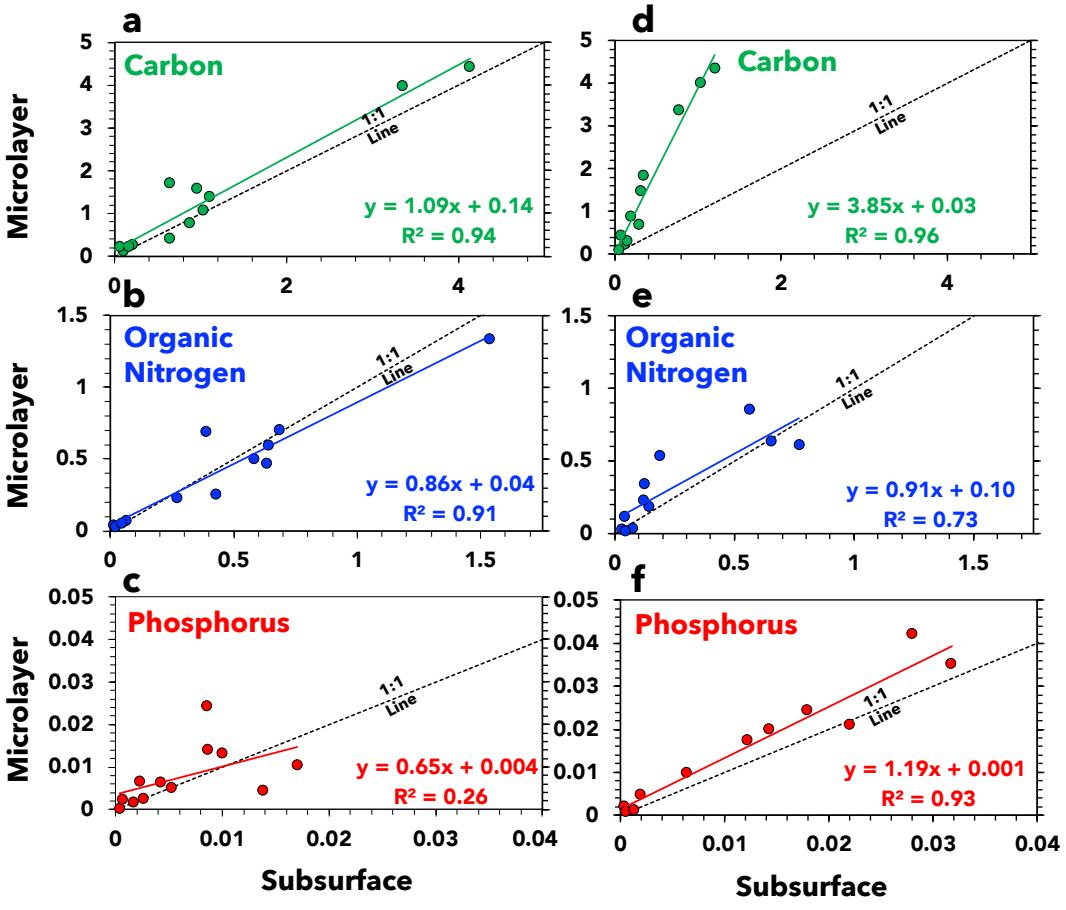

Figure 4 – Seawater Composition. The relative abundance of carbon, organic nitrogen, and phosphorus in (**a – c**) ETNP and (**d – f**) Florida Straits seawater samples. Axes represent PALMS ion signals in arbitrary units (Cziczo et al. 2006). Each data point represents the average value of at least one thousand spectra for each sample. Also included are reference 1:1 lines indicating equal signal in subsurface and microlayer samples.

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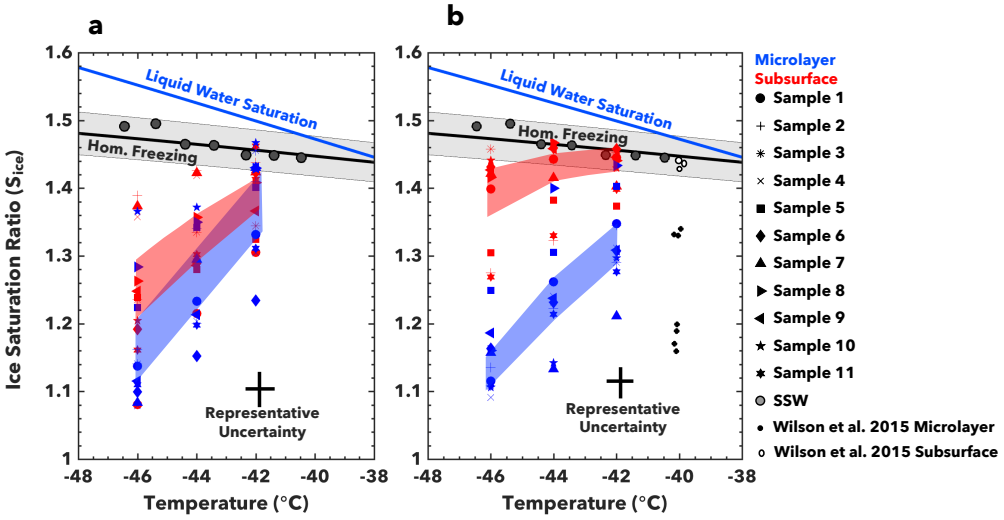

Figure 5 – Deposition Freezing. Conditions at the onset of deposition mode ice nucleation are shown for (**a**) ETNP and (**b**) Florida Straits seawater samples. The onset of ice nucleation is defined as when 1% of particles nucleate ice. Data points represent the average critical S_{ice} value at –46, –44, and –42 ˚C. Shaded regions indicate the average critical S_{ice} for all microlayer or subsurface samples, with a standard deviation of variability. Also illustrated are the conditions for homogeneous freezing for particles between 100 and 300 nm in diameter (Koop et al. 2000), as well as the onset of homogeneous nucleation as measured in SPIN with synthetic seawater (SSW) aerosol. Representative uncertainty in onset conditions arises due to variability in SPIN lamina conditions (Garimella et al. 2016).

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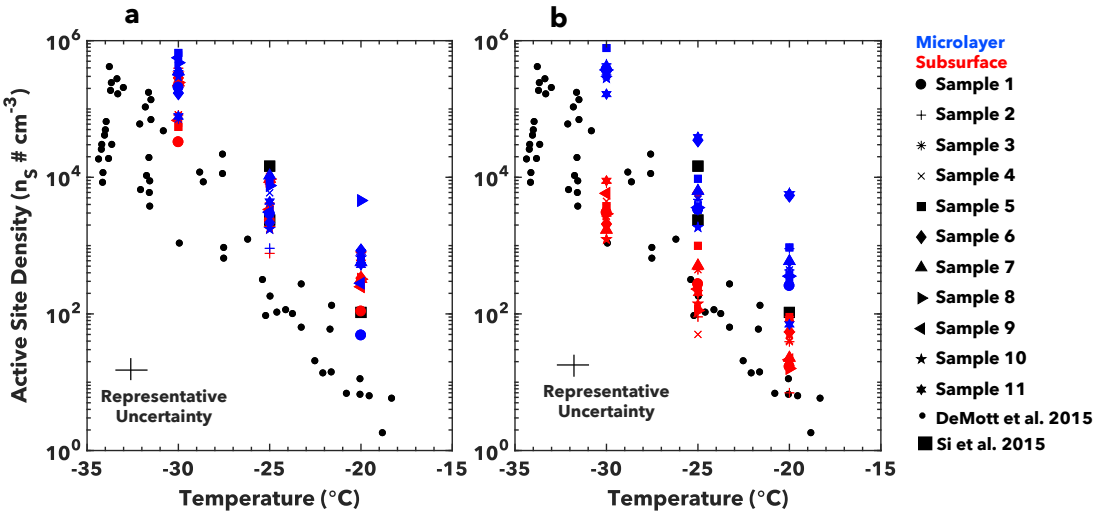

Figure 6 – Immersion Freezing. Active site density (n_s) for immersion-mode ice nucleation are shown for (**a**) ETNP and (**b**) Florida Straits seawater samples. Data points represent the average value n_s at –30, –25, and –20 ˚C. Representative uncertainties in n_s are derived from variability in replicate experiments, whereas temperature uncertainty arises due to variability in SPIN lamina conditions (Garimella et al. 2016).

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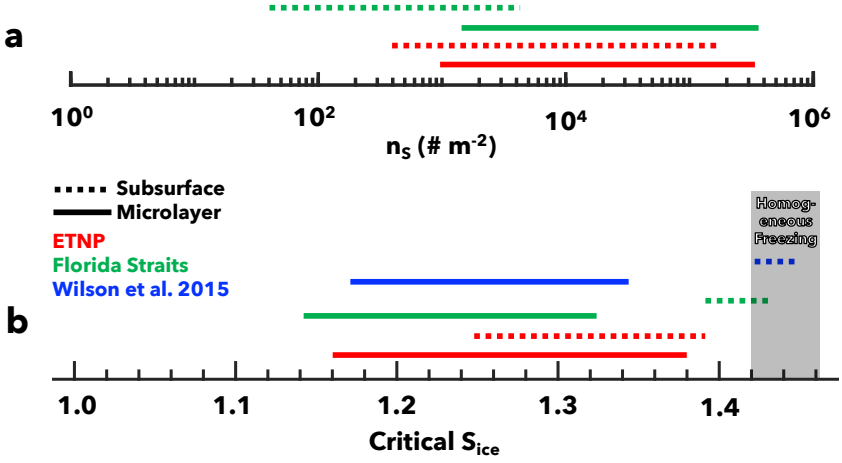

Figure 7 – Ice Nucleation Activity Comparison. (a) The INP active site density in the immersion mode, and (b) critical supersaturation required to attain 1% fractional activation in the deposition mode. Subsurface samples from the ETNP were more effective INPs than subsurface samples from less productive marine environments like the Florida Straits and the North Atlantic (Wilson et al. 2015).